



Cape Peninsula
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**NOVEL β -FeOOH/POLYMERIC COMPOSITES FOR REMEDIATION
OF WASTEWATERS**

by

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Declaration

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Date

Abstract

Water reclamation and sustainability through nano-based treatment processes has a promising prospect. The safe application of the numerous nanomaterials being applied for water treatment purposes is of utmost importance in this new phase of nanotechnology deployment. This is pertinent due to their potential adverse environmental and health concerns. This study was designed to investigate the suitability of polyamide matrix as immobilization support for the established catalyst- β -FeOOH nanoparticles. The synthesized polymeric nanocomposites (PNCs) were utilized for the remediation of 4-chlorophenol (4CP) and 4-nitrophenol (4NP). The analytes were selected to investigate the role of the attached groups (chloro- and nitro-) in the degradation intermediates, pathways and kinetics using the liquid chromatography/mass spectrometry time-of-flight (LCMS-TOF) instrumentation. The hydrothermally synthesized β -FeOOH nanoparticles and the PNCs fabricated via the *in situ* route were characterized using attenuated total reflectance-Fourier transform infrared (ATR-FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and nitrogen adsorption-desorption (Brunauer-Emmet-Teller and Barrett-Joyner-Halenda), which confirmed the clear-phase β -FeOOH nanoparticles and its successful incorporation into the polyamide matrix. *Daphnia magna* acute toxicity test was done to establish the safe application of the polymeric nanocomposites and the optimum treatment duration for the wastewater. The ozonation of the analytes solution (100 mL of 2×10^{-3} M) was done in a sintered glass reactor, with samples collected at different intervals over 60 min. The comparative oxidation results revealed that the 4-chloro- and 4-nitrocatechol pathways via hydroxylation were the major degradation route for 4CP and 4NP. Catechol intermediate was present as a primary breakdown product for the two analytes. Hydroquinone was observed as the transient degradation intermediate for 4CP but was absent for 4NP. Rather, an ozonation intermediate 2, 4-dinitrophenol was identified which was further oxidized to 3,6-dinitrocatechol. Several dimer products ($C_{12}H_8Cl_2O_2$, $C_{12}H_8Cl_2O_3$,

$C_{12}H_8Cl_2O_4$, $C_{12}H_8N_2O_6$, $C_{12}H_8N_2O_7$, etc.) were identified in the oxidation processes, favoured by alkaline conditions with more versatility shown by 4CP. Catalytic properties of the β -FeOOH/polyamide nanocomposites were evaluated during the degradation of 4CP and 4NP aqueous solutions through catalytic ozonation processes. The catalysed ozonation results showed 98.52% and 89.66% degradation of 4CP and 4NP using the optimum performing catalyst (1.25 wt% β -FeOOH loading) within 40 min relative to 62.94% and 55.21% degradation for the simple ozonation, respectively. The effect of pH on the degradation efficiency revealed that the catalysed ozonation is more favourable at higher pH values (pH 10 > 7 > 3). The COD and TOC values for real wastewater was effectively reduced by 54.62% and 89.22% by the polymeric nanocomposites compared to 33.92% and 47.06% removal obtained in the uncatalysed ozonation. The involvement of hydroxyl radicals in the breakdown of the phenols was confirmed by using methanol as a scavenger, which reduced the degradation efficiency of 4CP from 98.52% to 25.64% when it was added to the analyte solution. The composite exhibited excellent reuse potential with minimal decrease in its degradation ability over six cycles, and no leaching of iron was observed when applied in acidic, neutral and alkaline conditions. The complete degradation of 4CP after the treatment of the contaminated water for 1 h was established using the LCMS-TOF. However, the toxicity results showed that the treated water obtained at 1.5 h had better quality. Toxic intermediates persist in solution even though the parent analyte was completely degraded. Hence, toxicity assays should be encouraged on a complementary basis to the standard chemical methods. The study provided a great insight into the ozone degradation intermediates and pathways of 4CP and 4NP. The novel polymeric nanocomposites gave promising remediation ability for the removal of 4CP and 4NP from aqueous solutions and provided a safe deployment of the catalyst utilized.

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Dedication

This work is dedicated to the memory of my late father Mr Peter Igbede Akharamé

Academic outputs of the research reported in this thesis

Published Journal Articles

- **Akharame M.O.**, Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I. and Oputu, O.O. (2019). Comparative time-based intermediates study of ozone oxidation of 4-chloro- and 4-nitrophenols followed by LCMS-TOF. *Journal of Environmental Science and Health, Part A*, DOI: 10.1080/10934529.2019.1701340.
- **Akharame M.O.**, Fatoki, O.S. and Opeolu, B.O. (2019). Regeneration and reuse of polymeric nanocomposites in wastewater remediation: The future of economic water management. *Polymer Bulletin*, 76(2): 647-681. DOI: <https://doi.org/10.1007/s00289-018-2403-1>.
- **Akharame M.O.**, Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I. and Oputu, O.O. (2018). Polymeric nanocomposites for wastewater remediation: An overview. *Polymer-Plastic Technology and Engineering*, 57(17): 1801-1827. DOI: <https://doi.org/10.1080/03602559.2018.1434666>.

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- **Akharame M.O.**, Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I., Pereao, O. and Oputu, O.O. Beta-FeOOH/polyamide nanocomposites for the remediation of 4-chlorophenol from wastewater. (Manuscript under preparation).

Book

- **Akharame M.O.**, Oputu O.U., Pereao O., Fagbayigbo B.O., Razanamahandry L.C., Opeolu B.O., Fatoki S.O. (2019). *Nanostructured polymer composites for water remediation*. In: Gonçalves G. and Marques P. (Eds.) *Nanostructured Materials for Treating Aquatic Pollution*. Switzerland: Springer International Publishing. DOI: 10.1007/978-3-030-33745-2_10.

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- **Akharame M.O.**, Opeolu, B.O., Fatoki, O.S. Catalytic ozonation of 4-chlorophenol using beta-iron oxyhydroxide (β -FeOOH) nanoparticles: Efficiency and toxicity studies. 2nd Nanotechnology Seminar- Nanotech@CPUT 2019, 16th August 2019, Cape Peninsula University of Technology, Cape Town, South Africa.

- **Akharamé M.O.**, Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I. Magnetic beta-FeOOH/polyamide nanocomposites for the remediation of 4-chlorophenol from wastewater. The South African Chemical Institute (SACI)/Royal Society of Chemistry (RSC) Young Chemists' Symposium, 17th May 2019, Cape Town, South Africa.
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Poster Presentation

- **Akharamé M.O.**, Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I. Beta-FeOOH/polyamide nanocomposites for the remediation of 4-chlorophenol contaminated water: A case of efficiency versus toxicity. The Society of Environmental Toxicology and Chemistry (SETAC) 30th Europe Annual meeting, 3-7th May 2020, Dublin, Ireland (Abstract accepted).

Comparative time-based intermediates study of ozone oxidation of 4-chloro- and 4-nitrophenols followed by LCMS-TOF

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ABSTRACT

Greater insights on the degradation pathways and intermediates formed during the oxidation of organics can be achieved by more suitable and compatible instrumentation. In our research, we sought to explore the relative advantages of the liquid chromatography coupled to a time of flight mass spectrometer (LCMS-TOF) technique for the comparative time-based degradation intermediates and pathways of 4-chlorophenol (4CP) and 4-nitrophenol (4NP). The ozonation of the analytes solution (100 mL of 2×10^{-3} M) was done in a stirred glass reactor, with an ozone dose of 0.14 mg min^{-1} (O_3/O_2 10 mL/min). The comparative oxidation results revealed that the 4-chloro- and 4-nitrocatechol pathways via hydroxylation were the major degradation route for 4CP and 4NP. Catechol intermediate was present as a primary breakdown product for the two analytes. Hydroquinone was observed as transient degradation intermediate for 4CP, but was absent for 4NP. Rather, a novel ozonation intermediate 2, 4-dinitrophenol was identified which was further oxidized to 3,6-dinitrocatechol. Several dimer products were identified in the oxidation processes, favored by alkaline conditions with more versatility shown by 4CP. The study provided a great insight into the ozone degradation intermediates and pathways, with some intermediates scarce in literature identified.

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Ozonation; degradation pathways; degradation intermediates; phenols; endocrine-disrupting chemicals; liquid chromatography; time of flight mass spectrometer

Introduction

Phenols are part of the group of emerging micro contaminants known as endocrine-disrupting chemicals.^[1,2] Their presence in the environment is currently raising a lot of interest in the global scientific community, especially in surface, ground and wastewaters due to their xenobiotic tendencies.^[3–5] Of grave concern are their potential health implications even at extremely low concentrations ($\mu\text{g/L}$ or ng/L) and persistence in the environment; the adverse effects include possible acute toxicity, histopathological changes, mutagenicity and carcinogenicity.^[4] This makes it pertinent to carry out continuous investigations aimed at monitoring their presence in the different matrices of the environment, as well as elucidating their degradation pathways, intermediates and kinetics. Numerous advanced oxidation studies and literature abounds on the degradation intermediates and pathways of 4-chlorophenol (4CP) and 4-nitrophenol (4NP), respectively.^[7–12] The most common intermediates and degradation routes reported for both compounds center around chloro-/nitrocatechol^[13–16] and hydroquinone/benzoquinone.^[17–20] In general, the reasons alluded to most investigations include the need to provide data to aid understanding

or the substantiation of existing mechanisms, or proposing new degradation pathways.^[21–24] Whatever the purpose intended in researches, utilizing a suitable and compatible instrumentation or technique is of great importance.

The gas chromatography coupled to a mass spectrometer (GCMS) and high-pressure liquid chromatography (HPLC) coupled with a diode array or UV detector mostly reported for use in oxidation intermediates monitoring (see Table 1) has been posited to have some instrumental and method challenges.^[25–28] This creates the need to reevaluate and revalidate studies done using these instrumentations as gaps may still exist in the current body of knowledge. LCMS technique offers some versatility; constituent mobile phases and chromatographic column can be manipulated, while others such as ion source temperature, desolvation temperature, collision energy and source temperature can be leverage on for MS. Furthermore, the technique's compatibility with aqueous samples, which include nonvolatile, thermally labile and polar species,^[29] and ability of the soft ionization of the MS to generate data for the identification of parent compounds and intermediates provides leverage for intermediates identification.^[30]

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Regeneration and reuse of polymeric nanocomposites in wastewater remediation: the future of economic water management

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Abstract

The application of polymeric nanocomposites (PNCs) for wastewater remediation purposes is currently seen as frontier to explore the vast potentials of nanotechnology-based treatment solutions. Polymeric matrices act as bulk carriers for the immobilized nanomaterials, thereby helping to curtail their release into the environment during application processes and ease its recovery. In other instances, the polymeric component of the composite serves to synergistically improve the remediation processes. Research outputs in this area are exciting and have shown the possibility of providing a safe and efficient solution for wastewater treatment. Regeneration of synthesized PNCs to renew their active sites and prolong their life-span during use is an important aspect that will ultimately determine the large-scale application and progress of this technology. This review focuses on the different techniques utilized for the regeneration of PNCs, and their reuse potential in wastewater treatment and monitoring processes. Several regeneration mechanisms, mediums, processes and the nature of interacting bonds between PNCs/contaminants are discussed as presented in existing literatures. Highlighting this salient area in the development and utilization of PNCs for wastewater remediation purposes is our main intent.

Keywords Nanotechnology · Nanomaterials · Immobilized nanomaterials · Polymeric nanocomposites · Regeneration and reuse · Wastewater remediation

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Polymeric Nanocomposites (PNCs) for Wastewater Remediation: An Overview

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ABSTRACT

A decline in the world's freshwater resources poses a major domestic and industrial challenge. Amelioration efforts that proffer possible water management and reclamation technology is therefore, of utmost priority. One of the most promising solutions to water conservation is to recycle wastewater. The use of polymeric nanocomposites (PNCs) in water treatment/remediation processes provides possible solution to recycling. This overview focused on PNCs; to highlight trends in their fabrication, characterization and application procedures for wastewater remediation and monitoring. Key issues bothering on the regeneration and reuse of PNCs were discussed, along with projections for their rational design for safe application.

KEYWORDS

Nanomaterials; nanotechnology; polymeric nanocomposites; water and wastewater treatment; water reuse

GRAPHICAL ABSTRACT



Introduction

Nanotechnology is currently perceived as the gateway to the future, to solve numerous problems and create novel materials and products that will help fill many gaps and proffer solutions to several challenges being experienced in most fields of human endeavour. The technology is developed around particle size and surface area phenomenon which brings about much higher reactivity. It encompasses the modelling, synthesis, characterization and application of structures, devices and systems, by manipulating shapes and sizes at nanometre scale.^[1] Nanomaterials exhibit some unique properties due to their extremely reduced particle sizes such as high specific surface area, fast dissolution, high reactivity and strong sorption. Others

are superparamagnetism, localized surface plasmon resonance and quantum confinement effect.^[2]

Nanotechnology has generated a lot of interest in recent times in its application for the treatment and remediation of wastewater, especially in the quest for ways to maximize one of man's greatest resources, water. It is common knowledge that our freshwater resources are currently being stretched to the limit, with reports suggesting it is declining in quality and quantity, mainly due to anthropogenic activities.^[3,4] This has created a challenge to the global scientific community's efforts on seeking ways to ameliorate this problem and forestall possible water scarcity in the future. One promising solution is to prioritize water management and reclamation technologies for wastewater recycling and reuse.

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Nanostructured Polymer Composites for Water Remediation



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Abstract Nano-based advanced processes and technologies for water treatment operations provide innovative and progressive approaches with the capability to solve water scarcity, and contamination challenges across the globe. The incorporation of the numerous nanomaterials employed in this field into polymeric matrices bequeaths safer and more environmentally friendly materials-nanostructured polymer composites, for water treatment processes. In addition, the various functionalities of the polymers in combination with those of the incorporated nanomaterials often create synergistic treatment efficiencies in the hybrid composites. In this chapter, we focused on the complete process overview involved in the utilization of nanostructured polymer composites in water remediation and monitoring operations; this includes the different types of polymer matrices and nanomaterials in use, the design and synthesis methods, and characterisation techniques employed to elucidate their morphological, composite structural and functional properties. Scrutiny of their application potentials and efficiencies was done based on the different mode of applications which includes catalysis, adsorption, membrane filtration, microbial control, and monitoring and detection programs. This contribution harped on some areas of future concern

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Glossary

Clarification of basic terms and concepts

AOP	Advanced oxidation process
BET	Brunauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
β -FeOOH	Beta iron oxyhydroxides
COD	Chemical oxygen demand
CNTs	Carbon nanotubes
DAD	Diode array detector
EDCs	Endocrine-disrupting chemicals
EDS	Energy-dispersive X-ray spectroscopy
EIC	Extracted ion count
FTIR	Fourier transform infrared spectroscopy
GC/MS	Gas Chromatography/Mass Spectrophotometry
GC/MS/MS	Gas Chromatography/Mass Spectrophotometry/Mass Spectrophotometry
HO•	Hydroxyl radicals
HRTEM	High-resolution transmission electron microscopy
LCx	Effective lethal concentration
LC/MS	Liquid-Chromatography/ Mass Spectrophotometry
LC-MS/MS	Liquid-Chromatography-Mass Spectrophotometry/Mass Spectrophotometry
LOEC	Lowest observed effect concentration
MS	Mass spectrum
MWCNTs	Multi-wall carbon nanotubes
NOEC	No observed effect concentration
PNCs	Polymeric nanocomposites
POPs	Persistent organic pollutants
QAW	Qualitative analysis workflow
ROS	Reactive oxidative species
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy

STPs	Sewage treatment plants
TEM	Transmission electron microscopy
TIC	Total ion count
TOC	Total carbon content
TOF	Time of flight
USEPA	United State Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
WWTPs	Wastewater treatment plants
XRD	X-ray diffraction

Chapter: 1 Introduction

1.1 Background

Water is inarguably one of the greatest natural resources to humans and all living organisms. It is essential for the survival of all living things. The quality and quantity of water available to humans is a vital factor in determining their wellbeing (Chapra, 2018). In recent times, as a result of anthropogenic activities as well as natural occurrence, the quantity and quality of freshwater available for man's numerous needs is declining gradually (Zhu et al., 2018a; Zeng et al., 2013; El Kharraz et al., 2012). The presence of a wide array of contaminants in surface water and groundwater has become a crucial problem globally due to population growth, urbanization and industrialization (Gorza et al., 2018; Yin and Deng, 2015).

Inevitably, the reuse and recycle of wastewaters seems to be one of the best options in managing the diminishing freshwater resources. In some developing and industrialized countries, this is already in practice. However, the increasingly stringent water quality standards, coupled with emerging contaminants and micro-contaminants have brought new scrutiny to water treatment processes and procedures employed in conventional treatment systems (Qu et al., 2013). Prominent among these emerging contaminants are a wide variety of pollutants that are receiving significant attention because of their potential estrogenic effects and are classified as endocrine-disrupting chemicals (EDCs) (Goeury et al., 2019; Gore et al., 2018).

An endocrine disruptor is "an exogenous chemical substance or mixture that alters the function(s) of the endocrine system and thereby causes adverse effects to an organism, its progeny, the population and subpopulations of organisms" (USEPA, 1998). Recent studies have suggested that endocrine disruptors play a role in the pathogenesis of various disorders including male and female infertility, sexual underdevelopment, birth defects, endometriosis, and malignancies (Barber et al., 2019; Huang et al., 2019a; Al-Jandal et al., 2018; Vilela et al., 2018). Endocrine-disrupting chemicals include many groups of organic compounds such as alkylphenols, alkylphenol ethoxylates, polychlorinated biphenyls, selected pesticides, bisphenol A, pharmaceutical products, polybrominated compounds, steroids sex hormones and phthalates (Lauretta et al., 2019; Olujimi et al., 2012).

The realization that exposure to many environmental endocrine-disrupting chemicals is now widespread, coupled with proven or suggested trends for increased rates of certain endocrine-related diseases and disorders has given rise to growing concern globally (Cao

et al., 2019; Street et al., 2018; Attina et al., 2016). Hence, various investigations to establish their presence and proffer remedial solutions has gained momentum in the last decade (Gadupudi et al., 2019; Godfray et al., 2019; Goeury et al., 2019; Baycan and Puma, 2018; Cevenini et al., 2018; Giebner et al., 2018; Könemann et al., 2018), especially for treated wastewaters and effluents intended for discharge into water bodies or for recycling and reuse.

1.2 Justification of research

As a consequence of the declining freshwater resources and in order to forestall possible future water crisis, there is a great need for an innovative approach to water resources management worldwide, especially in a rapidly developing country like South Africa. In this regard, water management and reclamation technology are of utmost priority, so that wastewaters can be treated back to potable standards for domestic reuse. It is necessary to start developing, designing and incorporating novel treatment processes and procedures which has the potential to eliminate or minimize the presence of numerous emerging contaminants (especially EDCs) in wastewater to enable their reuse without any adverse health risk or implication.

Current wastewater treatment technologies and infrastructure fall short of completely eliminating persistent contaminants, and are inadequate to remove endocrine-disrupting chemicals found in wastewater (Giebner et al., 2018). These conventional methods which include biological processes, adsorption on activated carbon or other materials, thermal oxidation, chlorination, ozonation, flocculation-precipitation, reverse osmosis, etc. in most cases, are not adequate to reach the degree of purity required by international or local regulations to enable reuse of the treated wastewater (Rosman et al., 2018).

Recently, rapid and significant progress is on-going to design advanced technologies and procedures for wastewater treatment in order to eliminate pollution and also increase pollutants destruction or separation processes (Oller et al., 2018; Krýsa et al., 2018; Wang et al., 2018c; Yang et al., 2018; Covinich et al., 2014). Advanced oxidation processes are methods for water treatment that permits the total or partial degradation of compounds resistant to conventional treatments, reduction in toxicity or destruction of pathogenic organisms (Litter and Quici, 2010). However, the major setback for its wide application is the slow kinetics due to limited light fluence and photocatalytic activity (Qu et al., 2013).

Also, the use of nanomaterials and nanoparticles to remediate and disinfect wastewater has gained much interest in recent times (Lu and Astruc, 2018; El-Qanni et al., 2016), and nanocatalysts are being employed for degradation of organic contaminants and other persistent compounds (Feng et al., 2014). Due to their exceptionally large surface area, active sites and short diffusion length resulting in high sorption capacity and fast kinetics, recalcitrant contaminants are appreciably removed (Mthombeni et al., 2015; Qu et al., 2012). Many researchers have investigated the use of nanoparticles, and nanocomposites for remediation of wastewaters (Alqadami et al., 2019; Mudassir et al., 2019; Tony and Mansour, 2019; Fulekar et al., 2018; Mura et al., 2018; Neamtu et al., 2018). The output indicates the potential of these nanomaterials for removing some potential EDCs from wastewater systems. Nanotechnology-enabled procedures for wastewater treatment are perceived to be equipped to provide highly efficient, modular and multifunctional processes to provide high performance and cost-effective wastewater treatment solutions. Also, they possess the capabilities that could allow economic utilization of unconventional water sources to boost water supply (Qu et al., 2013).

Nano-based wastewater treatment processes have shown great promise in recent times. However, there are a number of potentially serious issues concerning the environmental fate of synthesized nanoparticles and their potential risk to human health (Tosco and Sethi, 2018; Dwivedi et al., 2015). The most likely routes through which these minute particles can get into humans is via skin contact, inhalation of water aerosols and direct ingestion of contaminated drinking water (Elsaesser and Howard, 2012; Stern and McNeil, 2007; Nel et al., 2006). Nanotechnology risk assessment research for establishing the potential impacts of nanoparticles on human health and the environment is crucial to aid in balancing the technology's benefit and potential unintended consequences (Yunus et al., 2012; Bhatt and Tripathi, 2011). A range of ecotoxicological effects from engineered nanoparticles have been reported on microbes, plants, invertebrates and fish species as well as mammals (Hou et al., 2019; Hou et al., 2018; Sardoiwala et al., 2018; Dubey et al., 2015; Poynton et al., 2012; Handy et al., 2008; Moore, 2006).

Health effects to the lungs similar to those of asbestos inhalation have been speculated for nanoparticles if inhaled in sufficient amounts, with recent studies showing a similar response by the human body to some forms of carbon nanotubes (CNTs) as asbestos particles (Buzea et al., 2007). These effects may significantly hinder the widespread use of nanomaterials for remediation purposes, especially where methods involve free-release of the nanoparticles to the environment. Immobilizing nanoparticles into a bulk carrier can

prevent their release into the environment while maintaining their reactivity (Boxall et al., 2012; Handy et al., 2008; Moore, 2006; DeMarco et al., 2003).

A significant number of studies on membrane technology have focused on creating a synergism or multifunctionality by adding nanomaterials into polymeric or inorganic membranes (Lofrano et al., 2016; Li et al., 2015; Mthombeni et al., 2015; Yan et al., 2014). Nano reactive composites were able to degrade pollutants such as 4-chlorophenol (Oputu et al., 2015a), and adsorb metal ions (Saad et al., 2018) in aqueous solutions. Guo et al. (2012) reported the synthesis of iron nanoparticles on graphene to form a composite which showed improved capabilities in the removal of methylene blue dye as compared to bare iron particles. Also, the use of magnetic zeolite-polymer composite as an adsorbent for the remediation of wastewaters containing vanadium, with promising results was reported by Mthombeni et al. (2015).

In recent years, novel size-dependent physicochemical properties make metallic iron nanoparticles of great potential in a wide range of applications which include environmental remediation (Li et al., 2015; Wang et al., 2014b; Liu et al., 2013; Xu et al., 2012). However, very little attention has been given towards iron-oxy-hydroxides materials despite their low toxicities, cheap and simple synthesis procedures (Oputu et al., 2015b). Catalytic properties of FeOOH based materials such as α -FeOOH (Yaping and Jiangyong, 2008) and γ -FeOOH (Chou et al., 2001) have been reported before in the presence of H_2O_2 . Oputu et al. (2015a) reported the incorporation of β -FeOOH on NiO by forming a heterojunction via the chemically bonded interface to reduce the loss of FeOOH as Fe^{2+} . The β -FeOOH/NiO composite catalyst showed significant improvement in the removal of 4-chlorophenol than bare β -FeOOH. In a similar way, β -FeOOH/Fe(III)-exchange resins were synthesized and used for the elimination of estrogen (17 β -estradiol) through heterogeneous photo-Fenton processes with H_2O_2 and UV. The procedure was reported as very promising for degradation of estrogenic compounds in water (Zhao et al., 2010b). However, the use of β -FeOOH immobilized onto polymer systems has not been explored as catalysts. This novel nanoparticle has been shown to have improved efficiencies in removing organics, particularly EDCs in wastewaters when on metal oxide (e.g. NiO) and resin supports. It might give better efficiency when immobilized onto polymer matrices with much more improved reusability.

1.3 Research aim and objectives

1.3.1 Aim

The aim of this was the synthesis of novel β -FeOOH/polymer composites for the remediation of synthetic wastewater and real wastewater samples from the Stellenbosch Wastewater Treatment Plant, South Africa

1.3.2 Specific objectives

The specific objectives of this research were to:

- ✓ Synthesize and characterise novel β -FeOOH/polymer nanocomposites.
- ✓ Investigate the treatment capabilities of the synthesised β -FeOOH/polymer composites in combination with ozonation for the removal of selected priority phenols (4-chlorophenol and 4-nitrophenol) from synthetic wastewater.
- ✓ Investigate the intermediates and pathways of the 4CP and 4NP during the degradation processes.
- ✓ Ascertain the treatment efficiency of the most effective nanocomposite for remediation of real wastewater samples from the WWTP.
- ✓ Establish the regeneration and reuse potential of the β -FeOOH/polymer composites.
- ✓ Assess the toxicity potential of the treated wastewater.

1.4 Significance of the research

Globally, freshwater resources are declining, especially in rapidly developing countries like South Africa. The drop in the annual rainfall levels in recent years has escalated the water scarcity challenge worldwide. Hence, there is a great need for innovative approaches such as reclamation technologies to manage water resources.

Synthesis of novel β -FeOOH/polyamide nanocomposites and establishing their treatment efficiencies for the removal of phenols will be beneficial to South Africa and the world at large for wastewater reclamation purposes. Also, the verification of their reusability and safe application through ecotoxicological studies will be relevant to the scientific community and the society at large.

1.5 Limitation of the study

The research was limited to laboratory-scale treatment and analyses. Application in a pilot wastewater treatment plant was not developed; although the system's potential for such application was tested with real wastewater.

Chapter: 2 Literature review

2.1 Endocrine disrupting chemicals

The contamination of water systems with endocrine-disrupting chemicals is a growing concern globally. This group of chemicals interfere with the normal functions of the endocrine system in organisms, and create abnormalities especially in their reproductive systems. Numerous endocrine disruptors has been identified and these include chemical compounds such as alkylphenols, alkylphenol ethoxylates, polychlorinated biphenyls, selected pesticides, bisphenol A, pharmaceutical products, polybrominated compounds, steroids sex hormones and phthalates (Lauretta et al., 2019; Olujimi et al., 2012). Phenol and its various derivatives have been reported to be active endocrine-disrupting chemicals (Wang et al., 2018; Zhou et al., 2019). Their toxicity is related to perceived hydrophobicity, the ready formation of free radicals, and easy localization of substituents (Michałowicz and Duda, 2007), with adverse effects on both plants and animals (Park et al., 2012; Erler and Novak, 2010).

2.2 Phenols

Phenols are part of the group of emerging micro contaminants known as endocrine-disrupting chemicals (Shoaff et al., 2019; Lv et al., 2019). Their presence in the environment is currently raising a lot of interest in the global scientific community, especially in surface, ground and wastewaters due to their xenobiotic tendencies (Tolosana-Moranchel et al., 2019; Fan et al., 2019; Michalík et al., 2018). Of grave concern are their potential health impacts even at extremely low concentrations ($\mu\text{g L}^{-1}$ or ng L^{-1}), as well as, their persistence in the environment. The adverse effects include possible acute toxicity, histopathological changes, mutagenicity and carcinogenicity (Michałowicz and Duda, 2007). Natural and anthropogenic EDCs are released into the environment by humans, animals and industry; mainly through wastewater treatment systems before being deposited in surface waters or leached into underground aquifers (Liu et al., 2009).

Phenols are aromatic compounds that have a hydroxyl group attached directly to the benzene ring. They are colourless, crystalline or liquid substances of characteristic odour and are mildly acidic in nature. In recent times, most industrial phenols are obtained from isopropyl benzene (cumene), which is oxidized by air in the cumene process (Figure 2.1). A two-stage process involving the oxidation of toluene to benzoic acid, followed by the decarboxylation of the benzoic acid also yields phenol (Figure 2.2). The production of

phenol is equally carried out through a one-step process, by utilizing nitrous oxide in the oxidation of benzene (Gardziella et al., 2013). It can also be synthesized from arenesulfonic acids by the fusion of alkali metal sulfonates with alkali in the presence of water; from aryl halides through nucleophilic substitution or by conversion of an aryl halide into a Grignard reagent or aryllithium compound and subsequent reaction with oxygen (Knop and Pilato, 2013). Derivatives of phenols also abound, they are molecules that contain other groups such as methyl, amide or sulphide attached to the benzene ring structure. Common examples (see Figure 2.3) regarded as priority pollutants are 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2-nitrophenol, pentachlorophenol, 2,4-dinitrophenol, 2,4,6-trichlorophenol, 4-nitrophenol, 4,6-dinitrophenol and 2,4-dimethylphenol (Olujimi et al., 2010).

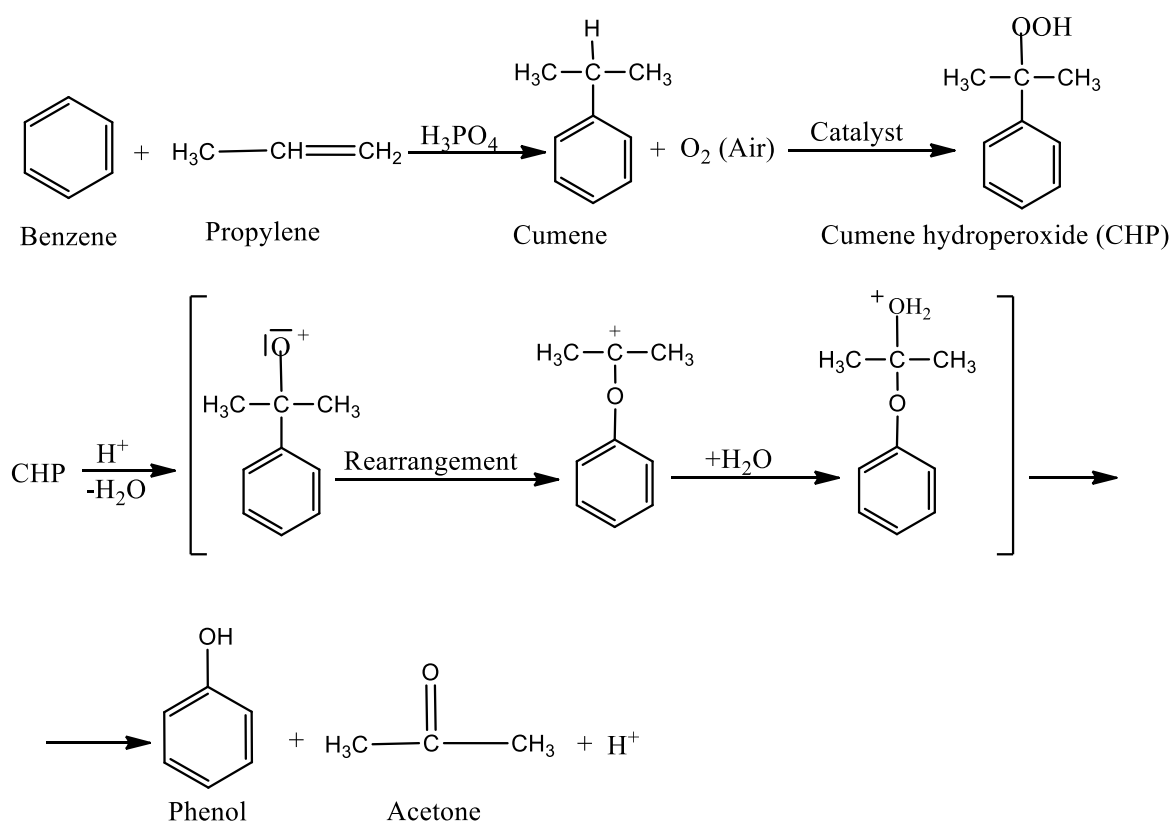


Figure 2.1: Cumene process for phenol production

Source: (Gardziella et al., 2013)

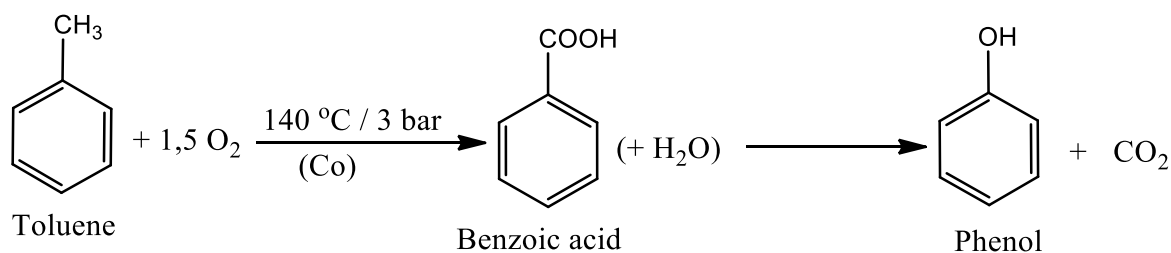


Figure 2.2: Toluene oxidation process for phenol production

Source: (Gardziella et al., 2013)

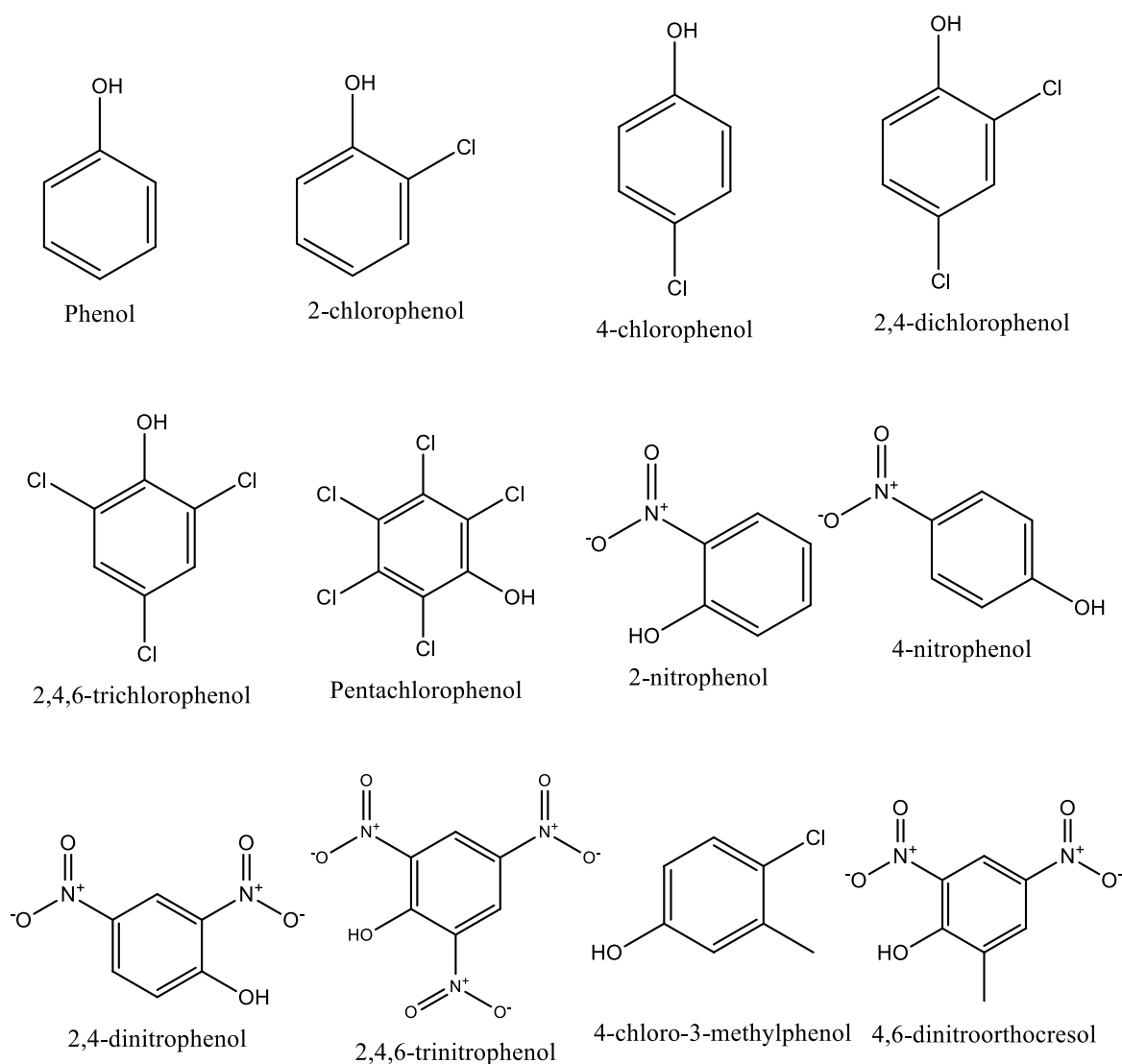


Figure 2.3: Chemical structures of some selected phenolic compounds

2.2.1 Sources and pathways of phenols in the environment

Phenols and its derivative compounds get into the environment through both natural and anthropogenic sources. Phenolics are natural components of many substances (e.g. tea, wine and smoked foods), present in animal wastes and decomposing organic material, and may be formed in air as a product of benzene photooxidation (Busca et al., 2008). The major sources of anthropogenic phenol pollution in the environment are effluents and wastewaters from paint and dyes, pesticides, coal conversion, polymeric resins, petroleum and petrochemical industries (Liotta et al., 2009). Phenol is also emitted from the combustion of fossil fuels and tobacco (Busca et al., 2008).

Phenol and phenolic compounds are used in so many industrial processes, hence their continual presence and contamination of the natural environment. They are used in the production of many disinfectants, in veterinary medicine as an internal antiseptic and gastric anaesthetic, as a peptizing agent in glue, an extracting solvent in refinery and lubricant production, as a blocking agent for isocyanate monomers, as a reagent in chemical analysis and as a primary petrochemical intermediate (Busca et al., 2008). Also, they are used as an intermediate in the production of phenolic resins, caprolactam used in the manufacture of nylon 6 and other synthetic fibres, and bisphenol A employed in the synthesis of epoxy and other resins. Other applications include medicinal preparations and products such as ointments, ear and nose drops, cold sore lotions, mouthwashes, gargles, toothache drops, analgesic rubs, throat lozenges, and antiseptic lotions (Ahmaruzzaman, 2008).

Due to the wide use and application of phenol and other derivatives as shown in Table 2.1, the introduction of these compounds into the environment is inevitable. Hence, phenols can be detected in air, water and soil water samples. Phenols, for the most part, are biodegradable (Basha et al., 2010), as bacteria in the environment can quickly break it down. Therefore, their levels in air, water and soil are generally quite low (Busca et al., 2008). However, when continuously introduced into the environment from a contamination source at high concentrations; phenols are considered as pollutants of high priority concern due to their toxicity and possible accumulation in the environment (Lin and Juang, 2009).

Table 2.1: Some chemical intermediates of phenols

Intermediate	Chemical formula	End-use/product
Bisphenol A	$C_{15}H_{16}O_2$	Used to produce epoxy resins for paints coatings and mouldings, and in polycarbonate plastics, familiar in CDs and domestic electrical appliances.
Caprolactam	$C_6H_{11}NO$	Major starting material for the manufacture of nylon and polyamide plastics for a wide range of products, including carpets, clothing, fishing nets, moulded components and packaging.
Phenylamine (aniline)	$C_6H_5NH_2$	Utilized for synthesizing isocyanates in the production of polyurethanes, with a wide range of uses from paints and adhesives to expanded foam cushions. Also, used as an antioxidant in rubber manufacture, and as an intermediate in herbicides, dyes and pigments, and pharmaceuticals.
Alkylphenols (3-methylphenol)	C_7H_8O	These compounds are used in the manufacture of surfactants, detergents and emulsifiers, and in insecticide and plastics production.
Chlorophenols (2,4-dichlorophenol)	$C_6H_4Cl_2O$	Used as an active agent in the manufacture of medical antiseptics and bactericides, and in fungicides and pesticides production.
Salicylic acid	$C_7H_6O_3$	Employed in the production of pharmaceuticals such as aspirin.

Adapted from: Basha et al. (2010)

2.2.2 Effects of phenol and its derivatives

Phenol and its various derivatives have been reported to be active endocrine-disrupting chemicals (Zhou et al., 2019; Wang et al., 2018b; Zheng et al., 2015; Zhong et al., 2012; Li et al., 2010; Takayanagi et al., 2006). The noxious effects of phenols and their derivatives concern acute toxicity, histopathological changes, mutagenicity and carcinogenicity (Michałowicz and Duda, 2007). They have been reported to have adverse effects on both plants and animals (Park et al., 2012; Erler and Novak, 2010). Their toxicity is related to perceived hydrophobicity, the ready formation of free radicals, and easy localization of substituents (Michałowicz and Duda, 2007).

From their various sources, phenol and phenolic compounds enter the environment where they are taken up by plants, animals as well as humans through several routes (inhalation, ingestion and adsorption). Exposure to phenols by any route can cause systemic poisoning, especially at high concentrations. Table 2.2 presents the effects of phenols on various metabolic systems in organisms.

Table 2.2: Effect of phenols on various metabolic processes

Metabolic system	Effects
Central nervous system	Initial signs and symptoms may include nausea, excessive sweating, headache, dizziness, and ringing in the ears. Seizures, loss of consciousness, coma, respiratory depression, and death may ensue. Coma and seizures usually occur within minutes to a few hours after exposure but may be delayed up to 18 hours.
Cardiovascular	Phenol exposure causes initial blood pressure elevation, then progressively severe low blood pressure and shock. Cardiac arrhythmia and bradycardia have also been reported following dermal exposure to phenol.
Respiratory	Mild exposure may cause upper respiratory tract irritation. With more serious exposure, swelling of the throat, inflammation of the trachea, tracheal ulceration, and an accumulation of fluid in the lungs can occur. Ingestion may lead to death from respiratory failure.
Gastrointestinal	Nausea, vomiting, abdominal pain, and diarrhoea are common

Metabolic system	Effects
	symptoms after exposure to phenol by any route. Ingestion of phenol can also cause severe corrosive injury to the mouth, throat, oesophagus, and stomach, with bleeding, perforation, scarring, and or stricture formation as potential sequelae.
Renal	Renal failure has been reported in acute poisoning. Urinalysis may reveal the presence of protein (i.e., albuminuria), casts, and green to-brown discolouration of the urine.
Hematologic	Components of the blood and blood-forming organs can be damaged by phenol. Most haematological changes (e.g., haemolytic, methemoglobinemia, bone marrow suppression, and anaemia) can be detected by blood tests or simply by the colour or appearance of the blood. Methemoglobinemia is a concern in infants up to 1-year-old. Children may be more vulnerable to loss of effectiveness of haemoglobin because of their relative anaemia compared to adults.
Ocular	Contact with concentrated phenol solutions can cause severe eye damage including clouding of the eye surface, inflammation of the eye, and eyelid burns.
Dermal	When phenol is applied directly to the skin, a white covering of precipitated protein forms. This soon turns red and eventually sloughs, leaving the surface stained slightly brown. If phenol is left on the skin, it will penetrate rapidly and lead to cell death and gangrene. If more than 60 square inches of skin is affected, there is a risk of imminent death. Phenol appears to have local anaesthetic properties and can cause extensive damage before pain is felt.
Reproductive and Developmental.	No studies were located concerning the developmental or reproductive effects of phenol in humans. Animal studies have reported reduced foetal body weights, growth retardation, and abnormal development in the offspring of animals exposed to phenol by the oral route.

Source: Basha et al. (2010)

2.2.3 Analytical techniques for identification and quantification of phenols

Different analytical techniques and procedures are being employed for qualitative and quantitative assays. Development of techniques such as GC-MS, LC-MS, GC-MS/MS, LC-MS/MS and their numerous modifications has provided researchers more leverage in analysing environmental samples. However, Liquid chromatography/mass spectrometry (LC-MS) has proven to be a reliable and effective technique that can be used for the determination and quantification of phenol, and an array of organic compounds. Its popular application is based on several reasons such as relatively low operating cost, minimal sample preparation, ease of operation, compatibility of the technique with many aqueous samples, and ability of the soft ionization of the MS to provide data for the identification of parent compounds and intermediates (Hisaindee et al., 2013). The LC-MS technique offers some versatility that allows certain parameters to be manipulated and leverage on for easy resolution of target analyte with well separated, high-intensity peaks for proper identification and quantification. For LC parameters, constituent mobile phases and chromatographic column can be manipulated, while others such as ion source temperature, desolvation temperature, collision energy and source temperature can be optimised for MS.

The techniques have shown much importance and usefulness in the analysis of a wide array of compounds, including non-volatile, thermally labile and polar species (Sosa-Ferrera et al., 2012). Recently, it was used for quantification of 4-chlorophenol and the degradation intermediates during the NiO/ β -FeOOH catalysed ozonation process with a mobile phase of 1% formic acid in water and acetonitrile, and a C8 column employed at a negative mode for the analysis (Oputu et al., 2015a). Oputu et al. (2015b) had previously utilized the same LC-MS technique for the analysis of 4-chlorophenol in another β -FeOOH catalysed ozonation, but with a C18 column and a mobile phase composed of 1/1 (V/V) formic acid/water. In both cases, the technique was able to effectively determine the analyte and its degradation products. Also, Kubo et al. (2014) in their investigation of using molecularly imprinted polymer as a preconcentration medium, applied online SPE-LC-MS for the determination of sulpiride, a pharmaceutical found in river water. Again, Andreozzi et al. (2003) in their monitoring campaign of STP effluents carried out in four European countries (Italy, France, Greece and Sweden) for assessment of pharmaceuticals, used the LC-MS technique which proved quite efficient for the determination of more than 20 individual pharmaceuticals belonging to different therapeutic classes.

2.2.4 Regulations and guidelines for phenols

The presence of phenols in the various matrices of the environment, especially wastewater has already been established by several researchers (Lv et al., 2016; Olujimi et al., 2012; Olujimi et al., 2010). However, more pertinent are standard model investigations to find out their specific environmental impacts and health effects to enable regulatory agencies at the regional and global level to set holistic policy initiatives for these pollutants of concern.

Phenol and some phenolic compounds are currently listed as part of the priority pollutants on the global watch list (USEPA, 2014). Hence, most industrialized countries have put in place guidelines for their regulations. For example, in the United States of America a maximum permissible limit that should not be exceeded at any time of $3.5 \mu\text{g L}^{-1}$ has been set for freshwater (USEPA, 1986), with $3.0 \mu\text{g L}^{-1}$ recommended for exposure through drinking water and ingestion of contaminated organisms (Zeatoun et al., 2004). Canada set $4.0 \mu\text{g L}^{-1}$ for mono- and dihydric phenol in freshwater (CCME, 1999) and later in the year 2002 made an update with 4-hydroxyphenol (quinol, hydroquinol, 1,4-benzenediol) maximum permissible limit set as $4.5 \mu\text{g L}^{-1}$; 3-hydroxyphenol (resorcinol, 1,3-benzenediol) set at $12.5 \mu\text{g L}^{-1}$; while all other non-hydrogenated phenols had $50.0 \mu\text{g L}^{-1}$ set for them. Following the global trend, a value of $3.0 \mu\text{g L}^{-1}$ has been recommended as the target water quality range for aquatic ecosystems in South Africa (DWAF, 1996).

2.2.5 Abatement for phenols

Phenols have been designated as part of endocrine-disrupting chemicals, bringing about a lot of interest in studying their occurrence, sources, fates, and possible mechanism of action and health effects to organisms in the environment. In all of these, most pressing to researchers are ways of remediating these noxious chemicals from our environment, especially wastewaters where most of them are ultimately deposited. The use of these compounds for various manufacturing processes and in churning numerous products is on the increase daily. Consequently, more of them will inevitably get into the environment bringing about increasing levels of contamination and possibly pollution which may further aggravate the precarious ecosystem balance on earth. Some common treatment methods used to remediate their presence in wastewaters are; bioremediation (Ryan et al., 2007), adsorption (Abdelkreem, 2013), ozonation (Esplugas et al., 2007), catalytic ozonation and application of nanotechnology (Oputu et al., 2015a; Oputu et al., 2015b).

2.3 Advanced oxidation processes

Advanced oxidation processes (AOPs) are now widely utilized for the removal of persistent organic compounds from wastewaters. It is perceived as a promising technology for the treatment of wastewaters containing organic compounds with high toxicity. The process can produce total mineralization, transforming organic compounds into inorganic substances (CO_2 and H_2O), or partial mineralization, converting them into more biodegradable substances (Covinich et al., 2014). AOPs are based on physicochemical procedures that produce powerful oxidative species like the hydroxyl radical ($^*\text{OH}$), and other reactive oxygen species like H^* , $\text{O}_2^*/\text{HO}_2^*$ and H_2O_2^* which enable the transformation of the target pollutant (Litter and Quici, 2010). Homlok et al. (2013), used an AOP to establish the relationship between chemical structures and degradability. The hydroxyl radicals generated in the system were majorly responsible for the high oxidation of the phenols, malic and fumaric acids. They noted that the high-efficiency degradation rates were due to $^*\text{OH}$ addition to unsaturated bonds and subsequent reactions of dissolved O_2 with organic radicals. The reaction rate of compounds in $^*\text{OH}$ radical initiated degradation process is of much higher magnitude when compared to ozone in same conditions, also $^*\text{OH}$ radicals are non-selective oxidants and could initiate a large number of reactions (Matilainen and Sillanpää, 2010).

Recently, many studies have been conducted to ascertain the treatment efficiencies and ability of AOPs to degrade recalcitrant organic compounds present in contaminated waters in order to develop standard models and obtain better treatment results (Wols et al., 2015; Xiao et al., 2015; Horáková et al., 2014; Karci, 2014; Klammer et al., 2013). Most of these reported positive output in their investigations and gave more insight into the versatility embedded in advanced oxidation technology. Generally, AOPs employ different reagent systems which include photochemical degradation processes (UV/O_3 , $\text{UV}/\text{H}_2\text{O}_2$), photocatalysis (TiO_2/UV , photo-Fenton reactions), and chemical oxidation processes (O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$), all geared towards producing radicals for the degradation of organics (Boczkaj et al., 2017).

AOPs as applied of late has shown capabilities to degrade organics in wastewater matrix. Yu et al. (2016) reported improved efficiency in the removal of sulfolane from contaminated groundwater by a combination of $\text{UVC}/\text{H}_2\text{O}_2/\text{O}_3$, $\text{UVC}/\text{H}_2\text{O}_2$ and UVC/O_3 in the treatment processes. All three treatment combinations efficiently degraded sulfolane, however, there was a synergist effect observed when $\text{H}_2\text{O}_2/\text{O}_3$ were combined. Huang et al. (2015) employed heterogeneous catalytic ozonation approach in the removal of dibutyl

phthalate (DBP) in aqueous solution in the presence of iron-loaded activated carbon. Positive output was reported, with the catalytic activity of the iron on activated carbon noted to contribute to the oxidation of the DBP. In other research, Xiao et al. (2015) investigated the kinetic modelling and energy efficiency of UV/H₂O₂ treatment of iodinated trihalomethanes. Their findings indicate high efficiency of the UV/H₂O₂ system for degradation of the iodinated trihalomethanes compounds in the contaminated water. Klammerth et al. (2013) compared the treatment efficiencies of photo-Fenton and modified photo-Fenton processes at neutral pH for the treatment of emerging contaminants in wastewaters. Both methods employed effectively removed over 95% of the contaminants in the wastewater. However, photo-Fenton modified with ethylenediamine-*N*, *N'*-disuccinic acid (EDDS) at neutral pH gave a more promising result.

Also, a lot of comparative studies between advanced oxidation processes and other treatment methods such as UV irradiation and ozone alone have been investigated. Bahnmüller et al. (2015) carried out a comparative study on the degradation rates of benzotriazoles and benzothiazoles under UV-C irradiation and the advanced oxidation processes using UV/H₂O₂. Their investigation highlighted the fact that the advanced oxidation process used was a better treatment method and gave more efficient degradation of the organics as compared to UV irradiation. Adak et al. (2015) supported the position above in their research on UV irradiation and UV/H₂O₂ advanced oxidation of roxarsone and nitarosone organoarsenicals. The UV/H₂O₂ process provided a faster and more efficient transformation of the organic arsenic to the inorganic form that can be more successfully removed through conventional means. Again, Ribeiro et al. (2015) in their overview of the oxidation processes applied for water pollutants posited that ozone treatment alone promotes the partial oxidation of pollutants and an increase in the effluent biodegradability. However, complete mineralization of pollutants is difficult. Lian et al. (2015) in their study on UV photolysis of sulfonamides in aqueous solution based on optimized fluence quantification, submitted that only part of the sulphonamides can be photodegraded during UV disinfection of water and wastewater and advanced oxidation processes are necessary for high removal efficiency for the selected compounds. Hence, to overcome these challenges, the advanced oxidation processes provides a combination of techniques for better treatment result and efficiency. To this effect, Horáková et al. (2014) investigated the synergistic effects of advanced oxidation processes to eliminate resistant chemical compounds (acid orange 7, hydrocortisone, verapamil hydrochloride). It was observed that decomposition of the model chemicals was strongly improved by the synergistic effects as applied in the advanced oxidation process via photocatalytic

reaction occurring on photocatalyst TiO_2 , presence of oxidative radicals and presence of wide-range UV.

Although advanced oxidation technology has shown much capability and versatility in the removal of organics and other pollutants in wastewater, there are still a lot of gaps and challenges inherent in its processes. It has been reported that the procedure has a major setback for being employed in large scale because of its slow kinetics due to limited light fluence and photocatalytic activity (Qu et al., 2013). Advanced oxidation techniques have also been associated with possible formation of more toxic intermediate products, which when not eventually degraded pose more danger to human health and the general environment. Quero-Pastor et al. (2014) in their study on degradation and toxicity in the ozonation of ibuprofen, reported that the toxicity of the intermediate compounds formed was more toxic than the parent compound. Also, there is a growing concern about the high cost associated with the advanced oxidation processes, especially in recent times of economic recession globally. Hence, more efficient, faster and cost-effective methods and alternatives are being investigated, such as the utilization of nanomaterials to catalyse the treatment processes.

2.4 Nanotechnology

Nanotechnology is now widely perceived as the gateway to the future, to solve numerous problems and create novel materials and products which will help fill many gaps and proffer solutions to several challenges currently being experienced in all fields of human endeavour. It has generated a lot of interest in recent times in its application for the treatment and remediation of wastewater, especially in the quest for ways to maximize one of man's greatest resources, water. To this end, nanotechnology-based water treatment processes and procedures are now being vigorously investigated and more studies conducted to find methods that can most possibly remove numerous recalcitrant organics, emerging new pollutants and other persistent compounds which seem to be a major challenge for conventional water treatment facilities currently being used.

Nanotechnology is developed around particle size and surface area phenomena which brings about much higher reactivity. It encompasses the modelling, synthesis, characterization and application of structures, devices and systems, by manipulating shapes and sizes at nanometre scale (Bhattacharya et al., 2013). Various procedures for its application in the monitoring, treatment and remediation of wastewater and contaminated groundwater exist, some of which are adsorption, sensing and monitoring,

disinfection and decontamination, membrane technology and fouling control, immobilization and other multifunctional processes (Qu et al., 2013). Hence, the technology is majorly based on the use of nanoadsorbents, nanocatalysts, bioactive membranes, nanosensors, nanostructured catalytic membranes, nanotubes, magnetic nanoparticles, granules, flakes, nanorods, nanocrystals, nanosheets, nanofibres, nanowires, nanoparticles and high surface area metal particles (Bhattacharya et al., 2013). These various nanomaterials exhibit some unique properties due to their extremely reduced particle sizes such as high specific surface area, fast dissolution, high reactivity and strong sorption. Others are superparamagnetism, localized surface plasmon resonance and quantum confinement effect (Qu et al., 2012). Typically, nanomaterials are materials smaller than 100 nm in at least one dimension (Qu et al., 2013). Their utilization in several fields in recent times is majorly due to their unique intrinsic and in several cases, enhanced electronic, optical, magnetic and mechanical properties which arise mainly due to their nanometre-scale size (Kango et al., 2013).

Nanotechnology applications and processes have been recently extensively investigated in seeking the best solutions in the treatment and remediation of various compounds in contaminated water and wastewaters. For example, dyes which are used in large quantities in various industrial processes, especially in the textile industry have continuously proven difficult to remove or degrade from wastewater by conventional treatment methods due to their extreme stability (Zhang and Kong, 2011). However, various reports suggest their easy removal by nanomaterials. Bhaumik et al. (2015a) demonstrated the degradation of Congo red dye in aqueous solution by application of polyaniline/ Fe^0 composite nanofibres. Interestingly, the nanocomposites retained their original dye removal efficiency up to the 5th cycle, showing high reusability potential. Vidhu and Philip (2014) carried out the biosynthesis of silver nanocatalyst using *Trigonella foenum-graecum* seeds, the nanomaterial formed showed capability for the degradation of hazardous dyes, methyl orange, methylene blue and eosin Y by applying NaBH_4 . Also, magnetic nanoparticles coated with aminoguanidine have been reported to possess high adsorption capability and the ability to quickly remove acid dyes with varying structures, and the adsorbents showed good potential for reusability (Li et al., 2013). Zhang et al. (2013c) synthesized a novel magnetic nanomaterial which was able to effectively remove both anionic and cationic dyes from aqueous solution, with the added potential for continuous reuse. Again, Zhang and Kong (2011) reported the application of novel Fe_3O_4 /carbon nanoparticles for the removal of organic dyes from aqueous medium. Their investigation revealed that the nanocomposite exhibited promising adsorbent qualities for the removal of organic dyes, especially cationic ones, from polluted water. The removal of

methylene blue from aqueous solution by solvothermal-synthesized graphene/magnetite composite with extraordinary adsorption potential and fast adsorption rates have been previously reported (Ai et al., 2011).

Nanotechnology has been employed for disinfection in some research studies, which is a critical aspect of water and wastewater treatment processes. Lin et al. (2013) demonstrated the disinfection capability of nanomaterials by applying silver nanoparticles-alginate composite beads for drinking water disinfection. The nanocomposites were able to effectively eliminate *Escherichia coli* from the contaminated water, with a hydraulic retention time (HRT) as short as 1 minute observed for one of the synthesis method (simultaneous-gelation-reduction) for the beads. Also, Wang and Lim (2013) showed how highly efficient and stable Ag-AgBr/TiO₂ composites effectively destroyed *E. coli* under visible irradiation. The *E. coli* were almost completely inactivated within 60 minutes by the photocatalyst with a low dosage of 0.05 g L⁻¹ under white LED irradiation.

Their effectiveness for the removal of heavy metals from contaminated water has been demonstrated by several researchers. Successful removal of Pb ions using hydroxyapatite nano-material prepared from phosphogypsum waste has been reported by Mousa et al. (2016). Similarly, Pb (II) has been remediated from contaminated water using magnetic biochar decorated with ZnS nanocrystals, the process was reported to be endothermic and spontaneous (Yan et al., 2014). Arsenic removal from aqueous solution by the application of polyaniline Fe⁰ composite nanofibres as adsorbent material was reported to exhibit excellent performance, with the advantage of a simple and low-cost synthesis process (Bhaumik et al., 2015b), while a novel facial composite adsorbent was synthesized, and reported to have potential to detect and remove Cu (II) ions from water samples (Awual, 2015). The application of functionalized multi-walled carbon nanotubes bearing both amino and thiolated groups have been investigated by Hadavifar et al. (2014) to ascertain their capability for the removal of mercury in simulated and real wastewater. Their findings indicate that the as-synthesized nanomaterial was efficient for the removal of Hg (II) from wastewater. Other studies which demonstrated the application of nanomaterials for heavy metals removal from water are chromium (Parlayici et al., 2015; Bhaumik et al., 2012) and cadmium (Salah et al., 2014; Alimohammadi et al., 2013).

Nanotechnology processes have also been applied for the removal of oil in wastewater (Fard et al., 2016; Chen et al., 2013; Wang et al., 2013a), phenols (Yoon et al., 2016; Zhou et al., 2013), pharmaceuticals (Xia and Lo, 2016; Xia et al., 2014; Wei et al., 2013), membrane fouling control (Kim et al., 2016; Zhang et al., 2013a; Vatanpour et al., 2011)

and nanosensor monitoring (Homayoonnia and Zeinali, 2016; Atar et al., 2015; Gupta et al., 2015). The numerous treatment processes and procedures where nanomaterials can be applied succinctly described the versatility inherent in the technology and the huge benefit that can be derived if properly harnessed.

2.4.1 Iron oxide nanoparticles

The use of iron oxides, hydroxides and oxyhydroxides for various nano remediation and treatment processes and procedures has garnered much attention in recent times. Iron oxide nanoparticles are chemical compounds that contain iron, oxygen and in some cases hydrogen, which are naturally occurring either in the form of the soil or by deposition in rocks and mountains (Shou et al., 2015). Their presence in the natural environment is boosted by the abundance of oxygen, hydrogen and iron at the surface and inner core of the earth (Guo and Barnard, 2013). They possess high energy of crystallization which allows them to mostly form minute crystals in natural environments and when artificially synthesized, which majorly account for the high specific surface area that makes them effective sorbents and also reactive oxidants (Cornell and Schwertmann, 2003). These unique properties coupled with the numerous forms in which they exist enable their wide application for the synthesis of various nano compounds that have been investigated and used for wastewater treatment processes. Generally, iron oxide nanomaterials are now widely investigated and employed for remediation purposes due to their low cost, extensive availability, reactive surface, chemical stability and high efficiency (Patel and Hota, 2016). Some of the oxides that have found wide application in several types of research are magnetite, Fe_3O_4 (Rajput et al., 2016; Shen et al., 2016; Pastrana-Martínez et al., 2015), maghemite, $\gamma\text{-Fe}_2\text{O}_3$ (El-Qanni et al., 2016; Dutta et al., 2014; Prucek et al., 2013), hematite, $\alpha\text{-Fe}_2\text{O}_3$ (Zhang et al., 2016; Satheesh et al., 2016; Hao et al., 2014), akaganéite, $\beta\text{-FeOOH}$ (Oputu et al., 2015a; Oputu et al., 2015b; Chowdhury et al., 2014), goethite, $\alpha\text{-FeOOH}$ (He et al., 2016; Taleb et al., 2016; Xu et al., 2016) and lepidocrocite, $\gamma\text{-FeOOH}$ (Sheydaei and Khataee, 2015; Darezereshki et al., 2014; Sheydaei et al., 2014). More members of the group are feroxyhyte ($\delta\text{-FeOOH}$), ferrihydrite ($\text{Fe}_5\text{HO}_8\cdot 4\text{H}_2\text{O}$), bernalite ($\text{Fe}(\text{OH})_3$) and wüstite (FeO).

Various methods and techniques have been designed and developed for the syntheses of the numerous iron oxide nanoparticles. Some of the preparation methods generally employed are precipitation (Rajan et al., 2016), co-precipitation (Shou et al., 2015), thermal decomposition (Glasgow et al., 2016), micro-emulsion synthesis (Liang et al., 2017), plasma injection (Grabis et al., 2008), electro-spray synthesis (Basak et al., 2007),

hydrothermal synthesis (Cheng et al., 2016b), sol-gel and polyol synthesis (Basti et al., 2016; Cui et al., 2013), laser pyrolysis (Bautista et al., 2005) and sonochemical synthesis (Shafi et al., 2001). The modification or at times combination of these different synthesis techniques has given rise to many iron oxide nanoparticles with varying useful properties which have found extensive application in wastewater remediation.

Iron oxide nanomaterials are particularly in great use for removal and degradation of heavy metals, dyes, phenols, pharmaceuticals, oil and grease, and a wide variety of other organic compounds from wastewater. Treatment and remediation techniques majorly employed when applying them are sorption, membrane filtration, catalytic and ion-exchange processes (Liu et al., 2015). However, catalytic processes seem to be receiving significant attention in recent times. For instance, magnetic polyoxometalate nanohybrid has been synthesized and applied for the degradation of ibuprofen in aqueous solution under solar light. The material showed high degradation capability for ibuprofen in the presence of H_2O_2 under solar light, with the added potential of ease of photocatalyst recovery (Bastami and Ahmadpour, 2016). Similarly, Akhi et al. (2016) reported the synthesis of carbon/MWCNT/ Fe_3O_4 composite material and their subsequent use for the simultaneous degradation of phenol and paracetamol. The prepared nanofibrous catalyst effectively degraded the phenol and paracetamol with maximum removal efficiencies of 99.9% and 99.0% respectively, when used in combination with H_2O_2 (15 mmol L^{-1}) with a reaction time of 25 minutes and process temperature at 45°C . Also, Kakavandi et al. (2016) synthesized $\text{Fe}_3\text{O}_4/\text{C}$ composite which was utilized in UV-Fenton system for the degradation of tetracycline. The composite material showed much enhanced catalytic ability, and under optimum condition, 79% of the contaminant was effectively removed within 44 minutes of reaction. The composite material also exhibited potential for reuse as it retained its stability and activity after several cycles. In the same vein, Cu-doped α - FeOOH nanoflowers was applied in a photo-Fenton-like catalytic process for the degradation of diclofenac sodium. The nanoflowers showed a high catalytic activity which the researchers said might be attributed to the photocatalytic mechanism and the synergistic activation of Fe and Cu of the nanocomposite in the presence of H_2O_2 (Xu et al., 2016).

Rashid and co-workers (2015) investigated the photocatalytic property of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ nanoparticles for 2-chlorophenol (2-CP) removal in simulated wastewater. Their findings indicate that the composite nanoparticles could effectively degrade 2-CP, with complete degradation of 25 mg L^{-1} 2-CP attained in 130 minutes at a catalyst dose of 0.5 mg L^{-1} and 100-W UV irradiation. Also, 97.2% degradation of 50 mg L^{-1} 2-CP was recorded

within 3 hours. Similarly, Wang et al. (2014a) synthesized and applied hydrogel coated Fe_3O_4 magnetic composite nanospheres (Fe_3O_4 MCNs) in combination with H_2O_2 for the remediation of phenol and chemical oxygen demand (COD) in contaminated water. The nanomaterial showed excellent degradation capabilities for the removal of both phenol and COD, with 98% and 76%, respectively achieved at optimum condition. Additionally, the composites were found to exhibit high catalytic recyclability and could be used over a wide pH range. Also, Fe_3O_4 -ZnO hybrid nanoparticles have been synthesized and employed for remediation of phenol in water. The composite nanoparticles were reported to demonstrate significantly enhanced photocatalytic activity with 82.5% phenol degradation achieved, which was quite higher than 52% recorded for ZnO nanoparticles only (Feng et al., 2014). Again, nanoscale zero-valent iron nanoparticles have been applied in photoelectron-Fenton processes for degradation of phenol in wastewater with many promising results. The researchers posited that the treatment method increased the biodegradability index of the effluent (Babuponnusami and Muthukumar, 2013).

2.4.1.1 Beta iron oxyhydroxides nanoparticles

Beta iron oxyhydroxides nanoparticles (β -FeOOH) also known as akaganéite is one of the numerous oxides of iron. Its occurrence is scarce in the natural environment, only likely found in chlorine-rich spots such as hot brines and in rust in marine environments with a characteristic brown to bright yellow colour (Cornell and Schwertmann, 2003). The β -FeOOH particles are made up of monoclinic system with a framework containing tunnel-like pores partially filled with chloride ions, which has given them unique properties for their applications as electrode materials, catalysts, ion exchange materials, and adsorbents (Ebrahim et al., 2016). They are thermodynamically metastable (relative to goethite) in ambient conditions, and their nanocrystals are lath-like and coalesce into spindles or rods (Guo and Barnard, 2013). Consequently, the anti-ferromagnetic materials have high surface areas, narrow pore size distribution with different crystal shapes (Ebrahim et al., 2016). During synthesis, their chemical, structural and physical properties such as crystals orientation, morphology and particle size and shapes, are majorly tied to the composition of the iron salt and initial hydrolysis pH of the medium (liu et al., 2016).

The use of β -FeOOH nanoparticles for environmental remediation purposes has spiked a lot of interest in the last decade with several investigations reporting their synthesis and morphology (Chowdhury et al., 2014; Zhang and Jia, 2014; Villalba et al., 2013), adsorptive properties (Ebrahim et al., 2016; liu et al., 2016; Roque-Malherbe et al., 2015) and catalytic properties (Chowdhury et al., 2015; Oputu et al., 2015a; Oputu et al.,

2015b). More so, their potential for remediation and degradation of pollutants from wastewater have been of immense interest. Their application for the degradation of 4-chlorophenol with high catalytic activities of the β -FeOOH/NiO composite was reported by Oputu et al. (2015a). In combination with ozonation, the 5% β -FeOOH/NiO composite effectively removed 85% of the 4-CP after 20 minutes, in contrast with the 47% recorded for ozonation alone. The composite material could possibly be used over a wide pH range (2.8 - 10) and exhibited good recyclability. Previously, Oputu and co-workers (2015b) had reported the catalytic activities of ultra-fine nanorods used with ozonation for the removal of 4-CP from water, which also gave impressive outputs. Similarly, Xiao et al. (2016) employed β -FeOOH/reduced graphene oxide nanoparticles for the removal of 2-chlorophenol. During the Fenton-like reaction, the degradation rate constant of 2-CP was increased 2 – 5 times after the addition of the composite material.

liu et al. (2016) investigated the use of spike-like akaganéite anchored graphene oxide for defluorination processes, where the mechanism involved was reported to be that of ion-exchange. Also, Obregón et al. (2016) reported the enhanced catalytic behaviour of BiVO_4/β -FeOOH composite, where the reaction rate for the BiVO_4 alone was estimated in $7.5 \times 10^{-5} \text{ S}^{-1}$ while its combination with β -FeOOH was estimated in $18.7 \times 10^{-5} \text{ S}^{-1}$. Again, akaganéite nanoparticles and sodium salts were synthesized and applied in high-pressure carbon dioxide adsorption experiments. The findings suggest that the synthesized material could possibly act as a high-pressure adsorbent (Roque-Malherbe et al., 2015).

In another report, Zhang and co-researchers (2015) investigated the treatment potential of novel TiO_2/β -FeOOH nanocomposites for the photocatalytic reduction of Cr (VI) under UV irradiation in an aqueous medium. The synthesized photocatalyst (tagged $25\text{TiO}_2/\beta$ -FeOOH) exhibited good treatment capabilities, with ~100% reduction efficiency obtained after 120 min. Similarly, akaganéite and goethite nanoparticles were applied for the remediation of oxolinic acid, widely used quinolone antibiotics in aquafarming. The β -FeOOH nanoparticles exhibited better binding of the oxolinic acid than α -FeOOH, this was attributed to the higher isoelectric point of the β -FeOOH (9.6 - 10) as compared to α -FeOOH (9.1 – 9.4). The report suggests that β -FeOOH can be applied to remediate oxolinic acid contaminated water (Marsac et al., 2015).

From the foregoing, the β -FeOOH nanoparticles and its composite materials exhibit interesting remediation potential and capabilities. Therefore, its use and application for more environmental remediation processes continue to garner more interest, especially

for the treatment and removal of numerous emerging contaminants like phenols and pharmaceuticals.

2.5 Nanocomposites

There is a growing concern in the global scientific community about the increasing use of nanotechnology for numerous applications in virtually all spheres of human endeavour. This stems from the potential deposition of these various nanomaterials in the environment and probable adverse effects that they may cause. Hence, the drive in the application of nanotechnology should be efficient and safe applications that leave the environment and living organisms with fewer pollutants. In this regard, nanotechnological procedures and processes should be subjected to analytical assays to ascertain how eco-friendly and safe they are after application.

Growing concerns are fuelled by preliminary results from several investigations indicating possible adverse effects from nanomaterials. For example, oxidative stress and nanotoxicity studies of TiO_2 and ZnO on gill tissue (WAG) of *Wallago attu* were reported to show acute toxicity. The researchers concluded that reactive oxygen species (ROS) mediated cytotoxicity and genotoxicity was exhibited by these metallic nanoparticles, with a dose-related increase in DNA damage, lipid peroxidation and protein carbonylation (Dubey et al., 2015). Poynton et al. (2012) investigated the toxicogenomic response of nanotoxicity in *Daphnia magna* exposed to silver nitrate and coated silver nanoparticles, where the biological processes disrupted by Ag nanoparticles include protein metabolism and signal transduction.

It is generally assumed that nanoparticles can easily enter cells, tissues, organelles, and functional biomolecular structures which could subsequently cause damage to the living organism (Fischer and Chan, 2007). However, some research findings are speculative that the small particle size may not be entirely responsible for their toxicity. Karlsson et al. (2009) in their comparison between nano and micrometre size, reported that the microparticles of TiO_2 caused more DNA damage compared to the nanoparticles; iron oxides (Fe_2O_3 and Fe_3O_4) micro and nanoparticles showed no significant difference in their toxicological effects; while CuO nanoparticles showed much higher toxicity than the micromolecules. Fu et al. (2014) in their report indicated that toxicity of nanoparticles could possibly be linked to the generation and overproduction of reactive oxygen species that leads to failure of cells to maintain normal physiological redox-regulated functions,

with resultant DNA damage, unregulated cell signalling, change on cell motility, cytotoxicity, apoptosis and cancer initiation.

Therefore, in the continued quest to maximize the inherent potentials and efficiencies associated with the use of nanotechnology, more studies are being conducted to fashion out the best ways to apply them for water treatment purposes. The application of various nanoparticles alone has been associated with numerous challenges such as loss of the particles, difficult recovery procedures after use and inherent cost implication, aggregation of the nanoparticles with resultant reduction of reactive surfaces and the health risks that might arise due to their release into the natural environment (Ebrahim et al., 2016; Muliwa et al., 2016; Samiey et al., 2014; Zhao et al., 2011; Lin et al., 2005). This has brought about the incorporation of synthesized nanoparticles in support materials. Thereby, preventing losses and aggregation of nanoparticles, making their recovery after use easier, eliminating the extra cost of recovery, and making their application process safer. Also, a lot of synergistic effects have been reported in some of these composite materials (Bhaumik et al., 2015a; Tang et al., 2014; Wu et al., 2014).

In this latest trend, various support materials have been investigated over time with different interesting research outcomes. Some materials that have been employed as support in composites are graphene and graphene oxide (Xiao et al., 2016; Zhang et al., 2016; Sharma et al., 2015; Guo et al., 2012), metals and metal oxides (Bastami and Ahmadpour, 2016; Xu et al., 2016; Rashid et al., 2015; Feng et al., 2014), activated carbon (Abussaud et al., 2016; Jamshidi et al., 2016; Nekouei et al., 2016), cellulose and chitosan-based materials (He et al., 2016; Haldorai et al., 2015; Sun et al., 2015; Xiong et al., 2014) and polymers (Basti et al., 2016; Ebrahim et al., 2016; Zhou et al., 2016). However, some of the support materials have their application shortcomings. For example, chitosan has been reported to have pH related challenges, where it readily dissolves in water at acidic conditions (Kim et al., 2015; Chiou et al., 2004), which could lead to the release of the embedded or attached nanoparticles to the environment. They possess intrinsic low surface area and pose difficulty during separation processes from aqueous phase (Badrudodoza et al., 2013). Also, their often poor mechanical strength leads to shrinkage or swelling of the composites (Kim et al., 2015), coupled with other operational challenges. For activated carbon, its disordered pore structures most being in the micropores range (pores with size $\leq 2\text{nm}$) with resultant sluggish mass transfer kinetics and long equilibration time (Li et al., 2015), may invariably pose a challenge for its effective application as support material. Additionally, they are susceptible to process engineering challenges such as dispersion of the activated carbon powder during flow

processes (Luo and Zhang, 2009). Graphene and its oxides support materials are prone to dispersity challenges due to their strong intermolecular interaction (van der Waals force), with resultant aggregation (Kamat, 2010). Their low solubility in both aqueous and organic solutions equally poses processability challenges (Yan et al., 2012). Similarly, nanomaterials incorporated into some metal oxide supports lose their reactivity or show no change in reactivity due to the very low lying Femi-levels of the oxidic materials (i.e. they tend to be too stable to give away their electrons easily) (Li and Antonietti, 2013). In an investigation into the catalytic effects of NiO/ β -FeOOH composite for the degradation of 4-CP, Oputu and coworkers (2015a) noted that TiO₂/ β -FeOOH and Al₂O₃/ β -FeOOH composites gave low efficiency during the catalytic ozonation of 4-CP. Polymeric support materials seem to be more suitable as they provide high thermal, mechanical and environmental stability, as well as excellent processability (Lofrano et al., 2016). Additionally, the wide array of polymeric materials with their numerous functional groups provides a huge opportunity for enhanced nanocomposites fabrication.

2.5.1 Polymeric nanocomposites

Polymeric nanocomposites (PNCs) are specially fabricated materials which contain appropriate inorganic nano-objects incorporated into or onto selected polymeric matrices (Khezri and Mahdavi, 2016). The use of polymeric nanocomposites is currently viewed as one way to solve the inherent challenges of using ordinary nanoparticles, powder, flakes, rods, sheets, and fibres (Lofrano et al., 2016). Deployment of polymers as support materials in nanotechnological processes and procedures for removal of various pollutants from wastewater have been researched extensively in recent times (Huang et al., 2019b; Sharma et al., 2019; Youssef et al., 2019; Peydayesh et al., 2018; Atta et al., 2016; Akl et al., 2016; Cho et al., 2016; Lü et al., 2016; Reddy et al., 2016; Tran et al., 2016; Wanna et al., 2016). Polymeric materials with embedded nanomaterials are most often transformed into composites with enhanced properties such as improved membrane permeability, fouling resistance, mechanical and thermal stability, higher adsorption and photocatalytic activities (Qu et al., 2012). These properties depend on the type of nanoparticle incorporated, their size and shape, their concentration and interaction within the polymer matrix (Kango et al., 2013). Also, the technique employed in the PNCs modification determines their selectivity, reusability and remediation capacity (Atta et al., 2016). Generally, the properties of nanocomposites are mainly influenced by the size scale of its component phases and the degree of interaction between the two phases (Hussain et al., 2006). Inherent advantages of polymers as support material for PNCs fabrication are their easy-forming and excellent pore-forming characteristics, selective

transfer of chemical species and ease of functionalization, and relatively low cost of the materials (Ng et al., 2013).

The selection of the appropriate polymer to use is guided mainly by their mechanical, thermal, electrical, optical, and magnetic properties. Additionally, properties such as hydrophobic/hydrophilic balance, chemical stability, bio-compatibility, opto-electronic properties and chemical functionalities should also be considered (Jeon and Baek, 2010). Polymer matrices can be used for PNCs fabrication singly (Zhou et al., 2016) or by a combination of two or more polymers (Reddy et al., 2016). In each case, the functionalities of the polymer backbone are considered in relation to the intended use of the PNCs.

Different polymer-based materials possess unique properties which make them ideal for deployment in certain areas or applications of wastewater treatment. For example, polypyrrole a conducting polymer is ideal for fabricating PNCs for monitoring and sensing purposes (He et al., 2014). However, the inherent versatility of polymers also allow the use of polypyrrole in the synthesis of excellent PNCs employed as adsorbents, singly (Muliwa et al., 2016; Hosseini et al., 2015; Sahmetlioglu et al., 2014) or in combination with other polymer-based matrices (Chauke et al., 2015) for the removal of various pollutants from wastewater. Furthermore, it can still be used in the synthesis of PNCs employed as catalysts for remediation purposes (Zhang et al., 2013b). Similarly, data presented in Table 2.3 showed that PNCs fabricated with polyethersulfone has been applied in photocatalytic processes (Hir et al., 2017), membrane filtration operations (Zinadini et al., 2017; Rahimi et al., 2016), and microbial control operations (Jo et al., 2016; Basri et al., 2010). Basically, polymeric materials offer a lot of versatility, processability and stability when applied as homogenous systems or as copolymers or graft polymers for PNCs synthesis (Lofrano et al., 2016). These unique properties contribute to making them support materials of choice for nanoparticles.

Polymer matrices are, however, of different categories. Those mostly utilized for PNCs fabrication can broadly be divided into two major groups called thermosetting and thermoplastic polymers, based on their interaction or reaction to applied heat. When subjected to heat, thermoplastic polymers become soft or molten and pliable, while the heating of thermosets brings about their degradation without going through the fluid phase (Sabu et al., 2016). Both groups of polymers have been used in the synthesis of PNCs employed for wastewater remediation, each with its inherent advantages and disadvantages. Also, PNCs have been fabricated by a mix of polymers from both groups

with resultant synergistic effect when tested for various applications (Han, 2013; Mirmohseni and Zavareh, 2010). Similarly, carbon microstructures obtained from thermal treatment of a blend of both polymers were reported as promising adsorbents by Wang and co-researchers (2012b).

Thermosets are considered an important class of polymers for PNCs fabrication due to their high thermal and structural stability; these properties depend largely on their chemical structure and crosslinking density, as well as, the processing conditions such as temperature and pressure (Shenogina et al., 2013). Their inherent high dimensional stability provides high mechanical, thermal and environmental resistance during various applications (Hameed et al., 2015). The major challenge with the processing and use of thermosets is their irreversibility once cured and susceptibility to decomposition at high temperature (Garcia et al., 2014). Hence, moulding appropriately as desired during processing is paramount because it cannot be transformed or remoulded after the crosslinking reaction. Common examples of thermosetting polymers are polyimides, polyurethanes, epoxies, polyesters and phenolics (Halley and Mackay, 1996). Thermosetting polymers have been employed for PNCs syntheses, and the composites formed have found various uses in water treatment and remediation processes (Cheng et al., 2016a; Benjwal and Kar, 2015; Muñoz et al., 2015; Motoc et al., 2013).

Thermoplastic polymers have been widely applied for the fabrication of PNCs due to their good mechanical properties, durability and versatility in processing that allows for their use in numerous forms (Coiai et al., 2015). Their unique properties are derived from their long-chain entanglement with resultant temporary crosslinks and the ability to slip past one another when subjected to intense local stress (Cogswell, 1992). This class of high application polymers include polyethylene, polypropylene, polystyrene, poly(vinyl chloride), polyvinylidene fluoride, polyethersulfone, polyethylene terephthalate, polyamide, styrene acrylonitrile, polycarbonate, polybutylene terephthalate, poly(methyl methacrylate), poly (p-phenylene oxide) and acrylonitrile butadiene (Najafi, 2013). Thermoplastic polymers have been employed singly or as a blend of polymers in the fabrication of high-performance filtration and antifouling membranes (de Lannoy et al., 2013; Lee et al., 2013), sensing and monitoring membranes (Pule et al., 2015; Devi and Umadevi, 2014), adsorbents (Ebrahim et al., 2016; Ravishankar et al., 2016), catalysts (Pathania et al., 2016; Ummartyotin and Pechyen, 2016), and also as disinfectant and antimicrobial membranes (Ghaffari-Moghaddam and Eslahi, 2014; Schiffman and Elimelech, 2011) employed for water or/and wastewater treatment and remediation

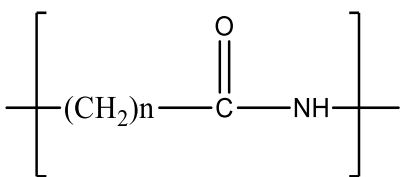
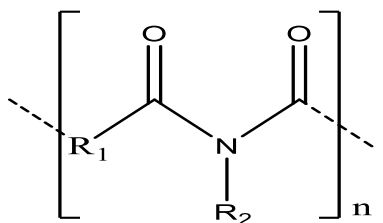
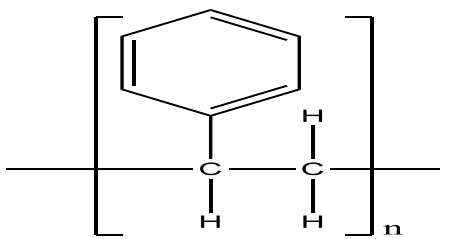
purposes. Table 2.3 shows some common polymer matrices utilized for PNCs synthesis and their numerous areas of applications.

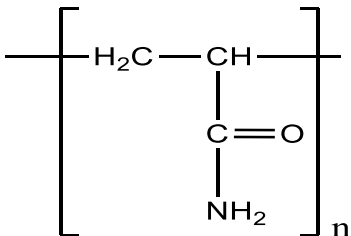
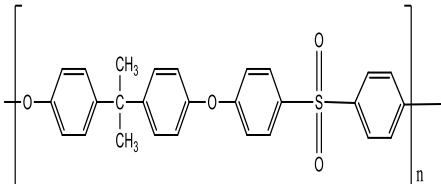
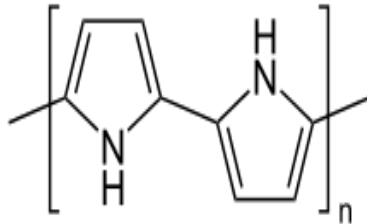
2.5.2 Polyamide polymer

Polyamide are part of the important engineering thermoplastic polymers. The polymer possesses exceptional mechanical, abrasion, wear, barrier, and crystalline properties (Farias-Aguilar et al., 2014; O'Neill et al., 2014; Espeso et al., 2006; Palabiyik and Bahadur, 2000). Its excellent hydrophilicity, thermal, and chemical stability has enabled it to be used in the fabrication of water treatment membranes, adsorbents and catalysts (Basaleh et al., 2019; Ali et al., 2018; Wang et al., 2015a; Wang et al., 2015b; Lombardi et al., 2011). Polyamides exhibit good compatibility with numerous nanomaterials (Özdilek et al., 2004) which create the opportunity for use in the production of many hybrid nanocomposites. They possess reactive sites in their chains via the active amines and carboxylic acid groups (Oh et al., 2019). This serves as anchor points for nanomaterials when incorporated into the polyamide matrix. Also, they are widely utilised in various fields due to their cost-effectiveness, lightweight and enhanced load resistant properties (Dinari et al., 2016).

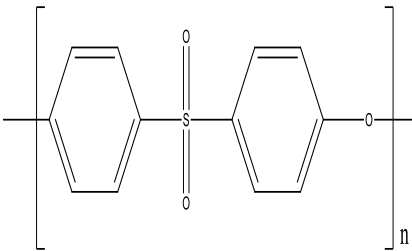
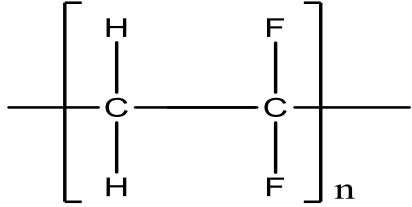
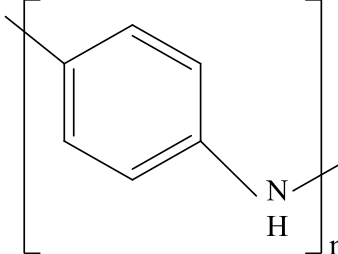
A major selling point for the polymer is the relatively easy syntheses procedures. Several of these are well established high-yield methods (Espeso et al., 2006). The syntheses procedures include the synthesis via the polycondensation route using bifunctional monomers from amines, amino acids and dicarboxylic acids (Wang et al., 2015a). Polyamide is widely produced through the ring-opening polymerization of lactams (O'Neill et al., 2014), and polycondensation reaction of caprolactam which has ring structures (Oh et al., 2019). More so, other methods are being researched for improved functional properties and ease of synthesis (Farias-Aguilar et al., 2014).

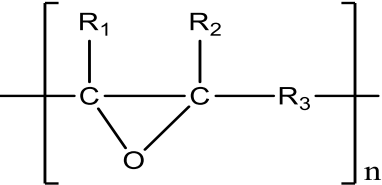
Table 2.3: Common polymers for PNCs synthesis and their reported area of applications

Polymer matrix	Chemical formula & structure of the repeat unit	Some reported application area	Target pollutant/application	Reference
‡Polyamide	$(\text{CONH}_2)_n$ 	Photocatalysis Membrane filtration Photocatalysis & microbial control	MB dye Desalination ($\text{NaCl}/\text{Na}_2\text{SO}_4$) Desalination (NaCl) Congo Red; E. coli	Ummartyotin and Pechyen (2016) Yin et al. (2016); Kim et al. (2014) de Lannoy et al. (2013) Pant et al. (2011)
†Polyimide	$(\text{CO-NR}_2)_n$ 	Sensing/detection	Bisphenol A	Cheng et al. (2016a)
‡Polystyrene	$(\text{C}_6\text{H}_5)_n$ 	Adsorption Demulsification Photocatalysis Sensing/detection	Pb(II) Oil in water MB dye 17β-estradiol COD detection/measurement	Ravishankar et al. (2016) Reddy et al. (2016); Yu et al. (2015) Vaiano et al. (2014) Pule et al. (2015) Gutierrez-Capitan et al. (2015)

Polymer matrix	Chemical formula & structure of the repeat unit	Some reported application area	Target pollutant/application	Reference
‡Polyacrylamide	$(C_3H_5NO)_n$ 	Photocatalysis & microbial control Photocatalysis Adsorption & photocatalysis Flocculation	Congo red; <i>E. coli</i> & <i>S. aureus</i> Congo red & MO dyes MG & Rhodamine B dyes Dewatering of sludge	Sharma et al. (2016) Pathania et al. (2016) Kumar et al. (2014) Huang and Ye (2014)
‡Polysulfone	$(C_{27}H_{26}O_6S)_n$ 	Membrane filtration Adsorption Microbial control	Antifouling Pb(II) <i>E. coli</i>	Lee et al. (2013) Abdullah et al. (2016) Schiffman and Elimelech (2011)
‡Polypyrrole	$(C_4H_5N)_n$ 	Photocatalysis & sensing/detection Adsorption	Rhodamine B dye Cr(VI) Cu(II) Pb(II) Vanadium	He et al. (2014) Yao et al. (2014); Setshedi et al. (2013) Hosseini et al. (2015) Sahmetlioglu et al. (2014) Mthombeni et al. (2015)

Polymer matrix	Chemical formula & structure of the repeat unit	Some reported application area	Target pollutant/application	Reference
‡Polydimethyl Siloxane	$(C_2H_6OSi)_n$ $\left[\text{---O---Si(CH}_3\text{)}_2\text{---} \right]_n$	Ion-exchange Sensing/detection Adsorption	Pb(II) & Hg(II) DO detection Toluene, sulfide, thiophenol & thioether	Chavan et al. (2015) Hsu et al. (2014) Scott et al. (2010)
‡Polyvinyl alcohol	$(C_2H_4O)_n$ $\left[\text{---CH}_2\text{---CH(OH)---} \right]_n$	Photocatalysis Sensing/detection Microbial control & Sensing/detection	MB dye Potassium ferricyanide <i>E. coli</i> , <i>P. aeruginosa</i> , <i>B. cereus</i> & <i>S. aureus</i> ; Cd(II)	Jung and Kim (2014) Mondal et al. (2017) Devi and Umadevi (2014)
‡Polyacrylonitrile	$(C_3H_3N)_n$ $\left[\text{---CH}_2\text{---CH(C}\equiv\text{N)---} \right]_n$	Membrane filtration Microbial control (filtration process)	MO, Acid brilliant blue & chrome blue-black R dyes <i>S. aureus</i> & <i>E. coli</i>	Liang et al. (2016) Zhang et al. (2011)

Polymer matrix	Chemical formula & structure of the repeat unit	Some reported application area	Target pollutant/application	Reference
‡Polyethersulfone	$(C_{12}H_8OSO_2)_n$ 	Photocatalysis Membrane filtration Microbial control	MO dye Direct Red 16 & Antifouling Antifouling Desalination (NaCl/Na ₂ SO ₄) <i>E. coli</i> & <i>S. aureus</i>	Hir et al. (2017) Rahimi et al. (2016) Zinadini et al. (2017) Bagheripour et al. (2016) Jo et al. (2016); Toroghi et al. (2014); Basri et al. (2010)
‡Polyvinylidene fluoride	$(C_2H_2F_2)_n$ 	Photocatalysis Catalysis Membrane filtration	Nonylphenol Organic contaminants Oil in water Desalination (NaCl)	Dzinun et al. (2015b) Alpatova et al. (2015) Yan et al. (2009) Obaid et al. (2016)
‡Polyaniline	$(C_6H_7N)_n$ 	Adsorption Microbial control & photocatalysis Photocatalysis Sensing/ detection Ion-exchange	Cr(VI) <i>E. coli</i> & MB dye MB, MG, MO & MR dyes MB & MG dyes Phenanthrene Pb(II) Trimethylamine & Cu(II) & Pb(II);	Ebrahim et al. (2016) Haspulat et al. (2013) Gülce et al. (2013) Tovice et al. (2014) Khan et al. (2016a) Zheng et al. (2008) Sharma et al. (2014)

Polymer matrix	Chemical formula & structure of the repeat unit	Some reported application area	Target pollutant/application	Reference
		microbial control	<i>S. aureus</i>	
†Epoxy	$(R_1COCR_2R_3)_n$ 	Electrocatalysis & sensing/detection Adsorption & Photocatalysis	Chlorine; Ibuprofen Pb(II), Cd(II) & Cr(II); MB dye	Muñoz et al. (2015); Motoc et al. (2013) Benjwal and Kar (2015)

Footnote: ‡ denotes thermoplastics; † denotes thermosets

2.5.3 Synthesis of polymeric nanocomposites

Synthesis of polymeric nanocomposites (PNCs) involves the incorporation of various inorganic nanomaterials into polymer-based matrices. The PNCs can basically be prepared via two major routes as illustrated in Figure 2.4; *in situ* synthesis and blending or direct compounding (Zhao et al., 2011). Both methods have their inherent advantages and disadvantages, and researchers most often tend to apply the one that is most convenient for them and/or the one that will give a better composite matrix. In all, the choice of synthesis employed is based on a number of factors such as polymeric system, area of application, size requirement etc. (Rao and Geckeler, 2011).

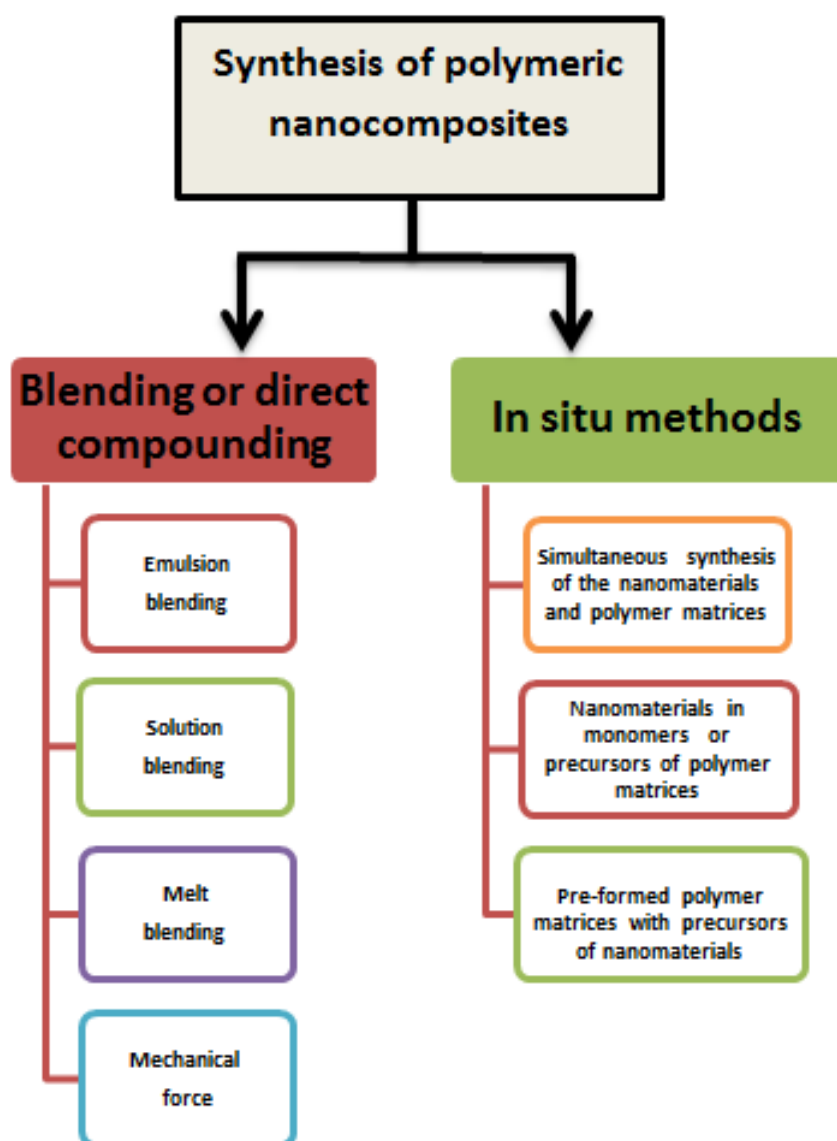


Figure 2.4: Synthesis routes for polymeric nanocomposites

2.5.3.1 *In situ* synthesis of PNCs

A wide range of PNCs have been synthesized following *in situ* procedures (see Table 2.4), with the developed nanomaterials possessing unique functionalities in their application for the remediation of water/wastewater. *In situ* techniques are centred on three basic processes which involve;

- Addition of already synthesized nanoparticles into monomers or precursors of polymeric materials
- Incorporation of pre-formed polymer matrices with precursors of nanoparticles, and
- Simultaneous synthesis of the nanoparticles and the polymeric support (Lofrano et al., 2016).

The application of *in situ* synthesis method seems to be more acceptable and used in recent times as can be seen in Table 2.4. The method brings about more uniform dispersion of the nanoparticles in the polymer support material with interpenetrating networks which enhances the compatibility between the constituents and build strong interfacial interactions (Kango et al., 2013). *In situ* methods were recently used to synthesize novel amino-amidoxime nanocomposites consisting of 2-acrylamido-2-methyl propane sulfonic acid P(AN-co-AMPS) and acrylamidoxime/2-acrylamido-2-methyl propane sulfonic acid amido-p(AN-co-AMPS) as the polymer supports while magnetite was the nanoparticles utilized. The technique employed pre-form polymerization, followed by synthesis of the nanoparticles *in situ* with the polymer matrix. The SEM micrographs were reported to show a spherical structure 5 – 12 nm in size, indicating the production of iron oxide nanoparticles. The nanocomposites were equally stated to possess high adsorption capacity for cationic MB dye and heavy metal ions (Atta et al., 2016). In a similar study, Akl et al. (2016) synthesized magnetite acrylamide amino-amidoxime nanocomposites using the *in situ* method. Pre-form polymers were utilized with the prior synthesis of cross-linked 2-acrylamido-2-methylpropane sulfonic acid-co-acrylamide amine amidoxime with MBA (AO/AMPS-MBA). This was followed by the *in situ* synthesis of the magnetite nanoparticles by immersion of 0.5 g of dried AO/AMPS-MBA into freshly prepared iron cation filtrate at room temperature for 24 hours and subsequent treatment with 100 mL of 28% ammonia solution. The developed PNCs were utilized for the treatment of U(VI) in aqueous solution with reported excellent sorption properties.

PNCs were synthesized by the conventional sol-gel process using tailor-made alkoxysilane-functionalized amphiphilic polymer precursors (M-APAS). The composite

materials were produced using pre-formed M-APAS, followed by the incorporation of SiO₂ nanoparticles through an *in situ* procedure. The PNCs formed was used for the removal of water-soluble dye (organe-16) and water-insoluble dye (solvent blue-35). They were reported as promising sorbent materials for the removal of both hydrophilic and hydrophobic pollutants from water (Cho et al., 2016). Lü et al. (2016) employed *in situ* procedures for the synthesis of poly(*N*-isopropyl acrylamide) grafted magnetic nanoparticles. In this case, the magnetic iron oxide nanoparticles were firstly prepared and modified with SiO₂, followed by addition of 0.2 g of the modified nanoparticle and 1.0 g of *N*-isopropyl acrylamide (monomer) into 38.8 g of water. Other subsequent steps were carried out to complete the polymerization process and attain the polymer-grafted magnetic nanocomposites which were envisaged as potentially promising and environmentally friendly materials for the treatment of emulsified oily water. Also, Tran et al. (2016) produced poly(1-naphthylamine)/Fe₃O₄ composite by firstly synthesizing the Fe₃O₄ nanoparticles before incorporation along with the monomer and other additives for the polymerization process.

Wanna et al. (2016) synthesized superparamagnetic iron oxide nanoparticles (SPIONs) functionalized polyethylene glycol bis(amine) through an *in situ* process whereby the nanocomposites were prepared by emulsion polymerization in an aqueous solution of previously prepared SPIONs. While, Reddy and co-workers (2016) fabricated polystyrene/Fe₃O₄ and poly(butyl acrylate)/Fe₃O₄ nanospheres by the prior synthesis of the Fe₃O₄ nanoparticles, and subsequent addition into the monomers and other additives for the polymerization step. Similar *in situ* process where the Fe₃O₄ was the first synthesis before incorporation into the polymeric support was reported by Yu et al. (2015).

Simultaneous *in situ* synthesis of both inorganic nanoparticles and the polymer support matrix has been equally reported with interesting results. Yang et al. (2014) carried out the simultaneous *in situ* synthesis of silver/polymer nanocomposites using UV photopolymerization. The first step they employed was the preparation of the organic silver precursor (silver dedocanoate), followed by its addition to UV curable monomer (3,3,5-trimethyl-cyclohexyl methacrylate). The mixture was then subjected to other synthesis processes and conditions to finally obtain the silver/polymer nanocomposites. Morphological studies confirmed the formation of highly dispersed silver nanoparticles in the polymer matrix with a diameter in the range of 3.0 – 4.2 nm. Zhu and co-workers (2012) also performed a simultaneous *in situ* synthesis for the fabrication of thermosensitive poly(*N*-isopropyl acrylamide)/Au nanocomposites hydrogels. This was effectively done by gamma-radiation-assisted polymerization of *N*-isopropyl acrylamide

monomer aqueous solution in the presence of $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$. The polymer nanocomposites obtained were reported to show excellent catalytic performance for the reduction of O-nitroaniline. Again, Sangermano et al. (2007) reported the simultaneous *in situ* synthesis of silver-epoxy nanocomposites carried out by photoinduced electron transfer and cationic polymerization process. Cationically polymerizable monomer 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate resin containing AgSbF_6 and 2,2-dimethoxy-2-phenyl acetophenone was subjected to UV irradiation for the formation of the nanocomposites materials. TEM micrographs confirmed the formation of silver nanoparticles in the polymer matrix with size distribution ranging between 10 – 50 nm.

More recently, simultaneous *in situ* synthesis was used by Morselli et al. (2016) for the formation of porous zinc oxide/poly(methylmethacrylate) nanocomposites. The PMMA/zinc acetate films were firstly prepared, followed by the *in situ* localized syntheses of ZnO nanoparticles and porous PMMA matrix by pulsed laser irradiation of the solid PMMA/ $\text{Zn}(\text{OAc})_2$ films. The ZnO nanoparticles were reported to have an average particle size of 9 nm. Similarly, Shimizu and co-workers (2016) prepared Cu/Ni alloy nanoparticles embedded in thin polymer layers using simultaneous *in situ* processes. Firstly, they prepared ion-codoped precursor films by reacting hydrolysed polyimide films (5 μm thick) with an aqueous solution of both copper chloride and nickel chloride at room temperature. The resulting material was subsequently subjected to high heat treatment under hydrogen atmosphere to obtain the Cu/Ni/polymer nanocomposites. The simultaneous *in situ* approach was reported to provide the ability for conscious manipulation of certain aspects of the nanocomposite's microstructure such as composition, size and interparticle distance.

2.5.3.2 Blending or direct compounding

Blending or direct compounding is perceived as a simple technique to synthesize polymeric nanocomposites. Blending techniques such as solution, emulsion, melt blending and application of mechanical force, involves the direct incorporation of the nanoparticles into the polymer matrix. This usually gives an easy, fast synthesis of PNCs. However, the inherent challenge of agglomeration of the nanoparticles may result in their non-uniformed distribution in the polymer blend (Kango et al., 2013).

Despite the challenge highlighted above for blending techniques, it has found continuous application in the synthesis of PNCs. Recently, the method was used for the synthesis of polyaniline/ β -FeOOH nanocomposites by Ebrahim and co-researchers (2016). The

polyaniline and β -FeOOH were prepared separately by chemical oxidative polymerization and co-precipitation techniques respectively. The PNC was subsequently formed by physically mixing different proportions of both polyaniline and β -FeOOH by grinding in a mortar. HRTEM images of the prepared PNC showed that the phases of β -FeOOH embedded in the PNC had the crystallinity and morphology of the pristine one, with diameter between 8.95 – 16.21 nm. The PNC also showed excellent removal efficiency for Cr (VI). Hwang and Hsu (2013) prepared organically modified silica materials (μ m and nm) and polypropylene (PP) composites using melt blending techniques. The PNCs were prepared through the blending of the inorganic additives with PP using a kneader. This was followed by moulding of the composite materials using conventional and mucell injection moulding processes separately. Similarly, Zu et al. (2014) synthesized polypropylene/silica composite particles via emulsion sol-gel approach in the presence of melt polypropylene. The thermal gravimetric and differential scanning results of the PNCs were reported to have interpenetrating structure and good thermal stability.

Again, polypropylene/nano- CaCO_3 composites were obtained from a two-stage modular extruder with the assistance of supercritical carbon dioxide (Sc-CO_2). The PP/ nano- CaCO_3 composites (100/10) were prepared by melt blending using Sc-CO_2 as blowing agent. The PNCs formed were reported to have improved impact strength, which was attributed to the uniform dispersion of nano CaCO_3 in the PP matrix (Chen et al., 2016). Various blending techniques using Sc-CO_2 assisted synthesis for the dispersion of inorganic additives into polymer matrices have been reported severally in previous works (Chen and Baird, 2012; Chen et al., 2012; Ma et al., 2007; Nguyen and Baird, 2007).

Table 2.4: Some recently fabricated PNCs and synthesis processes employed

Polymer material	Nanoparticles employed	Synthesis method	Target pollutant(s)	References
Acrylic acid/p(N-vinyl-2-pyrrolidone)	ZnO	<i>^bIn situ</i>	Methylene blue dye	Ali et al. (2016)
Polyacrylamide amino-amidoxime	Fe_3O_4	<i>^bIn situ</i>	Methylene blue dye	Atta et al. (2016)
Polyacrylamide amino-amidoxime	Fe_3O_4	<i>^bIn situ</i>	U(VI) ions	Akl et al. (2016)
Polyethersulfone	Fe-NiO	Solution blending	Salt rejection (NaCl & NaSO_4)	Bagheripour et al. (2016)
Alkoxysilane (functionalized amphiphilic polymer)	Silica nanoparticles	<i>^bIn situ</i>	Organe-16 and solvent blue-35	Cho et al. (2016)

Polymer material	Nanoparticles employed	Synthesis method	Target pollutant(s)	References
	(Aerosol 200)		dyes	
Poly(vinylidene fluoride)	TiO ₂	Solution blending	Nonylphenol	Dzinun et al. (2015b)
Polyaniline	B-FeOOH	Blending (Mechanical force)	Cr(VI)	Ebrahim et al. (2016)
[2-(methacryloyloxy)ethyl] dimethylhexadecylammonium bromide	Bentonite	^a <i>In situ</i>	Reactive black 5	Erdem et al. (2016)
Polyacrylamide	Modified montmorillonite	^a <i>In situ</i>	Dewatering of sludge	Huang and Ye (2014)
Polyethersulfone grafted with Poly(1-vinylpyrrolidone-co-acrylonitrile)	ZnO	Solution blending	Bacterial	Jo et al. (2016)
Poly(N-isopropylacrylamide-co-allylacetic acid)	Ag	^b <i>In situ</i>	Nitrobenzene	Khan et al. (2016c)
Polyaniline and polyether sulfone	Hydroxylated-MWCNT	^a <i>In situ</i>	Natural organic matter (NOM)	Lee et al. (2016)
Poly(N-isopropylacrylamide)	Fe ₃ O ₄ (modified with SiO ₂)	^a <i>In situ</i>	Emulsified oil	Lü et al. (2016)
Poly(dimethylamoniethyl methacrylate)	AuNP	<i>In situ</i>	Rhodamine B, Methyl orange and Eosine Y dyes	Mogha et al. (2017)
Polystyrene and Poly(butylacrylate)	Fe ₃ O ₄	^a <i>In situ</i>	Oil	Reddy et al. (2016)
Polyethylene glycol	Fe ⁰	Solution blending	Lindane (organochlorine pesticide)	San Roman et al. (2016)
Poly(1-naphthylamine)	Fe ₃ O ₄	^a <i>In situ</i>	As(III)	Tran et al. (2016)
Polyethylene glycol bis(amine)	SPIONs (Fe ₃ O ₄)	^a <i>In situ</i>	Pb(II), Hg(II), Cu(II) & Co(II)	Wanna et al. (2016)
Polystyrene	Fe ₃ O ₄	^a <i>In situ</i>	Oil	Yu et al. (2015)
Polypyrrole	Fe ₃ O ₄ (Magnetic secondary fly ash)	^a <i>In situ</i>	Cr(VI)	Zhou et al. (2016)
Poly(N-isopropylacrylamide)	Au	^c <i>In situ</i>	O-nitroaniline	Zhu et al. (2012)

a= synthesized NPs added to monomers or precursors of polymeric matrices; b= Pre-form polymer matrices with precursors of NPs; c= Simultaneous synthesis of NPs and polymeric matrices.

2.5.4 Characterization of PNCs

Characterization of PNCs comprises the use of different optical, electron microscopy, thermal and other techniques to elucidate the morphological, structural and functional properties inherent in them. These techniques often used to complement one another, are requisite and standard procedure that must be carried out as they provide basic and needed information specific to each fabricated PNC. Essentially, characterization is employed to provide data which help to analyse the different facet of PNCs. These include;

- Level of distribution of the nanomaterial in the polymeric matrix bearing its orientation or alignment as related to the synthesis method
- Effects of the embedded nanomaterial distribution or dispersion on the PNC
- Interaction of the nanomaterials with the functional groups present in the polymer matrix
- Effects of changes in process parameters and synthesis routes on the morphology and structural properties, and
- Provision of a wide spectrum of properties to ascertain possible application potential of the PNC (Mittal, 2012).

Transition electron microscopy (TEM) technique is currently being used to obtain morphological data such as shape, size and distribution of the nanocomposites. It provides qualitative information for the assessment of the inner structure and spatial distribution of the various phases through direct visualization (Monticelli et al., 2007). Selected area electron diffraction (SAED) microstructure data can also be gotten through TEM technique, to obtain structural information of PNCs like crystalline symmetry, unit cell parameter, and space group. Similarly, SEM micrographs provide data such as surface morphology, porous or crystalline nature, and dispersion level of the nanoparticles in PNCs. Atomic force microscopy (AFM) is used to analyse the surface morphology and roughness of fabricated nanocomposites. Also, X-ray diffraction (XRD), a rapid, non-destructive analytical technique used for phase identification of a crystalline or semi-crystalline material, and can provide information on unit cell dimensions and nanoparticle dispersion (García-Gutiérrez et al., 2007). The technique supplies necessary information for the elucidation of the structural properties of PNCs. Furthermore, FTIR technique is used to confirm the presence of the dispersed nanomaterials in the PNCs, mostly from spectra changes and addition of new peaks to the polymeric material. It also provides information about the nature of the interaction between the nanomaterials and polymer

functional groups when present. Energy dispersive x-ray spectroscopy (EDX) is used to further characterize PNCs to ascertain their composition and possible structure. Typically, this technique reveals the presence of elements present in the nanocomposite. Closely related to EDX, Raman spectroscopy and x-ray photoelectron spectroscopy (XPS) gives data pertaining to the nature of surface groups and chemical bonds in PNCs.

Thermal analysis has proven to be a useful tool to investigate numerous properties of polymers and has found great application in PNCs elucidation by providing further insight into their structures (Corcione and Frigione, 2012). Examples include techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA) and thermal-mechanical analysis (TMA). UV-vis spectroscopy has also found great application for the investigation of size and distribution of metallic nanoparticles in polymer matrices, related stability of the PNCs, and associated interactions between the nanoparticles and polymer matrices. The presence and/or absence of surface plasmon resonance (SPR) peaks, with the peak position, intensity and width provide valuable data about the nanoparticles for their elucidation (Sabu et al., 2016). Additionally, other techniques such as scanning tunnelling microscopy (STM), nuclear magnetic resonance (NMR) and proton nuclear magnetic resonance (^1H NMR), and many more are equally employed for characterization purposes as required.

2.5.5 Applications of PNCs for water treatment

Polymeric nanocomposites synthesized from a wide range of polymer matrices and numerous inorganic nanomaterials are currently being employed in wastewater treatment processes. The major areas of application tend to be photo(catalysis), sorption, membrane filtration, sensing and monitoring, as well as microbial control processes as shown in Figure 2.5. Each mechanism of contaminant removal requires specific functionalities to suit the operational design. This has brought about in-depth studies in the selection of various polymers and inorganic nanomaterials employed in the fabrication of functional PNCs for wastewater remediation. Hence, some polymers and inorganic materials tend to be more suitable in certain areas of applications than others due to their intrinsic properties.

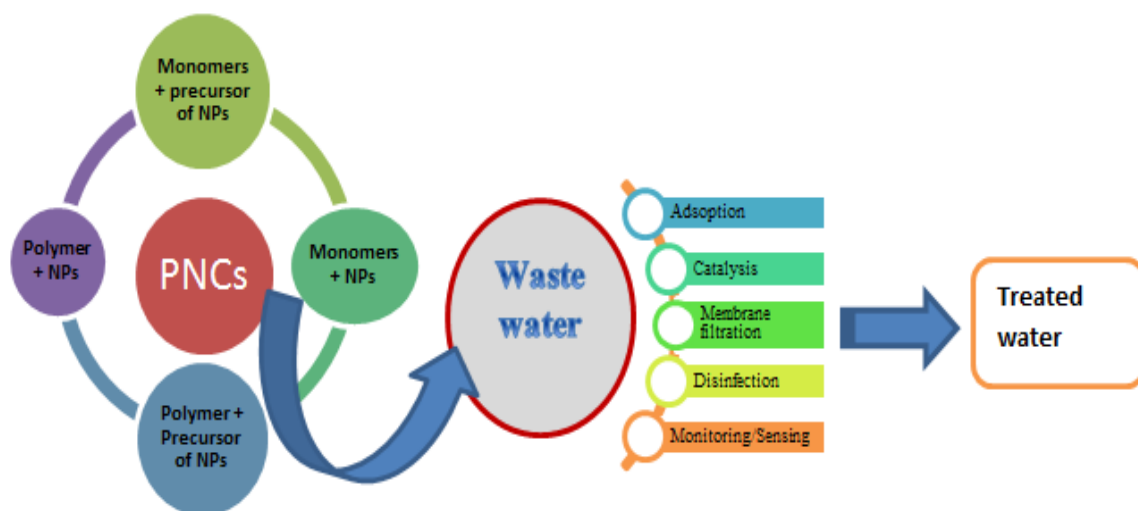


Figure 2.5: PNCs syntheses and some major application processes for wastewater treatment

2.5.5.1 PNCs as adsorbents

Adsorption is one of the frontline processes currently employed in wastewater treatment and management. It is mostly considered as a simple, low-cost, rapid and effective treatment process that has found extensive usefulness and application for the removal and remediation of various organic and inorganic pollutants from contaminated water. However, the use of traditional sorbents such as activated carbon, zeolite, clays etc. is being challenged by various new emerging microcontaminants, especially EDCs which are difficult to eliminate from contaminated waters (Wang et al., 2016c; Gao et al., 2013b; Ali, 2012; Anbia and Ghaffari, 2009). The use of PNCs as adsorbents for remediation of wastewaters is currently seen as a potential alternative due to their intrinsically high specific surface area and associated sorption sites, short intraparticle diffusion distance, and tunable pore size and surface chemistry (Qu et al., 2012). Also, the selection of sorbent materials for adsorption process is dependent on cost implication, availability, and suitability (Mthombeni et al., 2015), and polymer materials are readily available and relatively cheap, and stable enough to withstand different treatment conditions.

Adsorption is mainly a polishing treatment process for the removal of numerous pollutants in water/wastewater and has been increasingly carried out using PNCs. A variety of PNCs have been synthesized and investigated in various remediation studies in recent times. Typically, they have been applied for the removal of heavy metals (Hasanzadeh et al., 2017; Atta et al., 2016; Hayati et al., 2016; Muliwa et al., 2016; Ravishankar et al., 2016; Chauke et al., 2015; Hosseini et al., 2015), organic dyes (Zoromba et al., 2017; Cho et al., 2016; Erdem et al., 2016; Gao et al., 2013b), phenols (Yang et al., 2015),

pharmaceuticals (Kyzas et al., 2014), oil and grease (Lü et al., 2016; Reddy et al., 2016; Yu et al., 2015), and several other organic and inorganic contaminants.

The results from the current research pool demonstrate the remediation potential and effectiveness of the various synthesized PNCs to serve as excellent adsorbent materials. Zoromba and co-researchers (2017) recently synthesized PNCs using poly(aniline co-anthranilic acid) and magnetite nanoparticles which were employed for the removal of organic dyes from aqueous solution. The PNCs were reported to possess excellent remediation capabilities. Also, it was noticed that by changing the dopants in polyaniline, it was possible to enhance the dye adsorption and control selectivity which underline the versatility inherent in PNCs. Also, Hasanzadeh et al. (2017) reported the fabrication of iminodiacetic acid grafted poly(glycidylmethacrylate-maleicanhydride)/Fe₃O₄ nanocomposite material. The PNC applied as an adsorbent was employed for the remediation of Pb(II) and Cd(II) from aqueous solution with a removal efficiency of 91 – 100%. Even at the sixth reuse cycle, 80-90% abatement was achieved. Further application to industrial wastewater (battery manufacturing company) resulted in 95.02%, 92%, 89.25% and 82.34% removal of Pb(II), Zn(II), Cu(II) and Ni(II), respectively. In an earlier study, PNCs applied as adsorbents were synthesized by the assembly of Fe₃O₄ and graphene oxide on the surface of polystyrene. The composite formed was reported to possess a spontaneous and excellent adsorption capacity (73.52 mg g⁻¹) for the removal of Pb(II) ions, with a maximum removal efficiency of 93.78% at pH 6 (Ravishankar et al., 2016).

In adsorption processes, many variables are important and play various roles in the final functionality of the PNCs. These include the solution pH, contact time, temperature, agitation speed, adsorbent loading or dose etc. For instance, the extraction of most metal ions from solution phase is pH-dependent, as it affects the metal ions solubility, concentration of the counterions on the active functional group of the PNCs and degree of adsorbate ionization during the reaction (Hasanzadeh et al., 2017). Also, the functional groups present in the PNC or grafted to it coupled with their morphology is vital for the removal processes. Adsorption phenomenon can be based on various processes such as complexation, electrostatic interactions, hydrophobic effect, reduction and hydrogen bonding (Hasanzadeh et al., 2017; Ravishankar et al., 2016; Yao et al., 2014; Zhao and Liu, 2014). Typically, it may involve the combination of two or more of the aforementioned processes for adsorption to reach equilibrium. Hence, most treatment procedures using adsorbents have more than one mechanism for optimal removal efficiencies.

In the application of PNCs for removal of contaminants from water/wastewater, it is imperative and of critical interest that the process should be spontaneous and fast. In high volume potable water treatment or wastewater treatment plants, the processing time is a major consideration in choosing any treatment method. Therefore, the reaction kinetics and equilibrium conditions are critical parameters that must be optimized when PNCs are to be utilized. Generally, the major consideration for effectiveness of any PNC adsorbent should be hinged on its spontaneity, minimal contact time, high removal efficiency and excellent reuse capability, among other factors.

2.5.5.2 PNCs as catalyst

The use of PNCs in photocatalytic processes for the remediation of wastewater is one of the most promising and highly investigated areas of research. Their synthesis, characterization, application, as well as reuse potential studies, are active and core research interest in recent times. Basically, the photocatalytic process efficiency is determined by the nature of the photocatalyst and the irradiated light source (Dong et al., 2015). While the radiation source provides the activation energy equal to or higher than the band-gap energy (E_g) of the catalyst for the degradation reaction to proceed, and the catalyst efficiency is determined by its component materials consisting of the polymer matrix and nanomaterial(s) employed in their fabrication. In this regard, a plethora of polymer materials have been utilized as support materials such as hyperbranched polyester (Ghanem et al., 2014), poly(vinylidene difluoride)-co-trifluoroethylene (Teixeira et al., 2016), polyethersulfone (Hir et al., 2017), polyetherimide (Zhang et al., 2014b), polyamide (Ummartyotin and Pechyen, 2016), acrylic acid/p(*N*-vinyl-2-pyrrolidone) (Ali et al., 2016), polypyrrole (He et al., 2014), polyvinyl alcohol (Jung and Kim, 2014), polystyrene (Vaiano et al., 2014) and many more. TiO_2 tends to be the most sought-after and used inorganic nanomaterial mainly because it is non-toxic, inexpensive; possesses excellent photocatalytic property and high stability (Dong et al., 2015). However, its application is constrained due to its relatively large band-gap and the characteristic ability to absorb only a small portion of UV irradiation (Kanakaraju et al., 2014).

Despite this limitation, numerous PNCs fabricated by incorporation of TiO_2 nanomaterial into selected polymer matrix have been utilized in many wastewater treatment processes with encouraging results. Hir and co-workers (2017) reported the synthesis of PNCs using TiO_2 immobilized into polyethersulfone, used for the photocatalytic degradation of methyl orange dye from aqueous solution. The PNC (PT-13) showed excellent performance ability with high degradation efficiency (almost 80%) after 5 cycles of reuse. Similarly, He

et al. (2014) successfully fabricated a highly selective molecular imprinted PNC ($\text{MIP}_{\text{RhB}}\text{-PPy/TiO}_2$) with selective photocatalytic degradation for rhodamine B under visible light. The unique PNC showed high selectivity for the removal of the target contaminant (RhB) with a maximum remediation efficiency of about 85%. Additionally, the PNC was noted to exhibit high reusability and stability. Also, PNCs from TiO_2 and poly(vinylidene fluoride) employed for the fabrication of dual-layer hollow membranes were utilized for the degradation of nonylphenol with high photocatalytic activity reported by Dzinun et al. (2015b). Kanakaraju et al. (2014) elaborately reviewed the use of TiO_2 /polymer composites for the degradation of pharmaceuticals. Studies on the use of TiO_2 and other nanomaterial co-doped on polymer matrices have also been reported. For example, the synthesis of PVA/TiO_2 /graphene-MWCNT composite has been investigated with the PNC utilized for the removal of organic dye from aqueous systems. The research result showed that the composite had high degradation capability for the removal of methylene blue with almost 100% efficiency recorded in the first cycle. The third cycle reuse after regeneration had a removal efficiency higher than 90% (Jung and Kim, 2014).

Although, TiO_2 is popularly used for fabrication of PNCs photocatalysts employed for wastewater remediation, some other inorganic nanoparticles have equally provided exciting results. From recent research, Teixeira et al. (2016) synthesized various PNCs by incorporating TiO_2 and ZnO into poly(vinylidene difluoride)-co-trifluoroethylene, respectively. The comparative degradation efficiency of 15% wt of both nanoparticles in the polymer matrix showed that the degradation rates were similar. Added to this, the ZnO/P(VDF-TrFE) composite gave slightly better reusability potential losing only 11% of its photoactivity after three cycles in contrast to a 13% reduction for 15% $\text{TiO}_2/\text{P(VDF-TrFE)}$ composite. Similarly, Riaz et al. (2015) recently profiled extensively the photocatalytic activities of ZnO /conducting polymers composites. The various investigations cited used ZnO in the fabrication of high-performance PNC photocatalysts that were able to degrade numerous pollutants from aqueous solutions with varying efficiencies. Added to this, some reports suggested that PNC with ZnO were more effective, probably due to its ability to absorb a comparatively larger fraction of the UV spectrum than TiO_2 . Ummartyotin and Pechyen (2016) and Ali et al. (2016) reported the use of ZnO incorporated into nylon 6 and acrylic acid/p(N-vinyl-2-pyrrolidine), respectively. Both synthesized PNCs were utilized in combination with UV irradiation for the remediation of methylene blue from wastewater with 100% (Ali et al., 2016) and 60% (Ummartyotin and Pechyen, 2016) degradation efficiencies recorded. Also, the use of functionalized MWCNT in combination with the monomer 3,6-bis(2-(3,4-ethylenedioxythiophene))pyridine for the fabrication of photocatalytic PNC (poly(EPE)/f-MWCNT) has

been reported. The PNC utilized for the degradation of methylene blue under visible light irradiation showed excellent photocatalytic capability with 88% of the pollutant removed from the aqueous solution after 180 min (Liu et al., 2017).

Heterogeneous catalytic degradation of nitrobenzene and methylene blue using silver/polymer nanocomposites have been reported by Khan et al. (2016c) and Tang et al. (2015), respectively. The reducing agent, NaBH_4 was employed in the catalytic processes which were both reported to have huge potential for remediation of wastewater. Chao and co-workers (2015) also fabricated a composite material from silver nanoparticles and surface hydroxyl-functionalized poly(styrene-co-hydroxyethyl acrylate) microsphere. The synthesized PNC with small and denser nanoparticles reportedly showed high catalytic activity for the remediation of methylene blue from aqueous solution. Other nanomaterials that have been employed for the fabrication of catalytic PNCs with varying degree of treatment results are Fe^0 (San Roman et al., 2016), Fe^{2+} (Haspulat et al., 2013), Au (Mogha et al., 2017), Ni-ZnO (Kumar et al., 2014), ZnS (Pathania et al., 2016), Zr(IV) vanadophosphate (Sharma et al., 2016), Zr(IV) silicophosphate (Pathania et al., 2014), CdO (Gölce et al., 2013) and many more.

2.5.5.3 PNCs as membrane filters

The last decade witnessed a huge surge in the use of membrane filtration techniques and procedures for water treatment and remediation purposes. This was a sequence to the realization of the inherent potential, efficiency, economics and environmental friendliness of the process (Yang et al., 2012). The major basic principles involved in this technique are adsorption (hydrophobic/hydrophilic interactions), sieving, and electrostatic process (Padaki et al., 2015). Performance of membrane systems is largely dependent on the membrane composition which provides a physical barrier for the elimination and removal of target contaminants. In order to overcome some of the dire challenges of conventional membranes such as fouling, selectivity and permeability; nanomaterials are now being incorporated into membranes to improve their mechanical and thermal stability, fouling resistance, permeability and flux recovery, contaminant selectivity, as well as added functionalities such salt rejection, oil removal, and antibacterial and catalytic activities (Qu et al., 2012). These hybrid polymeric membranes with improved reusability potential have been applied in various membrane treatment processes and better efficiencies have been reported (Ghaemi, 2016; Lee et al., 2016).

The modification of these membranes has witnessed the use of numerous inorganic nanomaterials such as hydrophilic metal oxides nanoparticles (e.g., Al_2O_3 , TiO_2 , and zeolite), antimicrobial and antifouling nanoparticles (e.g., nano-Ag, C_6 fullerenes, CNTs) and photo(catalytic) nanomaterials (e.g., bimetallic nanoparticles, TiO_2) (Qu et al., 2012). Also, other inorganic nanoparticles (single or mixed) such as graphene oxide (Lee et al., 2013), reduced graphene oxide (Liang et al., 2016), goethite (Rahimi et al., 2016), SiO_2 (Obaid et al., 2016), ZnO/MWCNT (Zinadini et al., 2017), $\text{Fe}_2\text{O}_3/\text{MWCNT}$ (Alpatova et al., 2015) and exfoliated graphite nanoplatelets/nano-Au (Crock et al., 2013) have been utilized in numerous membranes fabrication with varying degree of efficiencies. On the other hand, polymer matrices commonly used to prepare these hybrid membranes include polysulfone (Lee et al., 2013), polyethersulfone (Kiran et al., 2016), polyvinylidene fluoride (Dzinun et al., 2015a), polyacrylonitrile (Liang et al., 2016) and polyamide (Yin et al., 2016). In addition to single polymer membranes, mixed-matrix polymer membranes have been synthesized with reports identifying synergistic effects (Lee et al., 2016; Feng et al., 2015). Once fabricated, these membranes are employed for processes such as reverse osmosis (Chae et al., 2015; Safarpour et al., 2015), forward osmosis (Emadzadeh et al., 2014; Ma et al., 2012), ultrafiltration (Lee et al., 2016; Feng et al., 2015), microfiltration (Fischer et al., 2015; Daraei et al., 2013), nanofiltration (Gholami et al., 2014; Peyravi et al., 2014), amongst others for the removal of arrays of water contaminants.

Fouling which has been one of the major challenges of membrane filtration technique due to its tendency to reduced membrane lifespan and increases operational cost is currently being highlighted in recent studies with many antifouling and self-cleaning membranes fabricated. Lee and co-workers (2013) utilized graphene oxide and polysulfone for the synthesis of membranes which were reported to possess high antifouling properties, with the operational use period lengthened to almost fivefold between chemical cleaning. This was attributed to the graphene oxide membrane having anti-biofouling capability due to its hydrophilicity and electrostatic repulsion characteristics. Also, a membrane fabricated from goethite ($\alpha\text{-FeOOH}$) and polyethersulfone was reported to possess excellent antifouling properties during long-term nanofiltration experiments with the protein solution. Additionally, the membrane gave high dye removal capacity (99%) for Direct Red 16 dye and showed good selectivity (Rahimi et al., 2016). Similarly, Zinadini et al. (2017) synthesized a mixed matrix nanofiltration membrane using ZnO/MWCNT nanoparticles and polyethersulfone. The PNC (0.5wt ZnO/MWCNT) reportedly showed high antifouling capacity which was attributed to its high hydrophilicity and low surface roughness induced by the embedded nanoparticle. Incorporating inorganic nanomaterials that may increase the hydrophilicity of the membrane helps to reduce their fouling tendency (Dulebohn et al.,

2014). In a related development, self-protected self-cleaning ultrafiltration membrane was fabricated utilizing TiO₂ nanoparticles, and polydopamine and polysulfone polymer matrix. The sandwich-like structure of the membrane was posited to provide both the good self-cleaning property and performance stability during the ultrafiltration process (Feng et al., 2015).

Another progressive trend in membrane technology is the fabrication of catalytic membranes. This group of hybrid membranes performs catalysis with membrane separation functions in order to enhance treatment efficiency. These membranes are already being applied in highly efficient reactive separations with the possible emergence of an efficient treatment route for wastewater. The fabrication of high permeability pluronic-based TiO₂ photocatalytic membrane with hierarchical porosity was reported by Goei and co-researchers (2013). The hybrid membrane showed great photocatalytic potential and excellent specificity for the complete removal of 2700 mg m⁻² Rhodamine dye in a membrane reactor process. The elimination mechanism of the pollutant was reported as majorly through photocatalytic activity, membrane rejection, and minor contributions from adsorption. Also, the membrane showed good fouling-control capability, high flux performance and reusability potential. Similarly, Zhang et al. (2014a) synthesized hollow fibre photocatalytic membranes from TiO₂ and a mixture of polyetherimide and 1-methyl-2-pyrrolidinone (ratio: 18: 25: 75 w/w). The membrane (calcined at 900°C) showed a good balance between mechanical properties and photocatalytic activity. It reportedly removed 90.2% of the Acid Orange 7 dye through filtration and photodegradation processes. Crock et al. (2013) fabricated a multifunctional membrane by adding exfoliated graphite nanoplatelets decorated by AuNP to casting mixtures of polysulfone, *N*-menthyl-2-pyrrolidone and polyethylene glycol. The resulting PNC was noted as permselective, highly permeable, catalytically active, with good resistance to compaction. The exfoliated graphite nanoplatelets were reported to be responsible for the hierarchical structure while the nano-Au produced the excellent catalytic activity.

Remediation of oily wastewater using membrane technology has always been riddled with fouling problems, which is either reversible or irreversible. Solute or colloidal particle deposition brings about reversible fouling which can be easily recovered by backwashing with pure water, while strong physical or chemical sorption of solutes and particles on the surface or in membrane pores generates irreversible fouling which requires removal with acid or alkali solutions (Yan et al., 2009). Membranes with capabilities to remediate oily wastewater are now fabricated to overcome the aforementioned challenge. Lü et al.

(2016) synthesized a thermosensitive poly(*N*-isopropyl acrylamide)-grafted magnetic nanoparticles (MIO@SiO₂) PNC which were utilized for the demulsification of oily wastewater. The PNC exhibited excellent oil removal ability by almost eliminating the presence of oil in the aqueous system. It showed high reusability potential with over 90% transmittance still obtained for the treated water even after the seventh reuse cycle. Also, Yan et al. (2009) employed their fabricated Al₂O₃-PVDF tubular ultrafiltration membrane for oily wastewater treatment. The research report suggests the high oil removal capacity and tolerance of the PNC with excellent reuse potential (100% flux recovery ratio) after washing with 1 wt% of OP-10 surfactant solution at pH 10.

Membranes with other important functionalities are currently being designed to meet the growing water treatment and remediation needs of the society. These include membranes for antimicrobial (Jo et al., 2016; Yuan et al., 2016), salt rejection (Obaid et al., 2016; Yin et al., 2016), chlorine tolerance (Xie et al., 2016; Han, 2013), and many such purposes. Membrane technology is currently being revolutionized by these waves of hybrid PNCs with varying treatment potentials.

2.5.5.4 PNCs as disinfectants and microbial control agents

Disinfection and microbial control in water and wastewater treatment are of utmost importance and priority. Nano-disinfection technology is now a vigorously pursued water treatment process due to the inherent challenges associated with conventional disinfectants, especially with the serious concerns about toxic disinfection by-products. Many nanomaterials such as nano-Ag, nano-ZnO, nano-TiO₂, nano-Ce₂O₄, CNTs and fullerenes possess antimicrobial tendencies with minimal oxidation, and are less prone to the formation of toxic by-products (Qu et al., 2012). Apart from the nanomaterials, the composition of the polymer matrix can also be responsible for the antimicrobial activities as well. This was depicted by Yuan et al. (2016) with the synthesis of recyclable *Escherichia coli*-specific-killing AuNP-polymer (pMAG:pMETAI) nanocomposites. The PNC (P4) which retained good antibacterial activity up to the third reuse cycle was able to specifically and effectively kill *E. coli* and eliminate their presence from the aqueous medium. The report indicates that the antibacterial ability of the PNC was due to pMETAI, a quaternary ammonium salt and widely used cationic fungicide.

Numerous PNCs have been synthesized with their antibacterial efficiency and effectiveness investigated. PNC obtained from PANI/PVA/nano-Ag (15% wt) was investigated for its antibacterial activity by evaluating against Gram-positive bacteria

Staphylococcus aureus and Gram-negative *E. coli* using the paper disk diffusion method. Results obtained showed very good antibacterial activity against the two bacteria. The nano-Ag was basically responsible for the antimicrobial activity of the composite, with its activity dependent on the Ag^+ that binds strongly to electron donor groups on biological molecules like sulphur, oxygen or nitrogen (Ghaffari-Moghaddam and Eslahi, 2014). Pathania and co-researchers (2014) fabricated a dual purpose PNC from PANI/zirconium(IV) silicophosphate (ZSP) nanomaterial. The photocatalytic PNC was investigated for its antimicrobial activity using optical density method. It successfully acted as an antibacterial agent against *E. coli* with the maximum inhibition at $320 \mu\text{g mL}^{-1}$ PANI-ZSP. The death phase of *E. coli* was subsequently observed after 20 h of incubation. Also, Alonso et al. (2012) demonstrated the high bactericidal activity of fibrous polymer silver/cobalt nanocomposites using fluorescence-based viability assay and under continuous operation flow condition ($0.7 \text{ mL}^{-1} \text{ min}$). The PNC exhibited excellent antimicrobial activity with cell viability always found close to 0% for bacterial suspension with initial concentration below 10^5 CFU/ mL after a single filtration through it. It further showed high performance against the different types of coliform (*E. coli*, *K. pneumonia* and *En. aerogenes*) and *S. aureus* during long-term operation, with an efficiency of 100% (0% viability) up to 1 h of operation and higher than 90% during the first 24 h of continuous operation.

Filtration membranes with antimicrobial activities have been explored for the prevention of fouling in treatment processes. Jo and co-workers (2016) successfully synthesized one of such PNC membrane from poly(ether sulfone) and ZnO grafted with hydrophilic polymers. The ultrafiltration membrane (0.5 wt% ZnO) exhibited excellent antibacterial activity, preventing fouling of the membrane. Additionally, it was noted that the membrane showed improved water flux, without a decline in the solute rejection capacity. Basri et al. (2010) investigated the antibacterial activity of silver-filled polyethersulfone membrane (with surface modification using 2,4,6-triaminopyrimidine) by targeting *E. coli* and *S. aureus*. The overall results showed the antibacterial potential of the PNC to inhibit almost 100% bacterial growth. The incorporation of AgNP in polymer matrix for antifouling membrane was also tested successfully by Mauter et al. (2011). The fabricated PEI/AgNP composite was reacted with oxygen plasma modified polysulfone UF membrane with or without 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC). Antimicrobial activity of the PNC membrane (without EDC) after 1 h incubation test with *E. coli* K12 concentration of $1 \times 10^6 \text{ cells/ mL}$ gave bacterial inactivation of over 94%, while membranes with EDC-facilitated binding of AgNP exhibited bacterial activation rate >

99.9%. The significant higher performance of the later was attributed to increase in atomic concentration of Ag bound to the membrane surface.

Currently, the use of PNCs for disinfection purposes is limited to secondary disinfection in treatment processes for now. Also, most PNCs with encouraging results from simulated contaminated water assays, have been found to exhibit lower treatment efficiencies when subjected to real samples from natural sources (Alonso et al., 2012). Hence, it is expected that more holistic studies to develop futuristic nano-disinfectant PNCs will take the front burner in the next decade in order to mitigate DBPs challenges. In this regard, their application in membrane processes will likely get more focus and attention.

2.5.5.5 PNCs as sensing and monitoring devices

The investigation and use of polymeric materials for the fabrication of sensors and other monitoring devices have recently become popular. This rising interest stems from the fact that polymer materials are relatively cheap, easy to process, and possess multifunctionality due to their structural, physical and chemical characteristics. This allows for easy modification and the possibility to add side-chains, and other inorganic components into the bulk matrices. The resultant effect is improved dielectric, conductive, electrolytic, molecular recognition ability, permselective, ion-selective and optically sensitive properties (Harsanyi, 1995). The nanomaterials commonly employed for the fabrication of sensing and monitoring PNCs possess intrinsically unique properties such as electrochemical, optical, and magnetic properties which help to improve their sensitivity, rate of detection and possible multiple detection abilities (Qu et al., 2012). The resulting PNC sensor and other devices are often designed to be pH-sensitive (Raoufi et al., 2014; Raoufi et al., 2012; Zamarreño et al., 2011), possess affinity for organic molecules and inorganic ions (Dutta Chowdhury and Doong, 2016; Khan et al., 2016b; Nie et al., 2016; Tovide et al., 2014), and monitoring of pathogens (Kochan et al., 2012).

The versatility of PNCs is evident in the numerous contaminants (heavy metals, trace contaminants (EDCs), persistent organic pollutants, and pathogens) that have been successfully determined or monitored in aqueous systems. Electrospun fibre colourimetric probe fabricated from polystyrene nanofibres and nano-Au was used for on-site detection of 17 β -estradiol associated with dairy farming effluent (Pule et al., 2015). The PNC probe exhibited a visual colour change from pink to blue with increasing concentration of the contaminant. It also showed high specific selectivity as it did not respond to the presence of cholesterol and other series of compounds (p,p¹-DDE, deltamethrin, 4-tert-octylphenol

and nonylphenol) known to induce oestrogenic activity. Similarly, Olowu et al. (2010) previously constructed an electrochemical aptasensor from poly(3,4-ethylenedioxythiophene)/nano-Au, that was utilized as a redox probe for measuring the concentration of 17 β -estradiol using cyclic voltammetry and square wave voltammetry in the presence of [Fe(CN)₆]^{3-/4-}. The transduced signal decreased due to interference of the bound 17 β -estradiol, with the current drop proportional to the concentration of the contaminant. Additionally, the probe gave excellent selectivity by being able to distinguish 17 β -estradiol from other structurally similar EDCs. Highly specific and selective sensor for dinitrotoluene (DNT) was fabricated from MWCNTs/PEI and molecularly imprinted polymer. The sensor exhibited excellent electrocatalytic activity to DNT with a good linear range current response of about 2.2×10^{-9} mol/L to 1.0×10^{-6} mol/L and a detection limit of 1.0×10^{-9} mol/L (Nie et al., 2016).

A sensor with selective Pb²⁺ detection capability and antibacterial activity was constructed from graphene oxide/CNTs/poly(O-toluidine). The sensor showed fast and selective response to Pb ions in aqueous solution, coupled with the ability to significantly inhibit *Bacillus subtilis* and *E. coli* bacteria compared to amoxicillin antibiotic (Khan et al., 2016b). Similarly, Fe³⁺ detection probe was fabricated using dopamine functionalized by graphene quantum dots. The highly selective and sensitive probe gave excellent performance for the detection of Fe³⁺ in the presence of other interfering metal ions with the linear range of 20 nM to 2 μ M and a detection limit of 7.6 nM obtained. The ability of a PVA/nano-Ag nanocomposite sensor to detect the concentration of cadmium in water, based on the linear change in surface plasmon resonance adsorption strength was equally reported by Devi and Umadevi (2014). Additionally, PNC sensors have been employed to determine ferricyanide (Mondal et al., 2017), free chlorine (Muñoz et al., 2015), ammonia and amines (Wang et al., 2016a; Baig et al., 2015; Lacy, 2013), bisphenol A (Cheng et al., 2016a), ibuprofen (Motoc et al., 2013), COD (Gutierrez-Capitan et al., 2015) and DO (Hsu et al., 2014) levels in aqueous systems.

2.6 Regeneration and reuse potentials of PNCs

Effectiveness of the remediation/monitoring capacities of PNCs, as well as, their reusability potential is a critical component of developing this nanotechnology-based treatment procedure. In general, the practical application of any technology is dependent on the cost implication weighed against potential benefits presented by competing alternatives- water treatment/remediation using PNCs is no different. The cost of synthesizing PNCs and their potential for regeneration and reuse is a major area of

interest, which will determine their large-scale application and progress of the technology. It is, therefore, imperative and expedient to give special consideration to the regeneration and reuse potentials of the various PNCs being synthesized and applied for treatment purposes; with a view of cost reduction.

Regeneration of PNCs is the process of subjecting these nanocomposites to various solutions and/or conditions in order to renew or reactivate their active sites after prior usage, with the intention to further use them in treatment processes. During application processes for treatment purposes, the active sites of PNCs are loaded with contaminants or their degradation products coupled with the loss of important functional groups. Hence, regeneration procedures are required to rejuvenate them. Suggested regeneration procedure should be relatively simple, fast and cheap. This will help to align the economy of scale, encourage and boost their application in water and wastewater treatment processes. Reported regeneration procedures in recent literatures include the treatment of PNCs with different concentrations of aqueous acidic solutions (Ravishankar et al., 2016; Hasanzadeh et al., 2017), alkaline solutions (Ballav et al., 2014a; Wang et al., 2012a), a combination of acidic and alkaline solution (Yao et al., 2014; Lee et al., 2016), methanol (Arya and Philip, 2016), ethanol (Reddy et al., 2016; Zhao and Liu, 2014; Chen et al., 2013), petroleum ether (Reddy et al., 2016; Keshavarz et al., 2015), EDTA solution (Ghaemi, 2016; Ghaemi et al., 2015), buffer solution (Jung and Kim, 2014), hydrogen peroxide solution (Luo et al., 2013) and mannose solution (Yuan et al., 2016). Additionally, water/deionised water or deionised distilled water under different conditions (elevated temperature, ultrasonication or UV irradiation) have been employed for regeneration purposes as well (Hir et al., 2017; Lü et al., 2016; Mogha et al., 2017; Goei et al., 2013).

A major regeneration mechanism for PNCs is desorption. It is the reverse process of adsorption/absorption which is intentionally done to release contaminants embedded or attached to the nanocomposites from prior remediation/monitoring usage. Essentially, the process renews the sorption sites by breaking the initial interacting bonds between the nanocomposites and the contaminants or its breakdown products. The nature of the interacting bond which may be weak (physisorption), moderate (chemisorption) or strong (electrostatic interactions) determines the likely solution(s) to be utilised in the desorption process; water can readily desorb contaminants trapped by weak bonds, while strong acidic solution may be required for desorption of those that are held by strong bonds (Mall et al., 2006). Microbial control processes with PNCs may also be posed with situations where the dead microbial cells adhere to the composite material, blocking the active sites.

Yuan and co-workers (2016) reported the use of large quantities of mannose solution to effectively wash-off dead cells of *E. coli* from applied PNCs to regenerate them. This was possible because of the lectin on the fimbriae in *E. coli* which had a mannose-binding domain with a high affinity for mannose. Washing of PNCs with chemical solutions to remove contaminants or their degradation products may follow mechanisms such as oxidation, hydrolysis, solubilisation, saponification or chelation to achieve regeneration (Lee et al., 2016). In most cases, a combination of two or more of these mechanisms is followed during the regeneration processes. An illustration of the regeneration/reuse cycle is as presented in Figure 2.6.

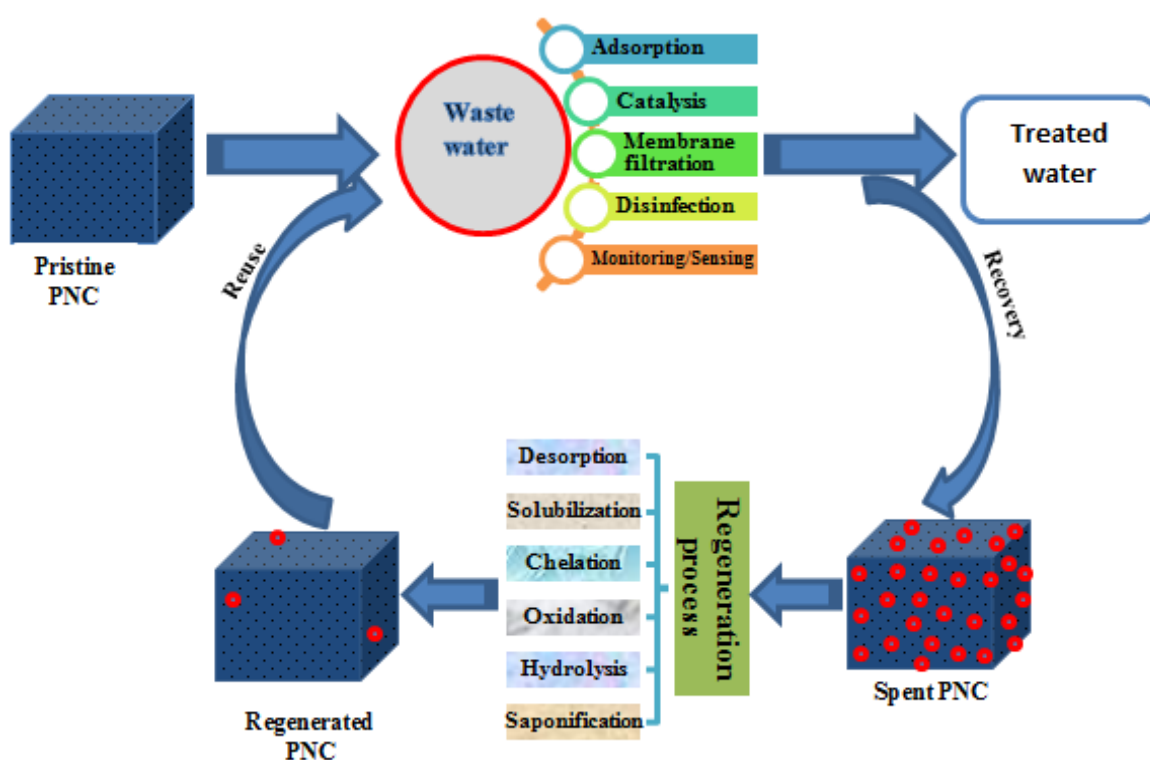


Figure 2.6: PNC regeneration and reuse cycle

2.6.1 Techniques and procedures for the regeneration of PNCs

2.6.1.1 Regeneration of PNCs with water

Regeneration of PNCs with different aqueous solutions (distilled water, deionized water, deionized distilled water and ultrapure water) is a core technique utilized for their reactivation purpose. These aqueous solutions are usually applied under varying conditions (see Figure 2.7) to achieve the desired result, mainly through a solubilisation mechanism. As reported by Mogha et al. (2017), water was utilized to regenerate PNCs

recovered by centrifugation, followed by drying in an oven to achieve regeneration and enable their reuse. The regenerated AuNP/poly(dimethylaminoethyl methacrylate)-immobilized reduced graphene oxide catalysts, utilized for the removal of rhodamine B, methyl orange and eosine Y showed minimal change in efficiency (< 5%) after 5 reuse cycles. Washing with distilled water was employed by Zhu et al. (2012) to regenerate AuNP/poly(*N*-isopropyl acrylamide) nanocatalyst previously used for the reduction of *o*-nitroaniline to 1,2-benzenediamine in contaminated water. The PNC retained about 75% of its initial treatment efficiency after the third reuse cycle. The observed loss of treatment efficiency (about 25%) was adduced to a probable increase in the size of the AuNP by agglomeration. Yan et al. (2009) carried out the cleaning and regeneration of Al₂O₃/poly(vinylidene fluoride) tubular ultrafiltration membranes by backwashing with clean water, which gave 91.5% permeate flux recovery for the membranes. The membrane fouling from the oily wastewater was reported to be mostly reversible caused by the colloidal layer which was easily controlled by mild cleaning. Also, Chan and co-workers (2016) employed deionized water for the cleaning (flushing) of synthesized zwitterion functionalized carbon nanotubes/polyamide nanocomposites membrane to achieve 100% recovery of initial water flux after their use in reverse osmosis process with feed water ladened with organic foulants (bovine serum and alginic acid, sodium salt). The flushing process added pressure to the water, making the removal of the organic foulants easier. Lü et al. (2016) performed the regeneration (demulsification) of filtration membrane nanocomposites by washing three times with hot water at 60°C to remove the attached oil. The thermosensitive poly(*N*-isopropyl acrylamide)-grafted magnetic nanoparticles PNCs were reported to possess the ability to desorb from the emulsified oil droplets, making regeneration with only hot water possible. Interestingly, Sarkar et al. (2015) reported the possible use of water under UV light to carry out photocatalytic degradation of organic dyes (methylene blue and methyl orange) adsorbed by their exfoliated layered titanate/poly(2-diethylamino)ethyl methacrylate-*g*-amylopectin nanocomposite to achieve regeneration. The use of water for regeneration purposes portends to provide a viable, easy and cheap route which will make it a method of choice when it can be applied. Also, it leaves little room for the contamination of the PNCs from the regeneration process. However, as evident in Table 2.5, regeneration using water is mainly restricted to scenarios where weak interacting bonds (physisorption) exist between the PNCs and contaminants or their degradation products. This involves PNCs applied for catalytic or absorption processes where superficial bonds are in play during the degradation or removal of contaminants from water.

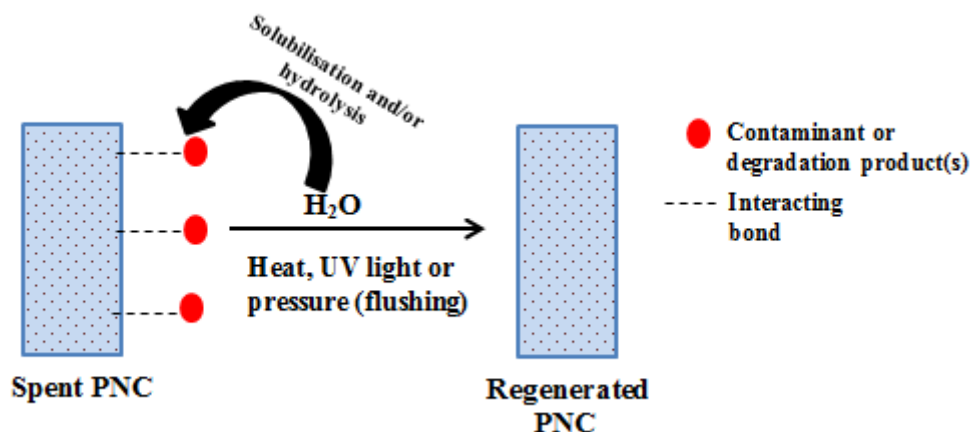


Figure 2.7: Scheme for water regeneration

2.6.1.2 Regeneration of PNCs with acidic solutions

The high usage of acidic solutions stems from the fact that it can be utilized for regeneration procedures where the interacting bond between the PNCs and the contaminants or their degradation products may be by electrostatic or chemisorption processes (Shan et al., 2015; Mahapatra et al., 2013). Such strong/medium strength bonds require greater action to loosen/break them. Wang et al. (2008) profiled aqueous solutions with pH ranging from 2 to 9 to determine their effectiveness on nanocomposites regeneration. The research showed that regeneration of montmorillonite/chitosan-g-poly(acrylic acid) PNC was more effective when the acidic solution with pH 2 was employed, yielding 69.8% desorption of the methylene blue contaminant; while the pH 9 solution was least effective, giving only 2.9% desorption. The report suggested that the contaminants (MB dye) were initially adsorbed by the nanocomposites mainly by electrostatic interaction. This trend was also reported by Pal et al. (2012), with the aqueous solution of pH 2.5 exhibiting maximum desorption capacity of 97.80% in the removal of MB blue dye from the nanocomposite as compared to 45.50% for the pH 8.5 aqueous solution. Desorption of dorzolamide from graphite oxide/poly(acrylic acid)-g-chitosan nanocomposite was effected with an aqueous acidic solution of pH 3 (adjusted with HCl). Agitation of the complex was carried out at 160 rpm at 25°C for the duration of 24 h. After 10 adsorption-desorption/reuse cycles, only 10% of efficiency loss was recorded (Kyzas et al., 2014). Hasanzadeh and co-workers (2017) reported that during desorption processes of Pb(II) and Cd(II) ions, the lower level acidic solution could possibly prevent further uptake of the metal ions when the concentrations tend towards zero at pH < 2. Again, Badroddoza et al. (2013) carried out the regeneration of their

synthesized Fe₃O₄/cyclodextrin polymer nanocomposites using an aqueous solution with pH 5.5. In this context, optimization of pH is most often required to achieve the highest regeneration efficiency for individual PNCs with respect to the contaminants of concern.

A wide range of inorganic and organic acids such as HCl (Atta et al., 2016; Liu et al., 2014a; Hasanzadeh et al., 2017; Islam et al., 2015; Jiang et al., 2015; Ballav et al., 2014b), H₃PO₄ (Badrudodoza et al., 2013), HNO₃ (Ravishankar et al., 2016), H₂SO₄ (Wang et al., 2009), acetic acid (Wang et al., 2009), citric acid (Lee et al., 2016), EDTA (Ghaemi, 2016; Ghaemi et al., 2015) and several others have been utilized for regeneration purposes. Varying concentrations (corresponding to different pH) of these acidic media are generally employed by different researchers to meet their application demand. Liu et al. (2014a) utilized 0.2 M aqueous solution of HCl to desorb Pb(II) and Cu(II) ions from their crossed-linked attapulgite/poly(acrylic acid-co-acrylamide) nanocomposites, with almost 100% regeneration attained for both heavy metals. The report posited that at higher acidic concentrations of HCl, the Pb(II) ions react with Cl⁻ to form water-soluble complexes which adhere to the surface of the adsorbent thereby preventing further desorption of Pb(II) ions. However, this phenomenon was not observed with Cu(II) ion. Similarly, montmorillonite/lignocellulose-g-poly(acrylic acid) hydrogel nanocomposites applied as adsorbent for remediation of MB dye from aqueous solution was regenerated by applying different concentrations of HCl solutions. The desorption capacity increased from 72.90 to 83.40% with increase in HCl concentration from 0.01 to 0.075 M, indicating that the higher acidic solution facilitated better desorption. Further increase in HCl concentration to 0.4 M caused a decrease in the desorption capacity which reduced from 83.40 to 42.88%, due to H⁺ ions competing with MB cations and the adsorbent's carbonyl groups most of which exist in the form of -COOH at high acidic levels (Shi et al., 2013).

Liu et al. (2014a) utilized an elution process for the desorption/regeneration of attapulgite/poly(acrylic acid) nanocomposite hydrogels using 0.5 M aqueous HCl solution. The adsorption-desorption cycle was repeated 10 times with the PNC retaining 99% of its initial adsorption capacity. Again, Islam and co-workers (2015) applied 1 M HCl solution as desorbing agent for the regeneration of phosphine-functionalized electrospun silica/poly(vinyl alcohol) nanofibers loaded with Mn(II) and Ni(II) ions. High desorption of approximately 99% was achieved, which was adduced to the protonation of P atoms of the phosphine groups and oxygen atoms of the integrated network of silica in the strong acidic solution. Wang et al. (2009) carried out desorption studies using distilled water and 0.5 M concentrations of CH₃COOH, HNO₃, H₂SO₄ and HCl, respectively on their fabricated attapulgite/chitosan-g-poly(acrylic acid) nanocomposite which was used as an

adsorbent for removal of Cu(II) from contaminated water. Result obtained showed desorption efficiencies of 0%, 13.03%, 84.91%, 85.31% and 86.26%, respectively. The 0% obtained using distilled water clearly shows that the interaction between the nanocomposite and the contaminant was mainly through the electrostatic process, and therefore, water was ineffective. The regeneration procedure with HCl gave both higher desorption capacity (208.18 mg/g) and desorption efficiency (86.26%) amongst the acidic medium applied. This ability to give better regeneration, coupled with the fact that it is one of the cheapest acids makes HCl one of the most preferred acidic medium.

Despite the popular use of HCl as highlighted above, other acidic media are also employed for regeneration purposes with various degrees of efficiencies recorded. Ravinshankar et al. (2016) regenerated their synthesized GO/Fe₃O₄/polystyrene nanocomposite by washing with 10% HNO₃ solution to desorb Pb(II) ions, and this was followed by washing and neutralizing with deionized water. The PNC which originally exhibited a removal efficiency of 93.78% at pH 6, subsequently dropped to 40.96% after the fourth regeneration/reuse cycle. This was attributed to the incomplete desorption of the absorbed sites of the nano-adsorbent. Sharma et al. (2014) profiled different concentrations of HNO₃ for the regeneration of Th(IV) tungstomolybdophosphate/polyaniline nanocomposites used to remove Cu(II) and Pb(II) ions from aqueous solutions. The 0.5 M HNO₃ solution reportedly gave a better rejuvenation of the PNCs as compared to the 0.1 M HNO₃ solution. This was attributed to the higher concentrations of H⁺ ions in the stronger acidic medium. The report also posited that the 0.1 M HNO₃ solution effected better regeneration than 0.1 M CH₃COOH acidic solution. Similarly, Semagne et al. (2016) used different concentrations of HClO₄ and HNO₃ to regenerate their fabricated PNCs in binary separation systems. Their investigation reports show that 1 M HClO₄ was preferably utilized for Pb(II) and Cu(II) system; 0.01 M HNO₃ for Cu(II)-Ni(II) binary system; 0.1 M HNO₃ for Pb(II)-Ni(II) system. Furthermore, 0.01 M HClO₄ gave a preferred result for Mn(II)-Pb(II) mixture; while 0.01 M HNO₃ favourably eluted Cu(II) from Cu(II)-Mn(II) solution. The selection of these solvents was based on the distribution coefficient (k_d) values of both metal ions in each system.

Gheami (2016) successfully regenerated his fabricated alumina/poly(ether sulfone) membranes used for the removal of Cu(II) from aqueous solution by dipping in 10 mM EDTA solution. The copper ions were removed from the membranes through the chelation process, with only a negligible reduction (4% relative to initial removal) in the removal efficiency recorded after the fourth reuse cycle. This was attributed to the high formation constant $[\text{Cu}(\text{EDTA})]^{2-}$ (5.0×10^{18}) for EDTA, which enable it to permanently

remove copper ions from the membrane adsorption sites by chelating them. Also, Ghaemi and co-researchers (2015) in a previous report successfully utilized EDTA for the regeneration of Fe_3O_4 (modified with SiO_2 , metformin and amine)/poly(ether sulfone) PNC used for removal of Cu(II) from contaminated water. In this case, the PNC employed through an adsorptive-membrane filtration process gave a removal efficiency of 81% after the 4th regeneration/reuse cycles, as compared to 92% obtained for the pristine PNC. The use of H_2O_2 , a weak acidic medium for the regeneration of PNCs was equally reported by Luo et al. (2013). In most of these acidic medium regeneration processes, protonation of the active sites of the PNCs is a major route taken to eliminate the contaminants, and subsequently effect their regeneration. The suggested mechanism for this process is shown in Figure 2.8.

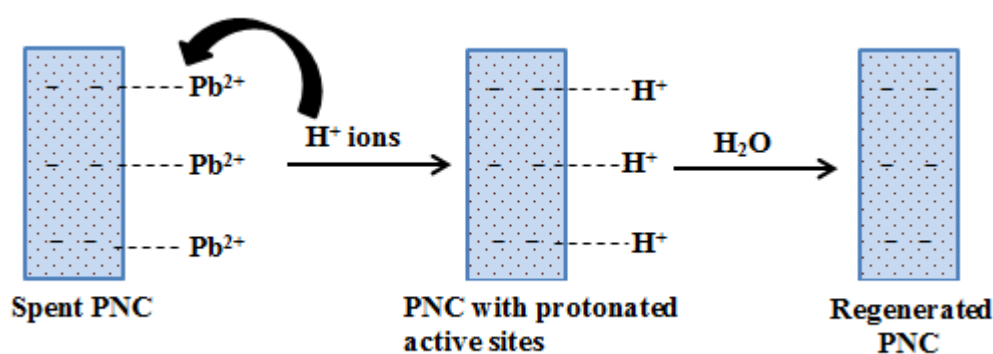


Figure 2.8: Protonation scheme for acidic medium regeneration

2.6.1.3 Regeneration of PNCs with alkaline solutions or in combination with acidic solutions

Alkaline or alkaline surfactant medium such as sodium hydroxide, sodium dodecylbenzene sulfate and non-ionic surfactant has found application in this technique (Yan et al., 2009). In general, this treatment process helps to regenerate PNCs with contaminants attached to them mostly through electrostatic and chemisorption interactions (Wang et al., 2012a; Sun et al., 2016; Kim et al., 2015). A major route to the regeneration may include desorption, saponification, or solubilisation, and mainly through hydroxylation processes. Evident successes of the technique include the use of aqueous KOH solution (0.5 M) for the rejuvenation of α -zirconium/polyaniline nanoadsorbent, which was used to remediate methyl orange dye (MO) from water. The regeneration investigation showed that more than 90% of the MO was desorbed from the spent nanocomposite when subjected to the KOH solution, and the PNC still gave a removal

efficiency of about 80% after the 5th adsorption-desorption cycle (Wang et al., 2012a). Patel and Hota (2016) utilized alkaline solution prepared using NaOH to carry out the regeneration of iron oxide/poly(acrylonitrile) nanocomposites employed for the adsorption of Congo red (CR) dye from aqueous solution. This was achieved by applying a 0.01 M NaOH solution for 3 h. Restoration of the adsorptive capacity of the PNC was done by this process, with 95% and 86% CR dye removal obtained for the 1st and 2nd cycle, respectively; while the 4th cycle gave 70%. Sodium hydroxide was used for the spiking of deionized water to attain a pH of 9.20, and further to 11.21 to carry out desorption of organic dyes (organe-16 and solvent blue-35) from silica/alkoxysilane functionalized amphiphilic polymer nanocomposites. The adjusted solution with pH 11.21 gave a better regeneration result for the hybrid composites, which was attributed to the pH dependency of zeta potential and isoelectric point (Cho et al., 2016). In contrast, Ballav et al. (2014a) utilized a 0.5 M NaOH solution for the regeneration of polypyrrole-coated halloysite nanotube clay composite with only 9.18% of the Cr(VI) ions desorbed. The reduction of Cr(VI) to Cr(III) by the electron-rich polypyrrole moiety was responsible for the poor regeneration level, as negligible adsorption of Cr(III) occurs at pH > 6 (Huang and Wu, 1977). Subsequent treatment with 2 M HCl released the Cr(III) ions and adsorption efficiency of 99.99% which remained unchanged after three reuse cycle was achieved. A similar phenomenon was observed by Setshedi et al. (2013), only 12% of the absorbed Cr(VI) could be extracted from their fabricated organically-modified montmorillonite clay/polypyrrole nanocomposite when 0.5 M NaOH solution was utilized. Further treatment of the PNCs with 2 M HCl solution subsequently facilitated the removal of the remaining reduced Cr(III), and simultaneously the active sites were regenerated by the doping Cl⁻ ions. The above phenomenon is depicted in Figure 2.9.

Many researchers have employed this mix of alkaline and acidic solutions alternately to achieve the desired regeneration for PNCs, especially through a combination of desorption/regeneration processes. Ballav et al. (2014b) reported the use of NaHCO₃ to condition their PNC applied as an adsorbent for Cr(VI) for the desorption process and subsequent washing with 2 M HCl to regenerate the sorption sites of the adsorbent. The adsorbent efficiency remained unchanged in the first three cycles with a removal capacity of above 99% recorded. Yao et al. (2014) utilized a 0.5 M NaOH solution in the desorption step for the removal of Cr(VI) loaded in their graphene/Fe₃O₄/polypyrrole nanocomposite. This was followed by treatment with 1 M HCl solution prior to reuse. After 6 cycles, the PNC was reported to still possess a removal efficiency of about 72.2%. Also, Kim et al. (2015) desorbed chromate ions adsorbed through electrostatic/chemisorption interactions by chitosan/MWCNT/polyaniline composite by soaking them in 1.0 M NaOH solution and

agitating. The regeneration process was then carried out with 0.1 M H_3PO_4 solution, followed by drying in an oven. The PNC retained about 85% of their removal efficiency after the 3rd cycle, as compared to initial efficiency of 99.1%. Similarly, Chauke et al. (2015) determined the reusability of graphene oxide/alpha cyclodextrin/polypyrrole nanocomposite by performing 5 cycles of adsorption-desorption studies using 0.5 M NaOH solution for the desorption of the Cr(VI), followed by regeneration with 2 M HCl solution. The first three cycles showed minimal loss of efficiency, however, a significant decrease in efficiency was observed for the 4th to 5th cycles. This was attributed to the probable oxidation of the polymer through repeated oxidation reactions which occur when using high concentrations of Cr(VI) solutions due to the high oxidising nature of the Cr(VI) species.

Conversely, some researchers subject the PNCs firstly to acidic solution for the desorption step before treating with the alkaline solution for the regeneration process. Barati et al. (2013) depicted this trend by using 1 M HCl solution and agitating for the desorption of Cu(II) and Ni(II) ions from their montmorillonite/poly(methyl acrylamide-co-acrylic acid) hydrogels. This was followed by the regeneration step using 0.1 M NaOH, with the PNC retaining more than 90% and 92% of their initial adsorption capacity after five cycles for Cu(II) and Ni(II), respectively. Regeneration of magnetite polyacrylamide amino-amidoxime nanocomposite was carried out by stirring in 2 M HCl solution for the initial desorption step. The PNC was later conditioned with dilute NaOH solution for the neutralization process before washing with distilled water. After three adsorption-desorption cycles, the PNC showed no loss in its adsorption capacity for Co(II) and Ni(II) ions removal with 98% and 96% recoveries of both metals achieved, respectively. However, there was low desorption of MB from the PNC due to strong electrostatic interaction between the MB dye and the PNC (Atta et al., 2016). Most often, the HCl/NaOH solutions mix is more widely used for PNCs regeneration procedure discussed above.

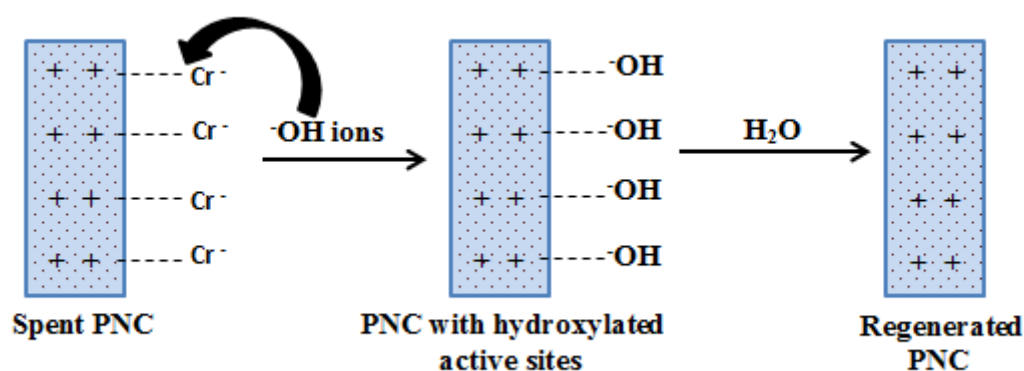


Figure 2.9: Hydroxylation scheme for alkaline medium regeneration

2.6.1.4 Regeneration of PNCs with organic solvents

Rejuvenation of PNCs with light organic solvents has been utilized by researchers with varying degree of regeneration efficiencies obtained. The organic solvents employed include methanol, ethanol, petroleum ether and toluene, which are used singly or in combination under different conditions. The regeneration process involves the washing, soaking or immersion of the PNCs in these solvents, and sometimes accompanied by agitation/ultrasonic treatment to effect the regeneration through mechanisms such as solubilisation and de-emulsification. For example, Nikkhah and co-workers (2015) utilized toluene and petroleum ether to regenerate their spent cloisite 20A nanoclay/modified polyurethane foams applied as adsorbents for oil remediation, by firstly immersing them in toluene. This was followed by washing with petroleum ether and drying in an oven. On a negative note, the investigation posited that the PNC exhibited reduced adsorption efficiency by washing with petroleum solvents. This was attributed to the structural strength weakening after washing with toluene, as the solvent penetrates the foam structure and possess the ability to react with isocyanate or the polyol chains of the polymer matrix with resultant reduction in strength of the foam. Ethanol was used for the regeneration of magnetic polystyrene nanocomposites employed for the removal of oil from water by Yu et al. (2015). The PNCs were rejuvenated by ultrasonic washing in ethanol, with subsequent washing and drying. The success of the regeneration procedure was depicted in the oil removal efficiency of the PNC which reached the oil-adsorption capacity of 2.294 times of their weight even after the 10th cycle, as compared to the 2.492 times obtained for the pristine PNC. Furthermore, Reddy et al. (2016) were able to regenerate synthesized Fe_3O_4 /polystyrene (FS_6) and Fe_3O_4 /poly(butyl acrylate) (FB_6) PNCs by mere washing with ethanol and ether solvents, respectively. The PNCs were

used to remediate edible oil and gasoline/n-hexane from the oil-water mixture or oil-in-water emulsions through a sorption process. Washing of the spent PNCs in ethanol gave regeneration for those utilized for the edible oil removal but was ineffective for the release of gasoline or n-hexane due to the difference in their polarity with that of ethanol. However, ether proved effective for the removal of the gasoline/n-hexane from the used PNCs with 98% / 99% and 99% / 97% desorption efficiency obtained for FS₆ and FB₆, respectively. Also, their investigation showed that the desorption of the edible oil from the PNCs was average (69% and 48% for FS₆ and FB₆, respectively) owing to the viscosity of the edible oil which raised the adherence of the oil to the surface of the PNCs. Retrospectively, possible improvement in the desorption of the oil from the PNCs may have been obtained in the regeneration step if the washing was aided by other additional conditions such as shaking or ultrasonic treatment (Figure 2.10). These activities can be used to speed up dissolution, by breaking intermolecular interactions.

Other reports from the literature include the regeneration of hydrophobic floating magnetic nanocomposites used for oil remediation by ultrasonic washing in ethanol, with minimal change in the water contact angle (about 153° to 139°) observed after the six cycles carried out in the study (Chen et al., 2013). Similarly, Gu and co-workers (2014) utilized ultrasonic washing in ethanol and drying in vacuum to carry out the regeneration of fabricated magnetic polymeric nanocomposites. The rejuvenated Fe₃O₄/poly(methyl methacrylate/styrene/divinylbenzene) composite (PMSD-II) showed excellent recyclability for diesel removal from water surface, as it still possessed a high water contact angle of 140.4° and an oil-absorption capacity of 3.22 g g⁻¹ even after the tenth cycle, relative to 141.2° and 3.63 g g⁻¹ reported in the first usage. Pavía-Sanders and co-researchers (2013) investigated the effect of ultrasonic washing with ethanol and drying in a vacuum on the morphology of synthesized magnetic iron oxide/poly(acrylic acid)-*block*-polystyrene nanocomposite. Infra-red spectroscopy was used to determine the state of the nanocomposite, which showed evident changes after the washing procedure, particularly between 1700 and 800 cm⁻¹. This was attributed to the probable reorganization of the polymer structures during the sonication washes. Also, the IR spectra showed an apparent loss of –OH (up to 40%) functionality after the removal of oil from the loaded PNC, presumably from the dehydration and esterification of the acrylic acid groups in the polymer matrix of the nanocomposite. Multi-walled carbon nanotube (MWCNT)/polyurethane nanocomposites synthesized and utilized for oil removal from water by Keshavarz et al. (2015), were regenerated by washing in petroleum ether and oven drying. The reusability of the nano-adsorbent (with 1% MWCNT) was determined through four cycles of regeneration and reuse, with a slight decrease in the oil removal

capacity after each cycle giving a final 85.45% of the initial oil sorption capacity in the last cycle. The reduction in the sorption potential was attributed to the incomplete regeneration of the active sites which were permanently filled by the chemically adsorbed molecules and probable loss of some of the MWCNT on the surface of the PNCs after each cycle. In all, careful selection of organic solvents for regeneration purposes is important to prevent adversely affecting the structural strength and functionality of the PNCs as depicted in the investigation carried out by Nikkhah et al. (2015) and Pavia-Sanders et al. (2013), respectively.

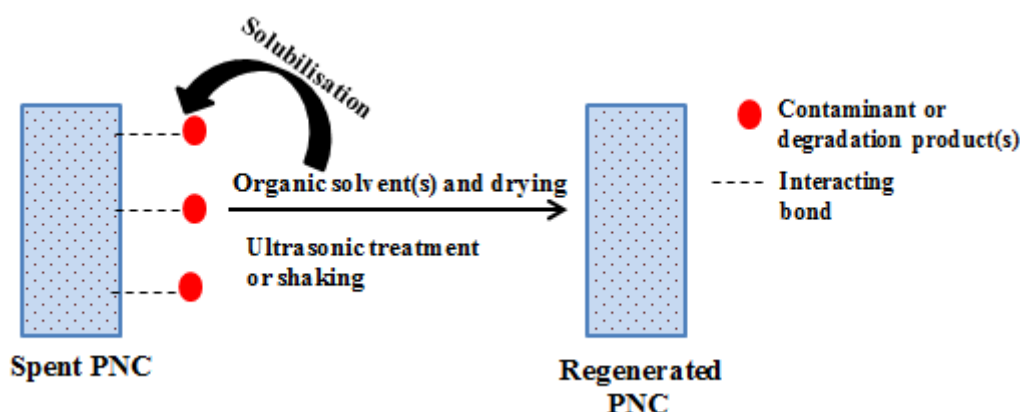


Figure 2.10: Scheme for organic medium regeneration

2.6.1.5 Regeneration of PNCs using non-specific medium

There exist in literature non-specific regeneration techniques/procedures which do not fall into any of the groups already discussed. The non-specific chemical mediums have equally produced good regeneration data as presented by some researchers. High-purity N_2 purgation was utilized for the recovery of TiO_2 /polyaniline sensor response by Zheng et al. (2008). The highly sensitive and selective sensor membrane for trimethylamine monitoring only lost 15% of its initial response magnitude after several operations which lasted for 4 months. The decline in the response was further attributed to the ageing of the polymer matrix. Yuan et al. (2016) reported the use of mannose solution for the regeneration of their AuNPspoly[2-(methacrylamido)-glucopyranose]-co-poly[2-(methacryloyloxy)ethyl trimethyl ammonium iodide] nanocomposite. Regeneration was achieved by washing the antimicrobial PNC with a large amount of the mannose solution to remove the dead cells of *E. coli* adhered to it, with subsequent reuse over three cycles showing no significant drop in performance. Graphenated-MWCNT/ TiO_2 /poly(vinyl alcohol) nanocomposites were rejuvenated by conditioning with buffer 7 and vacuum

drying. The PNC which was utilized for MB remediation in aqueous solution still exhibited an excellent efficiency > 90% after the 5th reuse cycle (Jung and Kim, 2014).

Expectedly, more non-specific procedures will evolve to meet the regeneration requirements of synthesized PNCs. In this regard, tailor-made procedures and techniques are expected from researchers in order to attain the maximum regeneration for their synthesized PNCs. Yang et al. (2015) demonstrated this by applying a binary alkaline solution of NaOH-NaCl mix (both at wt 5%) as the regenerating medium for their synthesized hydrated ferric oxide/polystyrene-divinylbenzene nano-adsorbents, utilized for the remediation of *p*-nitrophenol and phosphates from the water. The nanocomposites were further treated with 5 wt% NaCl solution prior to next usage to remove the residual OH⁻ inside them, which could hinder the contaminants remediation. Hua and co-workers (2013) utilized HNO₃-Ca(NO₃)₂ binary solution to regenerate their hydrous Zr(IV) oxide-based nanocomposite which had prior usage for the removal of Pb(II) and Cd(II) ions from aqueous solution. The process was performed using a mix solution of 0.1 M HNO₃ and 5 wt% Ca(NO₃)₂ at 298 K, with a regeneration efficiency > 95% achieved. Similarly, a binary alkaline solution of NaOH-NaCl (Pan et al., 2014) and the acidic solution of HCl-NaCl (Pan et al., 2010) have been successfully utilized for PNCs regeneration purposes. Of particular interest is the use of HCl/methanol (0.05 M) solution, to rejuvenate Fe₃O₄/starch-grafted-poly(vinyl sulphate) PNCs by Pourjavadi and co-researchers (2016). The PNCs utilized for MB and MG dyes remediation showed less than 7% loss of efficiency after 5 reuse cycles for both contaminants, with 99.1% and 97.2% initial removal efficiency obtained, respectively; while the 5th cycle reuse gave 92.5% and 91.7%, respectively. In this scenario, the synergistic effect of both the acidic medium and the organic solvent was channelled to achieve the excellent regeneration/reuse efficiency obtained. Also, the components of the PNC were possibly put into consideration, as using aqueous HCl solution may have an adverse effect on the starch grafted on the polymer matrix. Natural and cellulose-based polymers have been noted to readily dissolve in water at acidic conditions (Kim et al., 2015; Chiou et al., 2004).

2.6.1.6 Regeneration of PNCs using electrochemical techniques

Although water, chemical and organic solvent regeneration processes are more popular and widely used for the regeneration of PNCs as evident in literature due to their simple and economical procedures, utilization of electrochemical regenerative techniques tends to provide a safer and eco-friendly once-off solution for the regeneration of the PNCs and recovery of the contaminants (mostly heavy metals). To effect the deposition of the

metallic ions in their elemental form during the electrolytic process, a certain potential called the “potential of deposition” is required (Geckeler, 1980). The electrolysis of the metal-laden PNCs leads to the deposition of the metals on an electrode, which allows the recovery of the metal in its pure form without further processes required (Geckeler, 2001). In related research which can be adapted for PNCs, Xing et al. (2007) electrically regenerated ion-exchange resins employed for the removal of Cr(VI) from wastewater. Their rationale for this approach was to avoid the reintroduction of contaminants into solution as generally obtained with the alternative use of chemical medium. The electrical regeneration carried out on the principle of electrodialysis restored about 93% initial capacity of the resins under a constant current of 0.25 A, over a period of 24 h. Also, the electrically regenerated resins could remove Cr(VI) as effectively as those regenerated chemically, with the deposition of pure Cr(VI) in the anodic chamber as an added advantage.

Apart from heavy metals, Balamurugan et al. (2010) showed that synthesized poly(3,4-ethylene dioxythiophene-sodium dodecyl sulphate)/AgNP conducting electrode which exhibited electrocatalytic activity towards the oxidation of di-hydro nicotinamide dinucleotide were effectively regenerated through a redox process by the enhancement of the anodic peak current. The major challenge in the application of electrochemical regeneration is the high-energy dependent nature of the processes and the intended cost implication.

2.6.1.7 Regeneration of PNCs using thermal techniques

Thermal regeneration techniques have also been employed where possible for the regeneration of PNCs, as the method is generally restricted in its application scope and to situations where the applied heat can cleave the PNC-contaminant's bond (Geckeler, 2001). For example, Wang et al. (2016a) regenerated their chemiresistive PNC sensor utilized for monitoring ammonia and amines in water by heating in air at 80°C. Desorption of the ammonia and amines readily from the sensor were obtained through this process. Subsequent usage over a period of 7 days for 4 weeks with continuous regeneration, only gave a 12% decrease in the response of the sensor. Calcination processes were employed for the regeneration of polyethylene glycol/silica/bentonite composites utilized for the effective removal of dyes, volatile organic pollutant and petroleum product from aqueous solutions (Suchithra et al., 2012). The thermal regeneration of the PNCs was carried out by calcining the spent PNCs at various temperatures ranging from 50-300°C for a fixed time. The calcined PNCs (BSP 400) reused for the remediation of MB, MG,

phenol and toluene form aqueous solutions, gave similar adsorption efficiencies of 97.3%, 94.9%, 96.8% and 92.7%, respectively as compared to the results obtained for the pristine PNCs which was 99.8%, 97.0%, 99.6% and 98.5%, respectively.

Some scenarios where thermal regeneration technique have also been applied for PNCs regeneration include the application of hot water (as already discussed for water regeneration), to regenerate PNCs majorly employed for absorptive (oil removal) processes (Hir et al., 2017; Lü et al., 2016). The introduced heat or elevated temperature of the water aids the cleavage of the contaminants attached to the PNCs. However, the downside to this technique is that a large amount of energy is needed to keep the temperature at an elevated level (Gupta and Saleh, 2013).

Table 2.5: Regeneration processes and reusability potential of some selected PNCs

PNCs		Target pollutant(s)	Application route	Predominant interaction(s) between contaminant and PNC	1st cycle efficiency (%)	Maximum cycle & efficiency (%)	Mode of regeneration	Reference
Aqueous medium	*Pluronic P-123/poly(vinyl alcohol)/TiO ₂	Rhodamine B and water flux	Photocatalysis & membrane filtration	Physisorption	> 90% & 100% (initial flux)	5 cycles; > 82%; 91% (initial flux)	DI water (under UV irradiation for 2h)	Goei et al. (2013)
	Poly(dimethylaminoethyl methacrylate)/Au/RGO	Rhodamine B, Methyl orange and Eosine Y	Catalysis	Chemisorption (π - π)	82%, 74% & 93%, respectively	5 cycles; No significant change	DI Water; dried in vacuum	Mogha et al. (2017)
	Poly (ether sulfone)/TiO ₂	Methyl orange	Photocatalysis	Physisorption	80.34%	5 cycles; ~80%	DI distilled water	Hir et al. (2017)
	Poly(<i>N</i> -isopropyl acrylamide)/Fe ₃ O ₄ /SiO ₂	Oil (diesel)	Absorption	Physisorption	97% (water transmittance)	7 cycles; > 90%	Hot water	Lü et al. (2016)
	Poly(<i>N</i> -isopropyl acrylamide)//Fe ₃ O ₄ /SiO ₂	Oil (toluene in microemulsion)	Absorption	Physisorption	97% (water transmittance)	5 cycles; > 95%	Hot water	Chen et al. (2014)
	Poly (ether sulfone)/TiO ₂	Methylene blue	Photocatalysis & membrane filtration	Physisorption	70%	5 cycles; ~70%	Ultrapure water	Fischer et al. (2015)
Polyaniline/CdO		Methylene blue; Malachite green	Photocatalysis ; Photocatalysis	Physisorption; Physisorption	99%; 98%	5 cycles; 82% 5 cycles; 93%	DI water & dried at 100°C	Gülce et al. (2013)

	PNCs	Target pollutant(s)	Application route	Predominant interaction(s) between contaminant and PNC	1st cycle efficiency (%)	Maximum cycle efficiency (%)	Mode of regeneration	Reference
	Poly(1-vinylimidazole)/Fe ₃ O ₄ /SiO ₂	Hg(II)	Adsorption	Chemisorption (π-π)	> 96%	5 cycles; > 94%	0.5 M HCl	Shan et al. (2015)
	Iminodiacetic acid-g-poly(glycidymethacrylate-maleic anhydride)/Fe ₃ O ₄	Pb(II) & Cd(II)	Adsorption	Chemisorption	100% & 91%, respectively	6 cycles; ~90% & ~82%, respectively	0.5 M HCl	Hasanzadeh et al. (2017)
	Poly(vinyl pyrrolidine)/Fe ₂ O ₃ /Al ₂ O ₃	Hg(II), Ni(II), Pb(II) & Cu(II)	Adsorption	Electrostatic	89%, 67%, 52% & 21%, respectively	4 cycles; ~89%, 67%, 52% & 21%, respectively	0.05 M HCl	Mahapatra et al. (2013)
Acidic medium	Polyaniline/MWCNT	Nitrate ions	Adsorption (Ion-exchange)	Chemisorption	80%	5 cycles; 56%	1.0 M HCl	Nabid et al. (2012)
	Poly(acrylamide)/bentonite	Cu(II), Zn(II) & Co(II)	Adsorption	Chemisorption	~99.5%, 99.0%, 98.0%, respectively	3cycles; ~87.5%, 91.2%, 85.0%, respectively	0.1 M HCl	Anirudhan and Suchithra (2010)
	Poly(acrylamide)/bentonite	Malachite green; Methylene blue; Crystal violet	Adsorption (Ion exchange)	Chemisorption	~99.0%, respectively	4 cycles; ~90.0%, respectively	0.1 M HNO ₃	Anirudhan et al. (2009)
	Polystyrene/graphene oxide/ Fe ₃ O ₄	Pb(II)	Adsorption	Electrostatic	93.78%	4 cycles; 40.96%	10% HNO ₃	Ravishankar et al. (2016)

PNCs		Target pollutant(s)	Application route	Predominant interaction(s) between contaminant and PNC	1st cycle efficiency (%)	Maximum cycle efficiency (%)	Mode of regeneration	Reference
Alkaline /and acidic medium(s)	Triethylene tetramine /GO/CoFe ₂ O ₄	Cr(VI)	Adsorption	Electrostatic	100%	5 cycles; 78%	2 wt% NaOH	Sun et al. (2016)
	Polyaniline/ α -zirconium	Methyl orange	Adsorption	Electrostatic	100%	5 cycles; ~80%	0.5 M KOH	Wang et al. (2012a)
	Poly(vinyl fluoride)/Al ₂ O ₃	Oil (oil field wastewater)	Adsorption/ ultra- filtration	Physisorption	100% flux	1 cycle; 100% initial flux	OP-10 surfactant solution (pH 10)	Yan et al. (2009)
	Polypyrrole/graphene/ Fe ₃ O ₄	Cr(VI)	Adsorption	Chemisorption	100%	6 cycles; 72.2%	0.5 M NaOH / 1 M HCl	Yao et al. (2014)
	Poly(ethersulfone)/polyaniline/MWCNT	NOM and water flux	Adsorption/ membrane filtration	Electrostatic	80% & 100% (water flux)	3 cycles; ~80% & 100%, respectively	0.1 M HCl/ 0.1 M NaOH for 1 hour	Lee et al. (2016)

PNCs		Target pollutant(s)	Application route	Predominant interaction(s) between contaminant and PNC	1st cycle efficiency (%)	Maximum cycle efficiency (%)	Mode of regeneration	Reference
Organic solvents	Poly(tert-butyl acrylate)/graphene oxide	Tetrabromo-bisphenol A	Adsorption	Chemisorption (π - π)	100%	6 cycles; 95%	Ethanol	Zhao and Liu (2014)
	Polydopamine/modified graphene	Rhodamine B &	Adsorption	Electrostatic	100%	10 cycles; > 85%	Ethanol	Gao et al. (2013a)
		<i>p</i> -nitrophenol	Adsorption	Chemisorption	100%	10 cycles; > 80%		
	Polyurethane/graphene/ Fe ₃ O ₄	Oil (n-hexadecane)	Absorption	Physisorption	100% & 158 $\pm 1^\circ\text{C}$ water contact angle	8 cycles; > 90% & 155 $\pm 2^\circ\text{C}$ water contact angle	Ethanol	Liu et al. (2015)
	Poly(ethylene oxide)/poly(L-lactide)/oleic acid-coated Fe ₃ O ₄	Malachite green	Adsorption	Physisorption	~40%	3 cycles; ~40%	Ethanol	Savva et al. (2015)
	Poly(vinyl pyrrolidine)/Fe ₃ O ₄	Bisphenol A; Ketoprofen; Estriol; Triclosan; Metolacchor	Adsorption Adsorption Adsorption Adsorption	Physisorption Physisorption Physisorption physisorption	98%; 95%; 93%; 92%; 81%	5 cycles; ~97%, ~93%, ~90%, ~91%, ~80% respectively	Methanol	Fard et al. (2017)

PNCs		Target pollutant(s)	Application route	Predominant interaction(s) between contaminant and PNC	1st cycle efficiency (%)	Maximum cycle efficiency (%)	Mode of regeneration	Reference
Other non-specific mediums	Poly[2-(methacrylamido) glucopyranose]-poly[2-(methacryloyloxy) ethyl trimethylammonium iodide]/Au	<i>E. coli</i>	Microbial control	Physisorption	98.3% $\pm$ 0.1 – 98.6% $\pm$ 0.5	3 cycles; no significant drop in performance	Mannose solution	Yuan et al. (2016)
	Poly(vinyl alcohol)/TiO ₂ /graphene-MWCNT	Methylene blue	Photocatalysis	Physisorption	100%	3 cycles; > 90%	Buffer vacuum dry at 60°C for 24 h	Jung and Kim (2014)
	Poly(3-acrylamidopropyl)-trimethylammonium chloride/Cu	2-nitrophenol	Catalysis	Physisorption	100%	5 cycles; 46.57%, 60.75%, 51.45%, 75.42% respectively	Centrifugation and decantation only	Rehman et al. (2015)
		4-nitrophenol	Catalysis	Physisorption	100%			
		Eosin Y	Catalysis	Physisorption	100%			
		Methyl orange	Catalysis	Physisorption	100%			

*Pluronic P-123= poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

2.7 Effect of pollutants nature in regeneration and reuse processes

The nature and constituent of the pollutants play a major role in determining the type of interactions established between the pollutants and the PNCs during their remediation/treatment processes (see Figure 2.11). Subsequently, the interaction formed determines the choice of regenerating medium(s) and procedure to use for the regenerative step. For example, oils in wastewater when remediated with PNCs adsorbents are bonded to the composites mostly by physisorption interactions via absorption processes. In this scenario, hot water, light organic solvents and alkaline surfactants are generally employed to break the weak interacting bond (physisorption) through solubilisation and de-emulsification mechanisms to effect the regeneration of the PNCs (Lü et al., 2016; Abdulhussein et al., 2018; Yan et al., 2009). PNCs with hydrophobic and oleophilic properties are majorly employed for the efficient remediation of oils from wastewaters (Yu et al., 2015; Gu et al., 2014). Hence, regeneration with water is inadequate, except at elevated temperatures when the introduced heat helps to loosen the interacting bonds between the attached oil films/droplets and the PNCs. Similarly, surfactant, when added to water, reduces the interfacial tension between the oil and water, which allows the oil molecules to be detached from the PNCs and removed by the water/surfactant solution. Also, oils being non-polar compounds are readily dissolved by light organic solvents (methanol, ethanol, toluene etc.) to aid their release from the PNCs and ensure regeneration.

Organic contaminants in wastewaters are remediated through catalytic, sorptive or filtration processes. In this regard, the nature of their interaction with various PNCs ultimately determines the medium and procedure best suited for their regeneration. Typically, in most catalytic processes, the predominant interaction between the organic compound and the PNCs tends to be physisorption (Jung and Kim, 2014; Goei et al., 2013; Fischer et al., 2015), with few instances of chemisorption (Mogha et al., 2017). In Table 2, PNCs utilized for the remediation of several organic compounds such as bisphenol A, tetrabromobisphenol A, p-nitrophenol, ketoprofen, estriol, triclosan and metolachlor were effectively regenerated at different degrees of efficiency using organic solvents. This procedure was basically employed as these compounds and their degradation products readily dissolve in the organic solvents due to their composition and nature. Furthermore, water (applied under different conditions) also provides a successful route for the regeneration of PNCs employed in catalytic degradation of organic compounds, essentially because the interaction between the PNCs and the compounds/degradation products is through physisorption which allows easy dissolution.

However, for other organics whose mechanism of interaction with PNCs used for their remediation is through electrostatic or chemisorption via adsorption processes, acidic, alkaline or a combination of acidic/alkaline is required to give successful regeneration results (Ravishankar et al., 2016; Wang et al., 2012a; Lee et al., 2016).

For heavy metals, the major route for their remediation with PNCs is through adsorption processes brought about by electrostatic/chemisorption interactions (Hasanzadeh et al., 2017; Mahmoudian et al., 2017; Zhu et al., 2018b; Wang et al., 2013b). The nature of the bond formed between the PNCs and the heavy metal contaminants usually requires oxidising/reducing action(s) obtained from acidic, alkaline or alkaline/acidic solutions to effect their desorption from the PNCs and facilitate regeneration (Yao et al., 2014; Mahapatra et al., 2013).

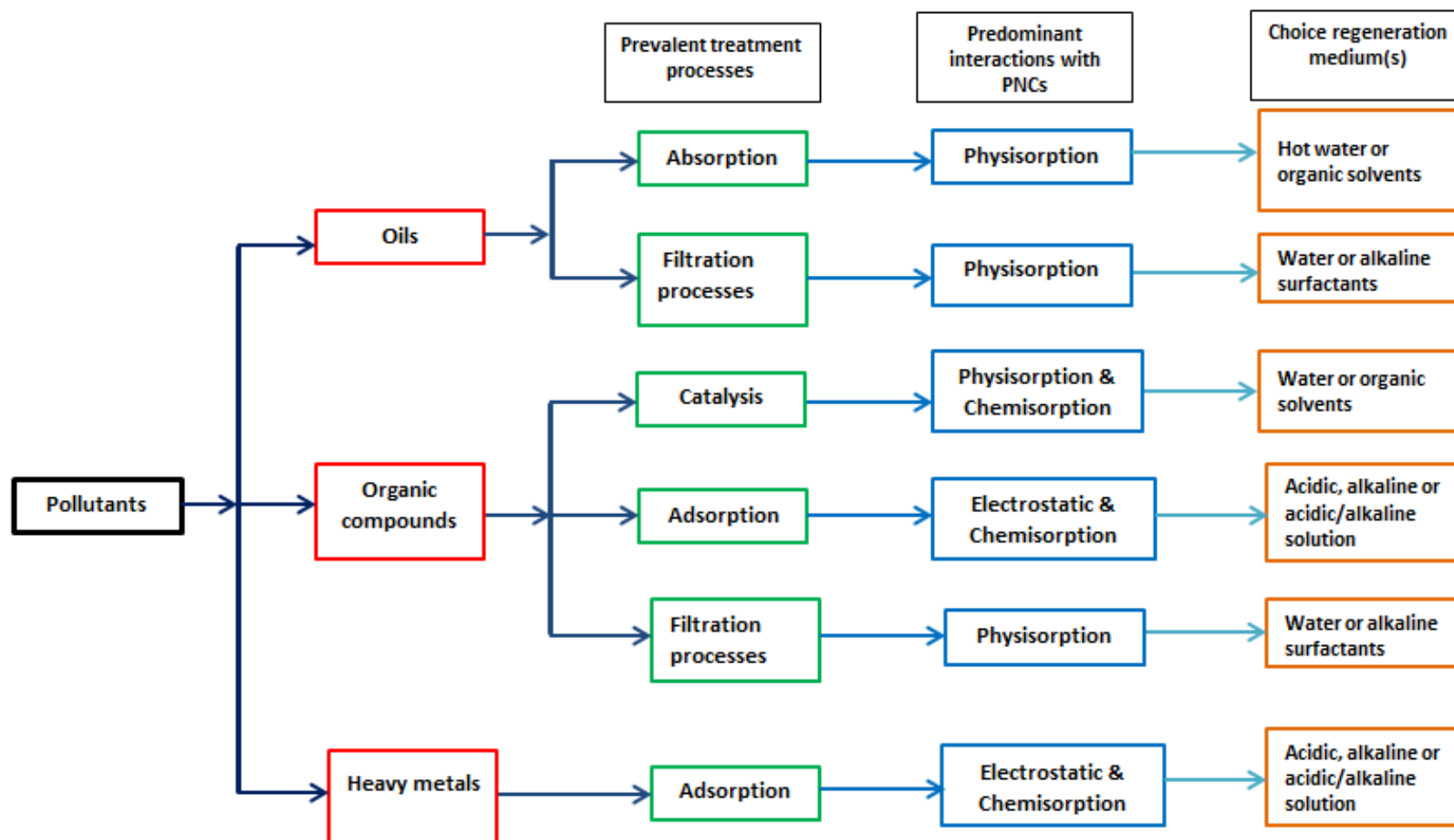


Figure 2.11: A scheme showing some pollutants and the choice of regeneration medium

2.8 Safe application and rational design of PNCs

Although the synthesis and application of PNCs for wastewater treatment operations is perceived as one of the ways to prevent possible contamination of the environment with nanomaterials during remediation processes, the safe application of these composites still requires monitoring with an intentional gathering of empirical evidence to either affirm or disprove their environmental toxicity. To improve on the existing conceptualized model for the rational design of nanomaterials (Li et al., 2015), it is therefore imperative to add a 'safe application' module following performance studies (Figure 2.12). At this stage, treated water or effluent would be subject to routine testing assays to assess safety and eco-friendliness of the PNCs.

The ecotoxicological tests will be used to determine potential associated health risks of the wastewater remediated with synthesized PNCs. These tests may be carried out using different trophic level organisms as required by the intended usage of the remediated wastewater. Hence, the assays may be a toxicity test on microalgae, crustaceans, fishes and lower aquatic organisms, seed germination and early plant growth, or effect on higher plants. Future studies on the synthesis and application of PNCs for water treatment processes will not be complete without appropriate toxicity assays on the remediated water and monitoring for leached nanomaterials.

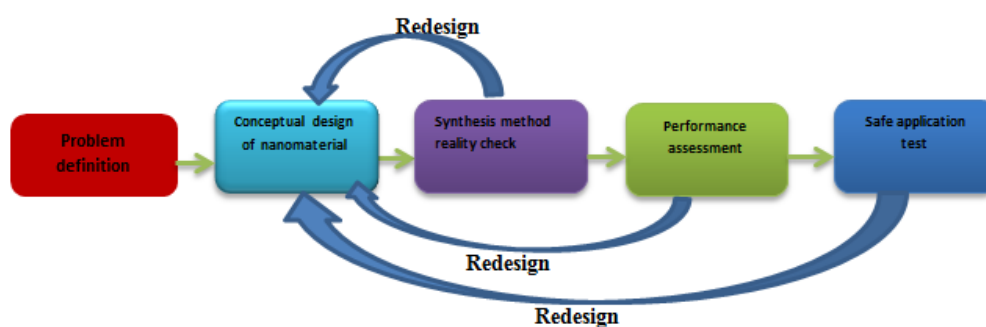


Figure 2.12: Rational design of nanomaterials

Adapted from: Li et al. (2015)

Chapter: 3 Experimental methodology

3.1 Chemicals and reagents

The 4-chlorophenol (99%) and 4-nitrophenol (99%) standards, as well as polymer materials and additives- ϵ -caprolactam (99%) and 6-amino caproic acid (99%), were purchased from Sigma Aldrich, South Africa. Daphtoxkit FM™ *Magna* was procured from Microbiotest Inc., Belgium. Analytical grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NH_4OH , KI, n-hexane, acetone and acetonitrile, HCl, ethanol (99.5%), formic acid (98%), nitric acid (98%), Na_2EDTA (99%), ascorbic acid (>99%), ammonium hydroxide solution (NH_3 content 28-30%), methanol (99.9%), acetonitrile (>98%), dimethyldichlorosilane (5% in toluene), toluene (99.5%), 10% nitric acid were also sourced from Sigma Aldrich, South Africa. Milli-Q water (Milli-Q Academic, Millipore) was used for reagent preparation and other experiments in the study.

3.2 Synthesis of β -FeOOH nanoparticles

The β -FeOOH nanoparticles were prepared using the method described by Oputu et al. (2015a). For a typical synthesis, 200 mL of Milli-Q water was mixed with 200 mL of absolute ethanol. The pH of the solution was adjusted to 10 by dropwise addition of NH_4OH (0.5 M), followed by the addition of 3.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to the mixture and stirring effectively for proper dissolution. The final pH of the solution was then adjusted to be 2.0 with HCl (0.5 M). The homogenous mixture was placed in a Teflon lined pressure vessel. The pressure vessel was heated at 100°C for 5 h and allowed to cool down to room temperature. The supernatant liquid was decanted followed by centrifugation and washing of the solids with ethanol to remove residual chloride ions. The washed solids were placed in the oven for drying at 60°C for 1.5 hours. Finally, the prepared β -FeOOH nanoparticles were stored in a desiccator. The experimental set-up used for the synthesis of the β -FeOOH nanoparticles is presented in Figure 3.1. The inside view of the reactor (with the Teflon vessel) is shown in Figure 3.2, while the mixture before and after the hydrothermal reaction is presented in Figure 3.3.

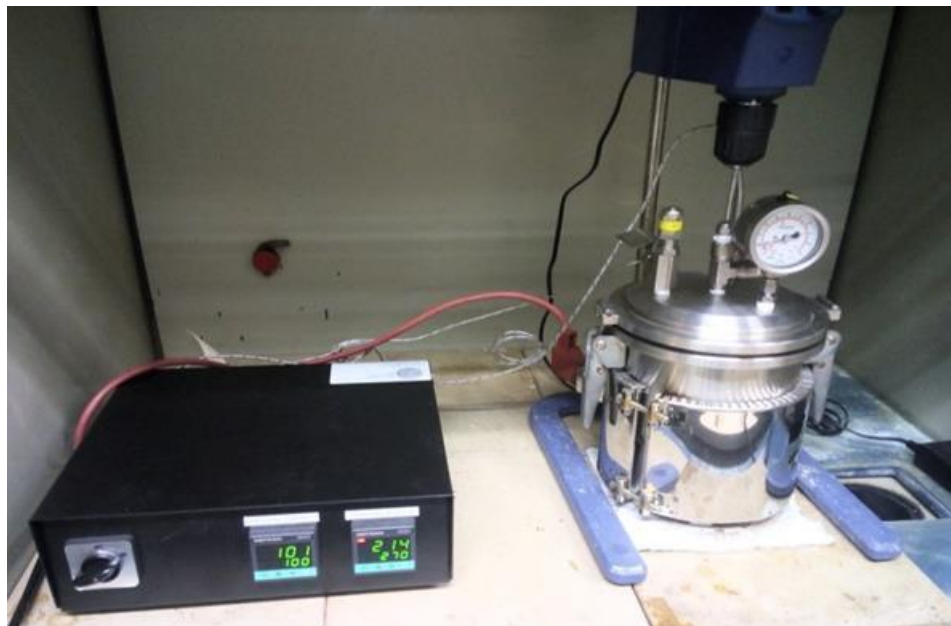


Figure 3.1: Temperature-controlled thermal reactor for the synthesis of the β -FeOOH nanoparticles



Figure 3.2: The homogenous mixture of water, ethanol and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ inside the Teflon lined reactor



Figure 3.3: Mixture of water, ethanol and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ before introduction into the reactor (left) and solution after 5 h at 100°C in the reactor (right)

3.3 Syntheses of $\beta\text{-FeOOH}$ /polymer composites

The polymeric nanocomposites were prepared using an *in situ* technique. The synthesised nanoparticles were added to the monomer prior to the polymerization step. The method of preparation of the $\beta\text{-FeOOH}$ /polymer composites was tailored according to that described by O'Neill et al. (2014). The starting material, ϵ -caprolactam (30 g) was placed into a 50 mL round bottom flask with a magnetic stirrer and kept in a fume hood under an inert nitrogen atmosphere. The temperature was raised from the room temperature to 80°C , with a magnetic flea added and set to a stirring speed of 1500 rpm throughout the polymerization.

The synthesized $\beta\text{-FeOOH}$ particles were added in the required amounts to give weight percentage (wt%) composites of 0.5 wt%, 0.75 wt%, 1.0 wt% and 1.25 wt%, respectively. After addition of the $\beta\text{-FeOOH}$, the temperature was increased to 150°C . A 10 wt% (3 g) of the initiator (6-aminocaproic acid) was added and the reaction allowed to continue for 30 min. Further increases of temperature to 200°C for 30 min, 225°C for 30 min and 250°C for 5 h were carried out.

The resulting viscous polymer was poured into boiling deionized water and allowed to cool. The nanocomposite was then chopped into small pieces using a stainless-steel knife and washed with boiling water for 2 h. The washing was repeated 4 times to remove any unreacted monomer. The thoroughly washed samples were then dried overnight under vacuum at 80°C. The experimental set-up and the polymerization scheme for the process are presented in Figures 3.4 and 3.5, respectively.



Figure 3.4: Experimental set-up for the synthesis of the β -FeOOH/polyamide nanocomposites

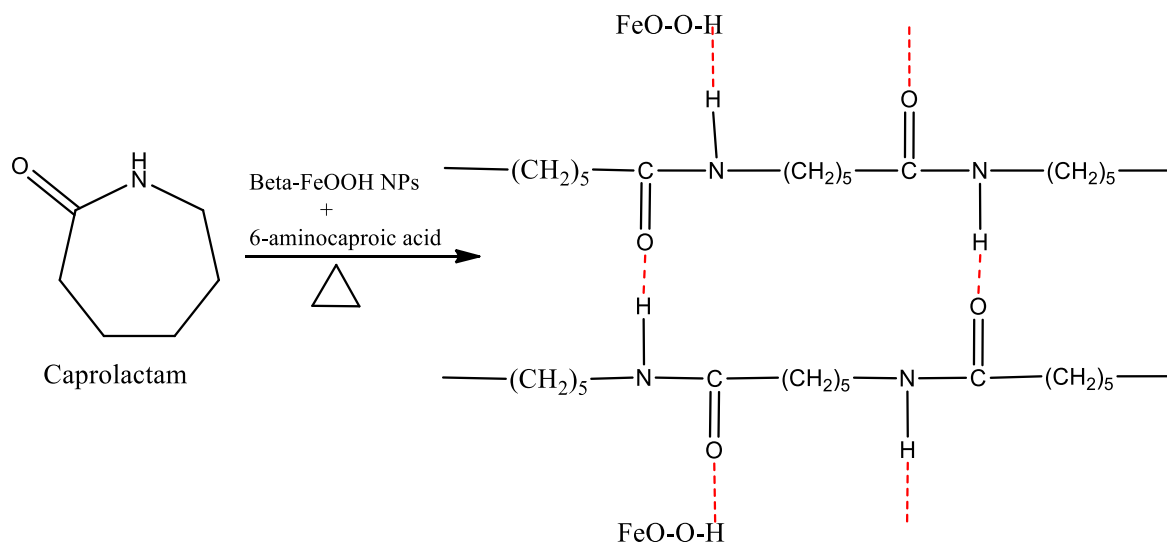


Figure 3.5: Proposed polymerization scheme of the β -FeOOH/polyamide nanocomposites showing suggested anchor points for the nanoparticles in the polymer matrix

3.4 Characterization of β -FeOOH nanoparticles and polymeric nanocomposites

The synthesized β -FeOOH nanoparticles and polymeric composites were both characterized to elucidate the morphological, structural and functional properties, as well as ascertain the elemental compositions. The characterization techniques used include the transmission electron microscopy (TEM) and scanning electron microscopy (SEM) – with the energy-dispersive X-ray spectroscopy (EDS) extracted from it. Other techniques used were the Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption analysis (BET and BJH) and X-ray diffraction (XRD).

3.4.1 Transmission electron microscopy (TEM)

For TEM analysis, the suspended samples were loaded on carbon-coated copper grids (Agar Scientific, UK). Excess sample was blotted with filter paper and allowed to dry. The samples were viewed and analysed using a FEI Tecnai 20 transmission electron microscope (FEI, Eindhoven, Netherlands) operating at 200kV (Lab6 emitter) and fitted with a Tridiem energy filter and Gatan CCD camera (Gatan, UK). The average diameter and length of the nanoparticles were determined using ImageJ software.

3.4.2 Scanning electron microscopy (SEM)

The SEM samples were prepared by sprinkling a small amount of the sample onto a carbon covered SEM stub. The samples were then evaporation coated with a thin film of carbon, ready for viewing in the SEM. SEM images were captured with a Nova NanoSEM 230 (Diepoldsau, Switzerland) with a field emission gun and operated at an energy level of 5.0 KeV, while the EDS spectrum was obtained with an Oxford X-Max 20mm² detector (Oxfordshire, UK) and data collected the data using Oxford INCA software.

3.4.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR technique was used to determine the functional groups of the β -FeOOH nanoparticles and the β -FeOOH/polyamide nanocomposites. It also provided information used for the confirmation of the incorporation of the nanoparticles in the polyamide matrix. The infrared spectra of the synthesized materials were captured within the range of 4000-400 cm⁻¹ using a UATR Two PerkinElmer FT-IR spectrometer (Llantrisant, UK) in ambient conditions.

3.4.4 Nitrogen adsorption-desorption analysis (BET and BJH)

Nitrogen adsorption-desorption analysis for surface area, pore volume and pore size were elucidated for the nanoparticles only. The Brunauer-Emmet-Teller (BET) surface area and the Barrett-Joyner-Halenda (BJH) pore volume and pore size were obtained with a TriStar II 3020, Version 2.00 Unit (Norcross, USA). Prior to the analysis, the samples were degassed at 100°C for 16 h under a gentle stream of nitrogen.

3.4.5 X-ray diffraction (XRD)

Powder XRD spectra were obtained using a Bruker D8 Advance powder diffractometer (Billerica, USA) with Vantec detector and fixed divergence and receiving slits with Co-K α radiation. The phases were identified using Bruker Topas 4.1 software (Coelho, 2007) and the relative phase amounts (weight%) were estimated using the Rietveld method. The samples were degassed at 35°C for 24 h before the measurements.

3.5 Optimization studies for the polymeric nanocomposites

Quality assurance and screening studies were conducted using simulated wastewaters prepared from analytical standards of 4CP and 4NP. The process was employed to ascertain the nanocomposite material most effective for the removal of the phenols of interest from contaminated water.

Stock solutions ($1000 \times 10^{-3} \text{ mol L}^{-1}$) were prepared by dissolving pre-determined quantities of the standards (4-chlorophenol and 4-nitrophenol) in a specified volume of Milli-Q water to form a solution. Working standard solutions ($2 \times 10^{-3} \text{ mol L}^{-1}$) were then prepared from the respective stock solutions. The prepared samples were transferred into amber bottles and stored at 4°C in the dark.

The synthesized nanocomposites in combination with ozonation were tested for their treatment and remediation capabilities using the simulated wastewater samples. The most promising nanocomposite material was thereafter used for further studies with real effluent samples from Stellenbosch WWTP, Western Cape, South Africa.

3.6 Pre-batch ozonation and ozonation degradation

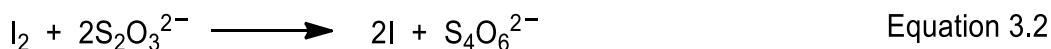
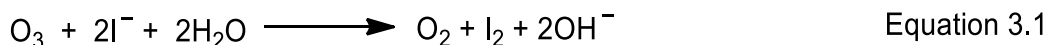
3.6.1 Calibration of ozone generator

An ozone generator purchased from Ecological Technology (1000BT-12, Eco-Tech, South Africa) was used to generate the ozone utilized for the ozonation degradation, with the oxygen gas (99.998% purity) sourced from Air *Liquide*, South Africa. The oxygen flow rate to the ozone generator was controlled using a mass flow meter (Bronkhorst M33). The calibration of the ozone generator was carried out by determination of the ozone dose/minute produced by the ozone generator at varying oxygen flow rates, ranging from 5 mL min^{-1} – 50 mL min^{-1} . The standard iodometric titration method was used to measure the ozone (Chou and Chang, 2007).

The O_2 gas was kept at a fixed flow rate using the mass flow meter and the O_2 passed through the O_3 generator where conversion to O_3 takes place. The generated O_3 was introduced into 100 mL 2% potassium iodide (KI) placed in the reactor and the gas flow was kept on for 20 min for each measurement. A constant temperature of 293 K was

maintained throughout calibration processes, as the solubility of O_3 is temperature dependent.

By calculating the amount of O_3/O_2 flowing through the reactor per minute, the composition of the gas feed into the reactor was determined. The quotients thereby represent the percentage of O_3 in the gas feed.



From equation 3.1 and 3.2 above, the O_3 concentration is equivalent to the I_2 concentration and this is further represented as shown in equation 3.3 below;

$$C_{O_3} = C_{I_3} = \frac{C_{S_2O_3^{2-}} \times V_{S_2O_3^{2-}}}{2V_{I_2}} \quad \text{Equation 3.3}$$

The O_3 concentration ($mg\ L^{-1}$), dosage ($mg\ min^{-1}$) and gas-phase concentration (%) were then determined by taking into account O_3 molecular mass, dose time/volume and moles of oxygen gas (at different volumes), respectively. The moles of oxygen in the gas feed was determined using equation 3.4, where P is 1 atm, V is oxygen flow rate, R is gas constant 0.0821 (atm Litres) and T is the experimental temperature at 293 K.

$$n_{O_2} = \frac{PV}{RT} \quad \text{Equation 3.4}$$

3.6.2 Determination of ozone mass transfer to the aqueous phase

Determination of O_3 mass transfer from the gas phase to aqueous media was evaluated by monitoring the aqueous concentration as a function of time. Ozone bubbles were introduced into 100 mL of Milli-Q water and aliquots were taken at regular intervals for analysis. The Indigo method proposed by Bader and Hoigné (1981) was employed for the O_3 quantification. The indigo trisulfonate decolourizes in an acidic solution rapidly and stoichiometrically. A 10 mL of 0.5 M phosphate buffer solution (pH 2) was measured into a

100 mL volumetric flask; a 1 mL of 1 mM indigo reagent (potassium indigo trisulfate) and 20 mL of Milli-Q water were added. The mixture was dosed with 1 mL of each of the $\text{H}_2\text{O}/\text{O}_3$ sample and stirred continuously. The volumetric flask was filled to the 100 mL mark with Milli-Q water; the magnetic stirrer was removed prior to the filling. The unreacted dye was quantified using a spectrophotometer (Jenway 6300, Bibby Scientific Ltd, UK) at 600 nm. Standard solutions of O_3 were prepared from solutions whose O_3 concentration was determined from iodometry.

3.6.3 Ozonation of phenolic compounds

Ozonation of the analytes (4CP and 4NP) was carried out to ascertain their degradation pathways, intermediates and products, as well as the degradation rates under different initial pH conditions. In this investigation, 100 mL of 2×10^{-3} M solutions of the analyte was used in all instances, respectively. The analyte solution was introduced into a sintered glass reactor fitted with a porous glass sprout with a porosity of 2, for the infusion of 10 mL min^{-1} ozone delivered by the Eco-Tech ozone generator. The duration of each experiment was 60 min with 1 mL sample drawn at intervals to quantify the phenol and identify the intermediates generated over time. Phosphoric acid (1 M) was used to adjust the analyte solutions with starting pH 3 (acidic), and sodium hydroxide (1 M) for the pH 10 analyte solutions. Operating conditions of the experiments included constant stirring at $20 \pm 1^\circ\text{C}$.

3.6.4 Catalytic ozonation degradation

Batch ozonation analyses were carried out following the procedure described by Oputu et al. (2015a). A 0.5 g of $\beta\text{-FeOOH}$ /polymeric composite was added to 100 mL, 2×10^{-3} M analyte solution by sonication. The dispersed $\beta\text{-FeOOH}$ /polyamide composite in analyte solution was fed into a homemade 200 mL glass reactor with a porous bubbler. The mixture was allowed to achieve equilibrium by stirring in the reactor without passage of O_3 gas for 1 h, with test samples drawn at different time intervals for analysis to quantify analyte removal by adsorption mechanism (where applicable). Thereafter, a mixture of O_2/O_3 was introduced into the glass reactor at a flow rate of 10 mL min^{-1} using a mass flow meter. Samples were drawn from the reactor at regular intervals for analyte determination. A pictorial view of the ozonation set-up is presented in Figure 3.6.

The degradation efficiency was calculated using the equation:

$$\text{Degradation efficiency (\%)} = \frac{(C_0 - C_t) \times 100\%}{C_0}$$

Equation 3.5

Where C_0 is the initial concentration of analytes; and
 C_t the concentration removed at time t (min).

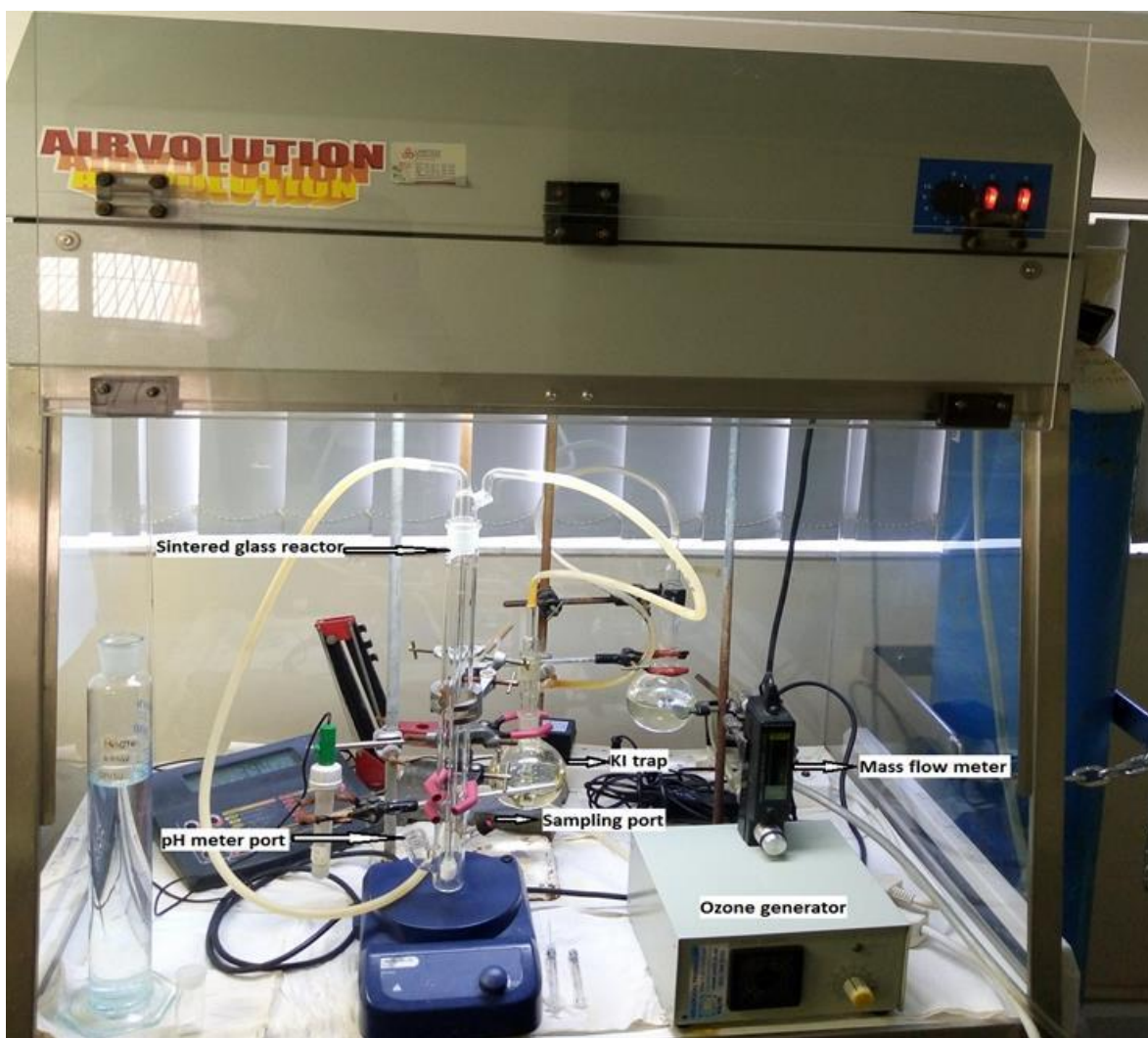


Figure 3.6: Experimental set-up for the ozonation process

3.6.5 Kinetic study and effect of pH on the catalytic ozonation

The procedure was carried out as described for the catalytic ozonation step in section 3.7.4. The analyte (4CP) solutions were adjusted to pH 3, 7 and 10, respectively prior to the experiments. Samples were taken at intervals and the 4CP concentrations measured using the LCMS-TOF instrumentation. The results obtained were used to determine the reaction rates of the different pH values. The data were fitted into the pseudo-first-order kinetics model following the Langmuir-Hanshelwood model (Li et al., 2018; Liu et al., 2014b). The equation is expressed as:

$$\ln = (C_0 / C_t) = K_1 t \quad \text{Equation 3.6}$$

Where C_0 is the initial concentration of analytes,
 C_t the concentration removed at time t (min), and
 K_1 (min^{-1}) is the first-order rate constant.

3.6.6 LCMS-TOF identification and quantification of phenolic compounds

The samples obtained from experiments in section 3.7.3 and 3.7.4 were analysed using LCMS-TOF technique with an Ace 5 C18 column (Agilent 6230 TOF LC-MS - Agilent Technologies, Inc, USA). The Agilent 1260 infinity series employed housed an auto-sampler, a binary pump and an 1100 diode array detector (DAD), operating on Mass Hunter software version 3.0. The phenols ionization was done by electron spray (ESI) nebulized over a drying gas (nitrogen) at 350°C and the ions captured in the negative mode using -175 V as the fragmentation. Mobile phases utilized for the analysis were 0.1% formic acid in water and 0.1% formic acid in acetonitrile. The experimental conditions and other necessary information are as presented in Table 3.1.

Table 3.1: LCMS parameters for quantification and identification of intermediates

Chromatograph	Agilent 6230 TOF LC/MS		
Detector	Agilent DAD 1100		
Column	Ace 5 C18 column, 3.9mm 5 μ		
Mass analyser	Time-of-flight		
Injection volume	5 μ L		
Mobile phase	A: water (0.1 % formic acid)		
	B: Acetonitrile (0.1 % formic acid)		
Flow-rate	0.3 mL/min		
Gradient elution	Time (mins)	%A	%B
	0	85	15
	35	0	100
	47	0	100
	50	85	15
Temperature	26°C		
Data Collection	Mass Hunter		

3.6.7 Regeneration and reuse studies

The regeneration and reuse potentials of the polymeric nanocomposites were studied using 100 mL of 2×10^{-3} M analyte solution during the catalytic ozonation degradation step. The used β -FeOOH/polyamide composites were regenerated using Milli-Q water assisted by sonication. The used nanocomposites were immersed in 50 mL of Milli-Q water at a temperature of 50°C and sonicated for 30 min; the procedure repeated 2 times. This was followed by thorough rinsing using Milli-Q water and drying in an oven at 50°C for 1 h. The regenerated β -FeOOH/polymeric composites were then reused for catalytic ozonation treatment processes.

3.6.8 Leaching studies

Investigation for the leaching of iron into the treated water during application of the β -FeOOH/polyamide composites were done at pH 3, pH 7 and pH 10. Phosphoric acid (0.5 M) and sodium hydroxide (0.5 M) solutions were used to adjust the 2×10^{-3} M 4CP to the acidic and alkaline pH respectively, prior to the catalytic ozonation step. The treated water

samples were drawn at the end of each catalytic ozonation process and the iron levels determined using an atomic absorption spectrophotometer equipped with AA WinLab Analyst software (Perkin Elmer 3300, Germany), with the data collected using AA WinLab Analyst software. Treated water samples from the regeneration cycles of the polymeric nanocomposites were also analysed for iron content.

3.7 Ecotoxicity studies

Toxicity bioassay was used to evaluate the possible associated ecological risk of the wastewater remediated with the polymeric nanocomposites. Samples tested included blank or control samples, 4CP contaminated water before and after the remediation processes. Water flea (*Daphnia magna*) an aquatic crustacean, was used to assess toxicity in freshwater systems. Water flea is a primary consumer and a major component of zooplankters in the ecosystem. The acute toxicity testing was carried out at 24 h and 48 h using mortality of the *D. magna* (ISO 6341).

Hatching of the daphnids from the ephippia was carried out using the supplier's (Daphtoxkit F MagnaTM, Microbiotests Inc., Belgium) instructions. The daphnids were fed 2 h prior to the commencement of the toxicity assays to prevent their "starvation to death" which may alter the accuracy of the results. The dilution percentiles of the water samples were prepared according to standard procedures to obtain 6.25, 12.5, 25, 50 and 100 percentile. The holding plate for the assays is fitted with six rows (one for each of the diluted samples and the control) and four columns which allowed for four replicates for each sample. In the four cells for each dilution, 10 mL of the samples was introduced, and five actively mobile neonates transferred into each. The plate was covered and incubated in the dark at 20°C and the mobility result scored at 24 h and 48 h, respectively. The neonates that could not swim after a gentle swirl of the samples for 15 seconds was considered immobilized even if they could move their antennae. The experimental data obtained were analysed using Toxrat Professional 3.2[®] for the determination of the statistical significance.

3.8 Wastewater sampling and analysis

3.8.1 Pre-sampling and sampling procedures

All glassware used was first soaked in 10% nitric acid followed by acetone for at least 30 min; rinsed in hexane and dried at 200°C for 4 h. The caps or lids of all sample kits were lined with PTFE. Effluent and influent samples were collected from the Stellenbosch WWTP, South Africa for analysis. The samples were collected in 2.5 litre pre-cleaned amber glass bottles. Samples were kept on ice and transported to the laboratory. Analyses of samples were done within 24 h after collection.

3.8.2 Physicochemical parameters determination

The determination of the physicochemical parameters of the water samples from the WWTP was done *in situ* with a field multi-parameter instrument. The samples pH, temperature, dissolved oxygen (DO), conductivity (EC), total dissolved solids (TDS) and the oxidation-reduction potential (ORP) were measured using a Lovibond® water testing potable meter- SensoDirect 150 (Tintometer®, Sarasota, USA).

3.8.3 Chemical oxygen demand analysis

Chemical oxygen demand (COD) analysis was conducted on WWTP influent samples prior to and after the ozonation processes. This includes water samples subjected to remediation processes using ozonation alone and catalysed by the synthesized nanocomposites. The closed reflux colourimetric was used to determine the COD values (ASTM, 1995). Samples were digested with potassium hydrogen phthalate (KHP) standards and potassium dichromate solutions. The digestion process converted the hexavalent chromium ions to the trivalent ions and quantification was carried out at 400 nm and 600 nm). In the experiment, a 2 mL aliquot of each sample and standard solutions were digested simultaneously (to ensure instrument accuracy) for 2 h in a reactor block at 150°C. Afterwards, the samples were removed and allowed to cool overnight. The COD levels of the samples were read using a DR 1900 spectrophotometer supplied by HACH, South Africa at 600 nm and presented as mg O₂ L⁻¹.

3.8.4 Total organic carbon analysis

As described for the COD analysis, TOC was conducted on water samples prior to the batch ozonation and the analysis repeated after the treatment procedure. The analysis

was done through thermocatalytic oxidation accompanied by the TOC measurement using a DR 1900 spectrophotometer supplied by HACH, South Africa (APHA, 1998). A 0.4 mL buffer solution (sulphate) was added to 10 mL of the sample and the pH value adjusted to 2; the mixture was then stirred to obtain a homogenous solution. TOC persulfate powder pillow was added to each acid digestion vials for both samples and standards. This was followed by the introduction of 0.3 mL of the sample (organic-free water in the case of the standard) into the vials. The pH reagent pillow is carefully added inside the acid vial after carefully nipping (by snapping) the top, followed by heating at 105°C for 2 h. The vials were removed and kept upright to cool for about 1 h before the TOC values were read at 610 nm.

3.9 Quality control and quality assurance

To ensure the quality of data, accuracy and precision of result in the study, the following quality control and assurance steps were taken into consideration;

- ❖ Analytical grade reagents and Milli-Q water were used to control external contributions.
- ❖ Analysis of control samples to ensure instrument consistency.
- ❖ Strict adherence to recommended standard methods during sampling, sample handling, preservation and analysis.
- ❖ Assessment of reproducibility of analytical procedures by analysing triplicate samples.

3.10 Data analysis

The OriginPro[®] software was utilized for the FTIR, XRD, nitrogen adsorption-desorption isotherm, and other graphical charts. ImageJ software was used to determine the nanoparticle diameter and length from the TEM spectrum. Microsoft excel was utilized to analyse some data as appropriate.

Chapter: 4 Results and discussion**4.1 Characterization of β -FeOOH and β -FeOOH/polyamide composites**

The β -FeOOH nanoparticles and the β -FeOOH/polyamide nanocomposites were characterised to establish functional groups and properties of the materials. The TEM image (Figure 4.1a) showed that the β -FeOOH nanoparticles were rod-like shaped with an average diameter and length of 5 nm and 15 nm, respectively. The ultra-small nanoparticles were also well dispersed, with a D-spacing calculated to be 7.62 Å obtained from the selected area diffraction (SAED) in Figure 4.1b; the high-resolution TEM is presented in Figure 4.1c. The TEM image of the 1.25 wt% β -FeOOH/polyamide composites (Figure 4.2) gives a visualized evidence of the embedded nanomaterials in the polymer matrix. Clearly, rod-like shapes distinctive to the β -FeOOH nanoparticles can be seen in the polymeric nanocomposites. This suggests the incorporation of the nanoparticles in the polyamide matrix.

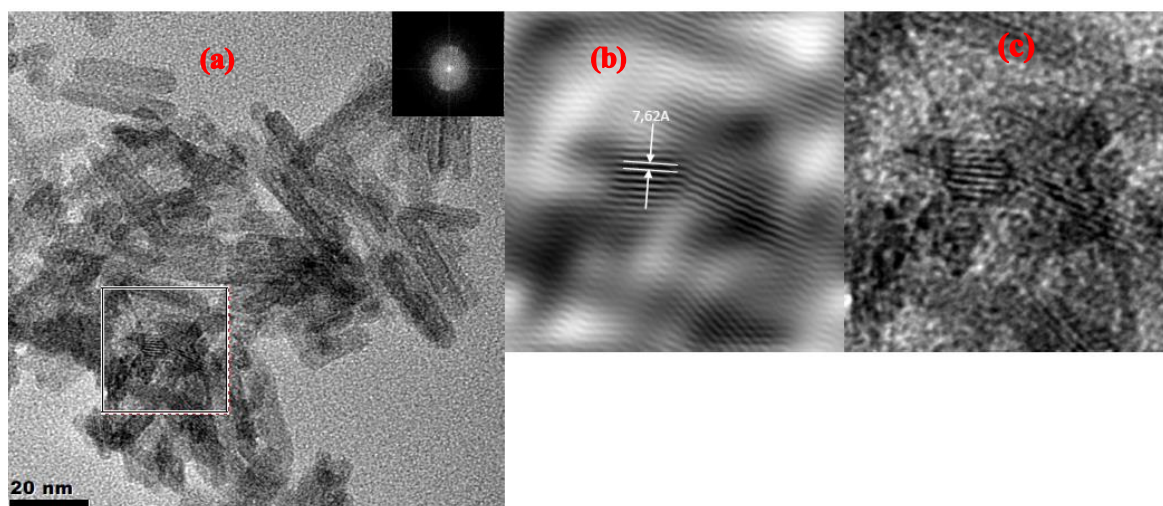


Figure 4.1: (a) TEM images of β -FeOOH nanorods (insert: SAED patterns of the nanorods), (b) D-spacing for the β -FeOOH nanoparticles and (c) HRTEM of β -FeOOH nanoparticles

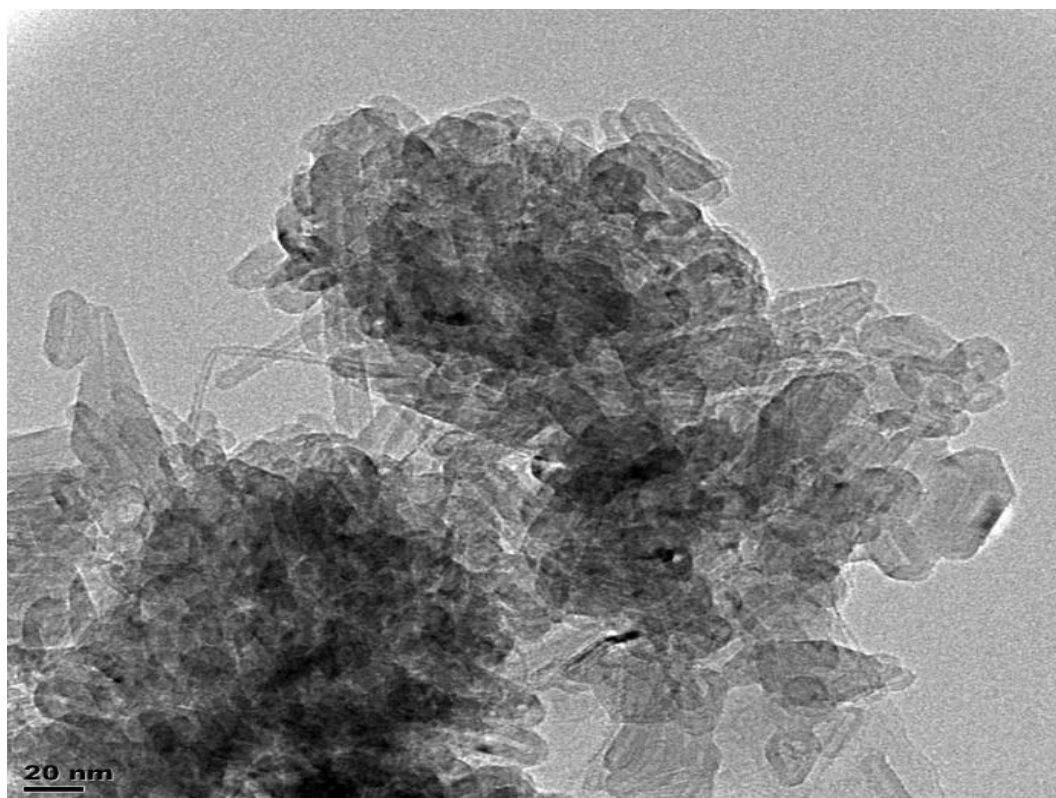


Figure 4.2: TEM image of 1.25 wt% β -FeOOH/polyamide composite

The SEM image (Figure 4.3) for the β -FeOOH shows the characteristic surface of a mesoporous material and also supports the possible tunnel-like channels found in the nanoparticles (Yuan et al., 2004). Investigation of the elemental composition of the synthesized β -FeOOH confirmed the presence of iron, oxygen and chlorine ions as evidenced in the EDS spectrum (Figure 4.4). The elemental analysis in percentage ($n=3$) was 47.01, 43.75 and 9.24 for iron, oxygen and chlorine respectively. The chlorine peaks in the spectrum and the elemental percentage obtained suggested its presence in the hollandite channels of β -FeOOH (Song and Boily, 2012), possibly offering stability to the tetragonal structure of the nanoparticles (Yue et al., 2011).

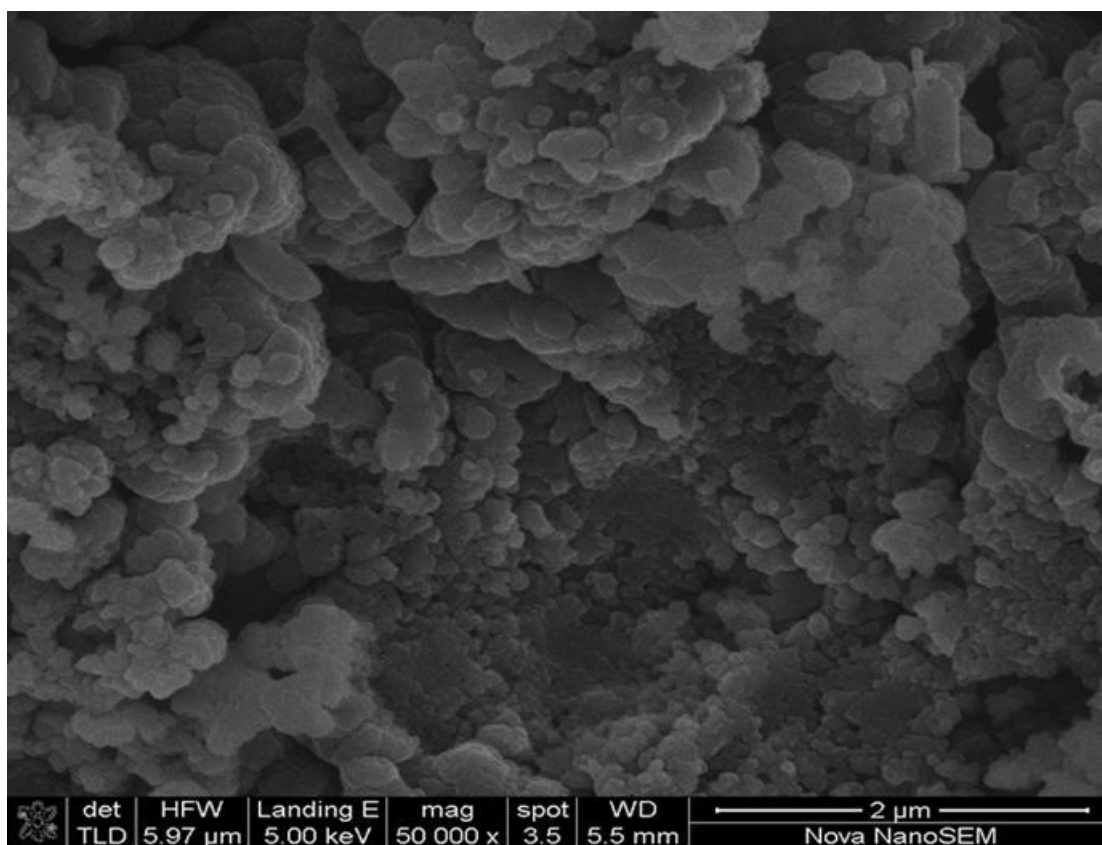


Figure 4.3: The SEM image of the β -FeOOH nanoparticles showing the characteristic surface of a mesoporous material

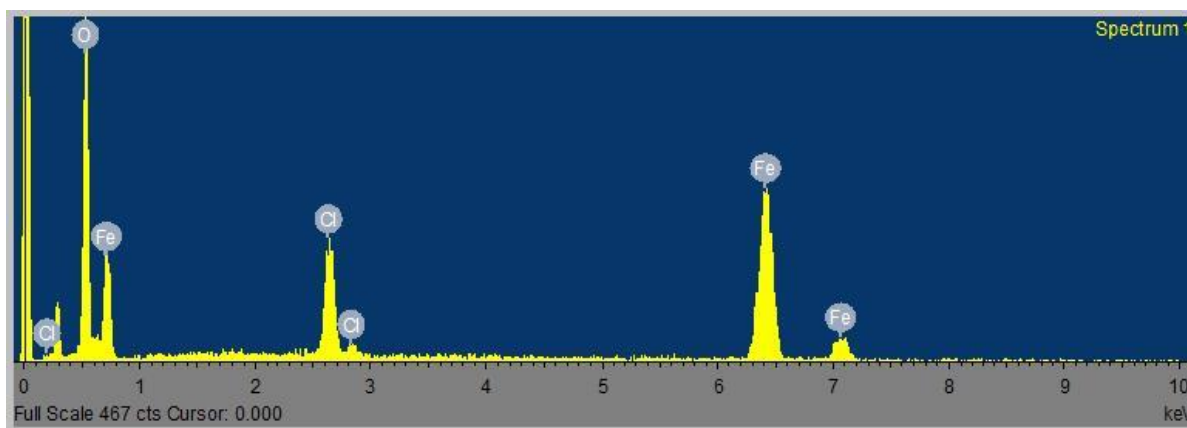


Figure 4.4: EDS spectrum for β -FeOOH nanoparticles with only chlorine, iron and oxygen identified

The FTIR spectra for the β -FeOOH nanoparticles, polyamide and the 1.25 wt% β -FeOOH/polyamide composite captured within the range of 4000-400 cm^{-1} is presented in Figure 4.5. The β -FeOOH nanoparticles showed characteristic absorption peaks at a wavelength of 3339 cm^{-1} and 1624 cm^{-1} for O-H vibrations of absorbed water molecules (Oputu et al., 2015b). Additionally, FTIR bands due to the vibration modes of the FeO_6 coordination octahedron were observed at wavelengths of 847 cm^{-1} and 651 cm^{-1} (Xu et al., 2013). The FTIR spectrum for the polyamide is distinctive for the material with some prominent peaks which include the stretching and bending vibrations of hydrogen bonds in amide II occurring at 3324 cm^{-1} and 1536 cm^{-1} . A bending vibration in the same bond of amide in mode I corresponds to the intense band at 1635 cm^{-1} , and this band overlaps the carbonyl group ($-\text{CO}-$) band located in the same region. The observed bands at 683 cm^{-1} and 574 cm^{-1} were assigned to the twisting vibrational bands of hydrogen in mode I and II of amide, respectively. The band at 3086 cm^{-1} represents the intramolecular bond which occurred between the amide and the carbonyl group ($-\text{CONH}_2-$) in the polyamide, while the doublet band at 2933 and 2866 corresponds to the vibrational symmetrical and asymmetrical stretching of the $-\text{CH}_2$ and $-\text{CH}_3$ groups, respectively (Farias-Aguilar et al., 2014). The FTIR spectrum for the polymeric nanocomposite was similar to that of the pure polyamide with slight band shift and decrease in intensity of the band at 3086 cm^{-1} which represents the $-\text{CONH}_2-$ intramolecular bonds. The incorporated β -FeOOH nanoparticles utilizing these same positions as anchor points (see Figure 3.5 under the syntheses of the nanocomposites) in the polymer matrix might be the reason for the observed phenomenon. The immobilization of the nanoparticles at these points may also be responsible for the slight band shift observed at wavelength of 2933 cm^{-1} and 2866 cm^{-1} .

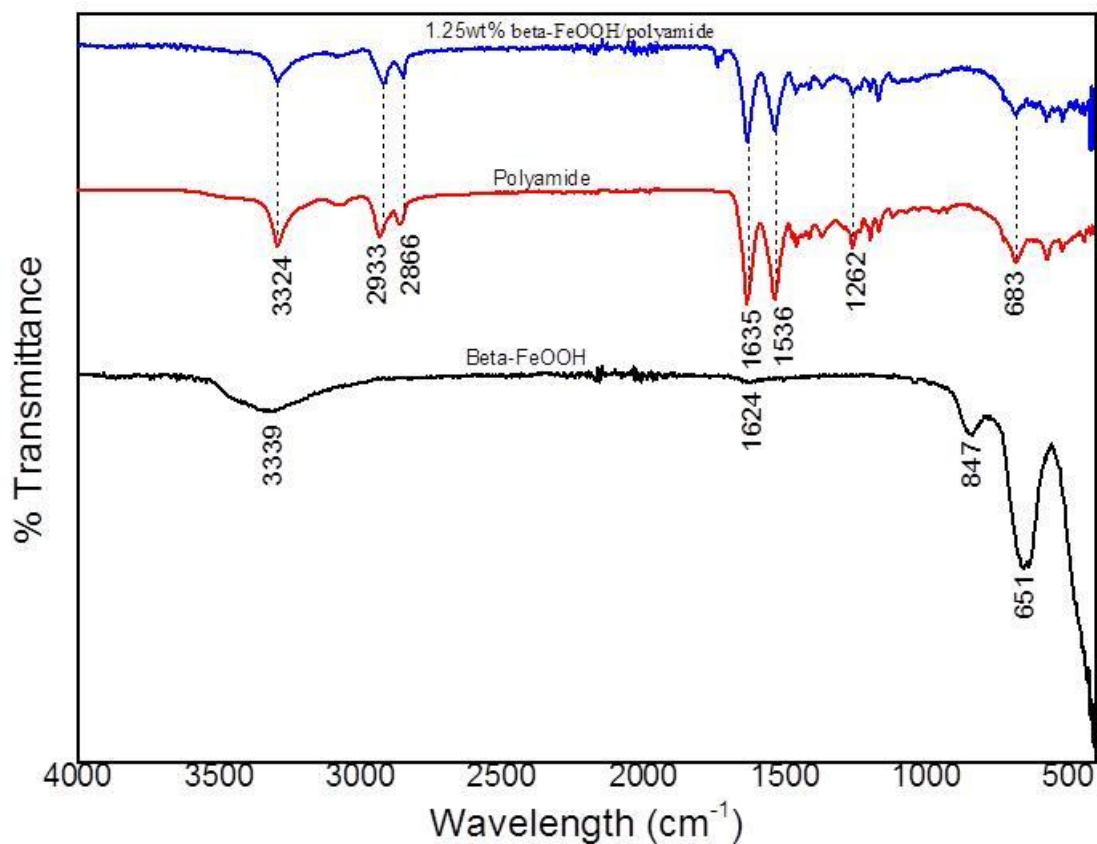


Figure 4.5: FTIR spectra of beta-FeOOH, polyamide and the 1.25 wt% beta-FeOOH/polyamide composite

The nitrogen adsorption-desorption isotherm presented in Figure 4.6 shows a type IV with a H1 hysteresis loops associated with mesoporous materials (Kruk and Jaroniec, 2001). The Brunauer-Emmet-Teller (BET) surface area of the β -FeOOH nanoparticles was $154.34 \text{ m}^2 \text{ g}^{-1}$, while the Barrett-Joyner-Halender (BJH) pore volume and pore sizes were $0.32 \text{ cm}^3 \text{ g}^{-1}$ and $69.32 \text{ \AA}$, respectively.

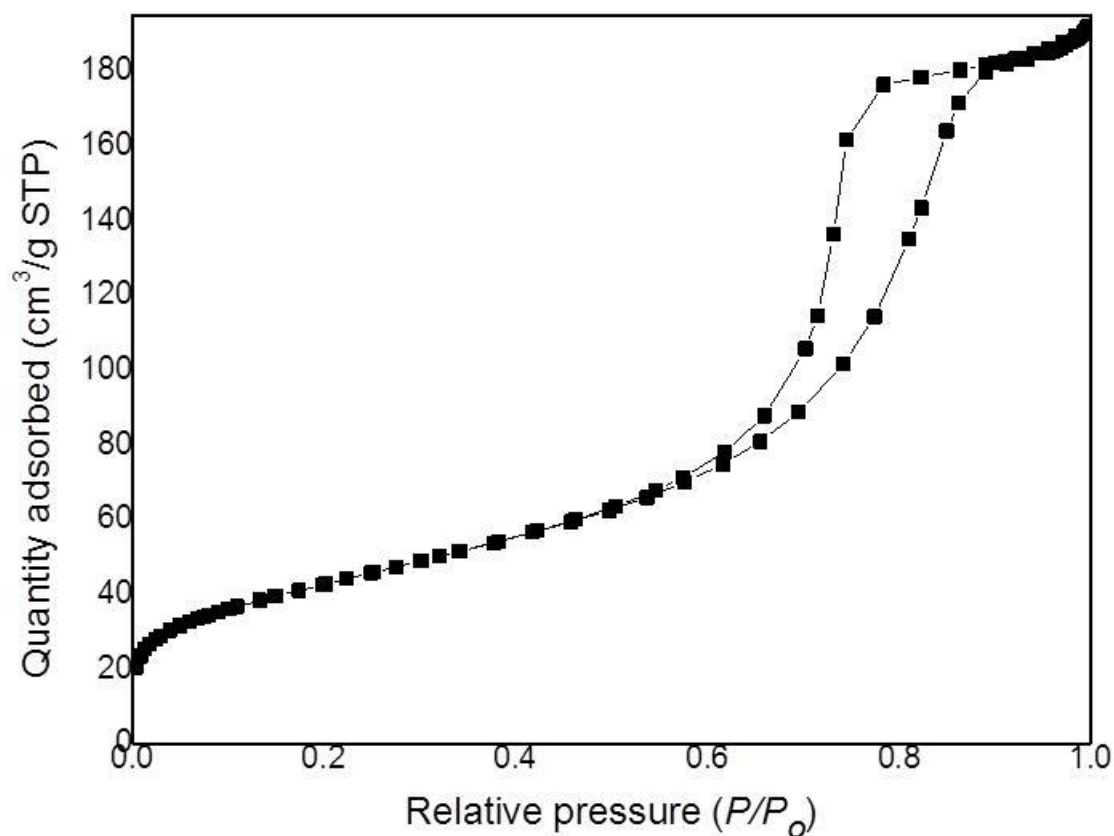


Figure 4.6: Nitrogen adsorption-desorption isotherm of β -FeOOH showing the type IV with H1 hysteresis loops associated with mesoporous materials

X-ray diffraction technique clearly identified the phase composition and purity of materials. The crystal patterns of the synthesized β -FeOOH nanoparticles, polyamide and the 1.25 wt% β -FeOOH/polyamide composite are presented in Figure 4.7. The patterns obtained for the β -FeOOH nanoparticles are the characteristic match which corresponds to the diffraction peaks of the nanomaterial (Joint Committee on Powder Diffraction Standards card number 34-1266). Additionally, no impurity phase was detected from the observed patterns. The observed weak and broad peaks are indicative of the minute crystalline sizes ranging in the nanometre scale of the nanoparticles (Yuan and Su, 2003). Also, the more intense (211) peak (more intense than 310) in the nanomaterial is indicative of the prevalence of the rod-like shape of the crystals (Schwertmann and Cornell, 1991). This was confirmed on the TEM spectrum (Figure 4.1a).

The XRD patterns for polyamide are matched with several experimental patterns found in literature (Wang et al., 2015a; Farias-Aguilar et al., 2014), showing the two characteristic crystallographic forms- α monoclinic and γ pseudo-hexagonal (Khanna and Kuhn, 1997).

The α -phase of the XRD pattern of the diffraction peak can be identified at approximately $2\theta = 24.7^\circ$, while the γ -phase was observed at 20.5 and 22° . The difference in the hydrogen bonds orientations is largely responsible for the different polyamide polymorphs. The γ pseudo-hexagonal phase was the product of parallel chain arrangement, while the anti-parallel chain arrangement forms the α monoclinic phase (Farias-Aguilar et al., 2014). The phase composition of the 1.25 wt% β -FeOOH/polyamide composite largely resembles that of the polyamide that formed the bulk of the synthesized material. However, identifiable peaks of the β -FeOOH nanoparticles can be observed in the diffraction patterns of the composite at $2\theta = 27$ and 35° . Also, the notable polyamide α monoclinic peak at $2\theta = 24.7^\circ$ became broader with a smaller peak at $2\theta = 23.5^\circ$ observed in the polymeric nanocomposite. This shows phase integration between the two starting materials with the β -FeOOH nanoparticles embedded into the polyamide matrix via the *in situ* polymerization process.

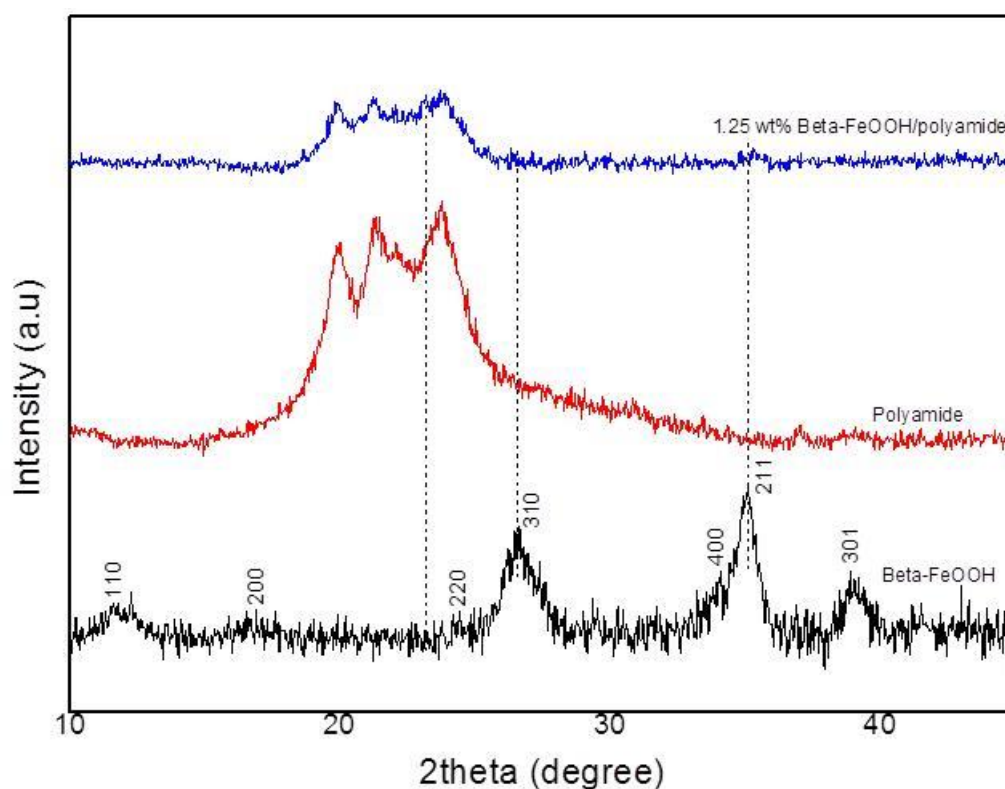


Figure 4.7: XRD patterns of β -FeOOH nanoparticles, polyamide and the 1.25 wt% β -FeOOH/polyamide composite

4.2 Ozonation set-up optimization analysis

4.2.1 Calibration of the ozone generator

The quantity of ozone generated with different flow rate settings (5 -100 mL min⁻¹ O₂) was investigated to establish the optimum value for the ozonation studies. The oxygen flow rate was controlled using a mass-flow meter and the oxygen passed through the ozone generator for conversion to ozone. The analysis was done 4 weeks apart to check for consistency and the result obtained are presented in Table 4.1. The resulting trend showed that increasing the flow rate of the oxygen yielded corresponding increments in the ozone produced. However, at 50 mL min⁻¹ further increases in the flow rate led to a decrease in the ozone generated. The shorter contact time that oxygen gas had with the corona discharge plates due to the corresponding higher pressure from the gas resulted in reduced ozone production (Lukes et al., 2005). A decline in the percentage concentration of the O₂/O₃ mixture was obtained with increasing flow rate because the ozone generator could not convert the increasing oxygen molecules into ozone by the factor by which the oxygen was raised. This gave credence to the fact that the residence time of the oxygen gas between the corona discharge plates played an important role in the ozone generation.

Table 4.1: Ozone concentrations versus flow rates

O ₂ flow rate (mL min ⁻¹)	Average Conc. O ₃ (mg L ⁻¹)	Standard deviation	O ₃ (mg min ⁻¹)	Gas phase O ₂ (mg min ⁻¹)	Conc. (%) O ₂ /O ₃
5	19.45	0.66	0.10	2.08	4.68
10	27.60	0.91	0.14	4.16	3.32
20	31.98	0.31	0.16	8.31	1.92
50	35.95	0.86	0.18	20.79	0.86
100	31.75	1.97	0.11	41.57	0.38

4.2.2 Reactor mass-transfer efficiency analysis

Ozone solubility can be determined in a liquid phase when it reaches a steady-state value in a batch experiment set-up under fixed conditions (Biń, 2006). The steady-state is attained when the rate of ozone breakdown in solution by natural process equals the rate it is replenished (Roth and Sullivan, 1981). The efficiency of ozone or gas mass-transfer in a bubble reactor set-up is influenced by certain operating variables which include temperature, gas flow rate, pressure and gas-contacting device (Levanov et al., 2018;

Miyamoto et al., 2014; Sotelo et al., 1989; Caprio et al., 1982; Singh et al., 1982; Whitehead and Dent, 1982). Temperature, a key variable was maintained at 20°C (293 K) for the duration of all experiments. The porous frit of the bubbler and the ozone flow rate at different settings gave the corresponding pressure values. The ozone concentration measured through iodometry as a function of time, with different oxygen flow rates, is presented in Figure 4.8. The aqueous ozone concentrations at equilibrium increased steadily until the oxygen flow rate of 50 mL min⁻¹ was reached. Further increment in the oxygen flow rate to 100 mL min⁻¹ resulted in a decrease in ozone concentration with increasing time. For the 50 mL min⁻¹, the decline in measured ozone occurred at 50 min to 60 min, going from 30.12 mg L⁻¹ to 29.22 mg L⁻¹. The observation was more pronounced for the 100 mL min⁻¹ oxygen injection which decreased from 30.02 mL min⁻¹ of measured ozone to 25.01 mL min⁻¹, at a corresponding time of 10 min to 60 min. This can be adduced to the spontaneous equilibration of the ozone associated with high flow rates (Chu et al., 2008). The trend confirmed that at higher oxygen flow rates, the efficiency of the corona discharge ozone generator reduced significantly.

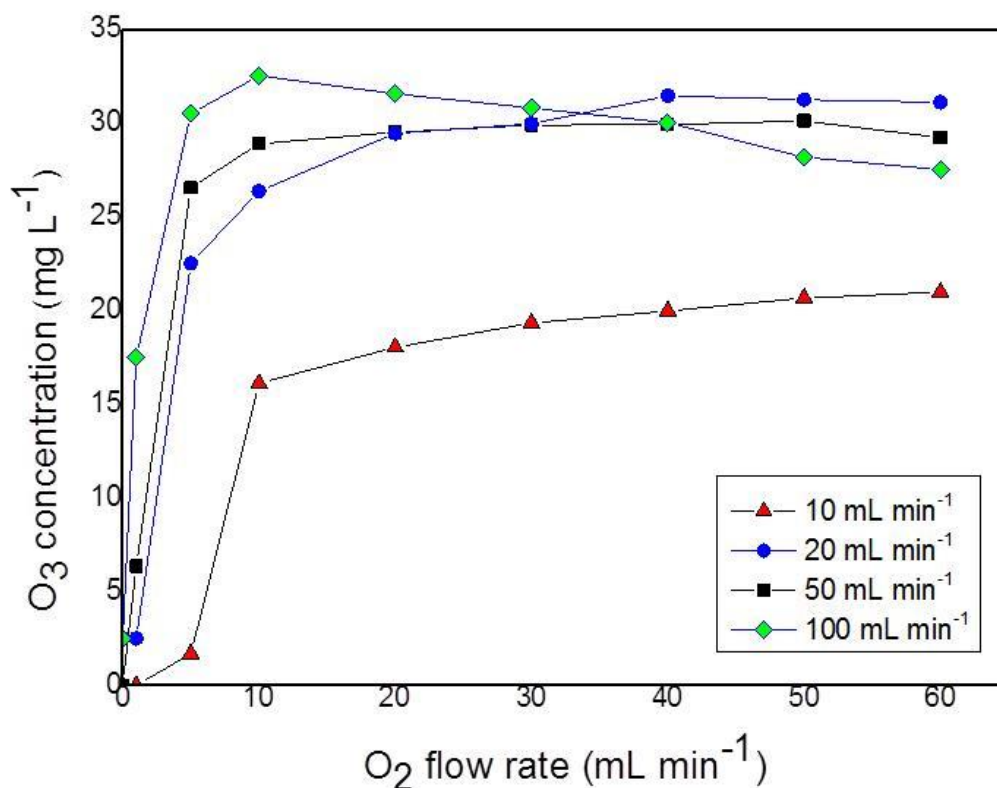


Figure 4.8: Effect of oxygen flow rate on reactor ozone generation

4.2.3 Gas flow and phenolic compound concentration optimization

To ascertain the best-suited ozone gas flow rate to employ for the ozonation processes, a 2.5×10^{-3} M concentration of 4CP was utilized as the substrate. Varying ozone gas flow at 5 mL min^{-1} , 10 mL min^{-1} and 50 mL min^{-1} were employed for the degradation of the 4CP substrate with samples collected and analysed at different time intervals. Results of the 4CP degradation obtained with time are presented in Figure 4.9. The lowest flow rate (5 mL min^{-1}) had a slow degradation rate with 27.76% of the initial analyte concentration remaining after 100 min. The 50 mL min^{-1} flow rate recorded almost complete degradation at 40 min. Both flow rates were considered undesirable for the intended study. The 10 mL min^{-1} was adopted as the best-suited flow rate to utilize with the substrate concentration reduced to 2.0×10^{-3} M to ensure the experimentation is accommodated within 60 min. The steady increment in the mass-transfer efficiency obtained for 10 mL min^{-1} in the previous section supported the decision to use it as the ozone gas flow rate set-point for all experiments conducted afterwards.

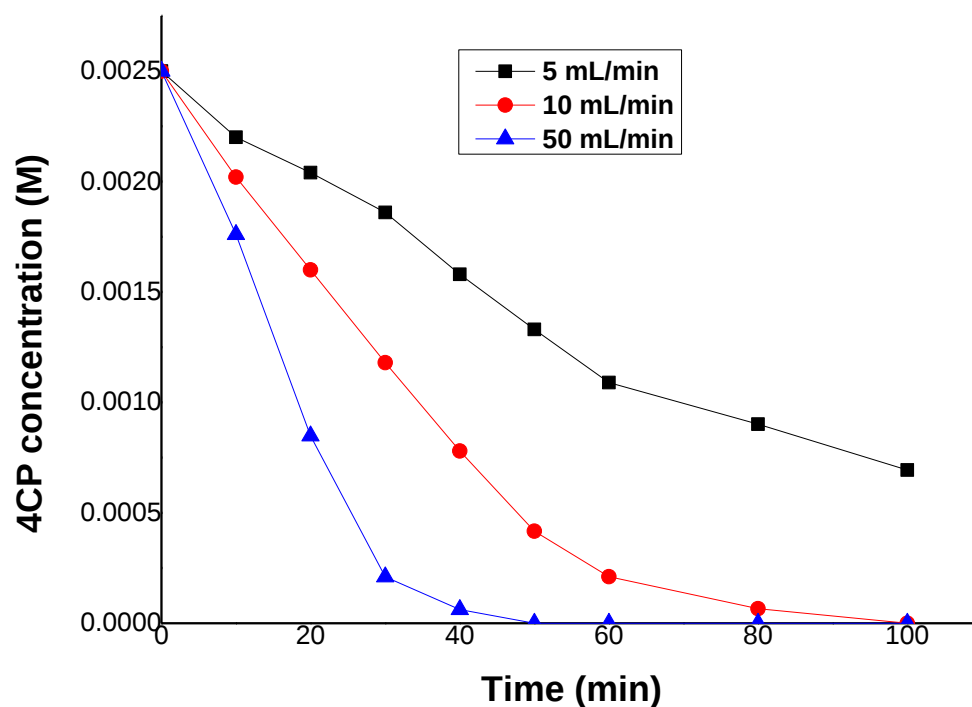


Figure 4.9: Effect of flow rate on 4CP ozonation

4.3 Catalytic ozonation experimental results

4.3.1 Catalyst size screening

Large scale application of polymeric nanocomposites was the goal of this study. Our approach to ensuring ease of field application was to optimize the size of the polymeric nanocomposites by grading into size ranges that could be easily recovered rather than powdered products. Three grade sizes of the 1.25 wt% β -FeOOH/polyamide composites were prepared and tested for their degradation capabilities (Figure 4.10). The catalytic ozonation of 2×10^{-3} M 4CP revealed that the size range of 500-600 μm produced the best result, with 98.52% degradation after 40 min. The other size ranges of 400-500 μm and 600-700 μm gave 92.81% and 85.84%, respectively. The 500-600 μm composites occurred mostly in the region where the ozone was being introduced into the analyte solution during the ozonation operations. To achieve optimum degradation requires the stability of the catalysts in suspension and around the reaction zone (Oputu et al., 2015b).

Further studies were conducted using the 500-600 μm polymeric nanocomposites. The size range contributed to the recovery of the composites after each application cycle. The composite settles out immediately once stirring was stopped; the recovery was achieved by a simple filtration process. The β -FeOOH/polyamide possesses paramagnetic characteristics as they are attracted towards an applied external magnet (see Figure 4.11). This property will be of great advantage during field applications and will advertently enhance the recovery of the polymeric nanocomposites.

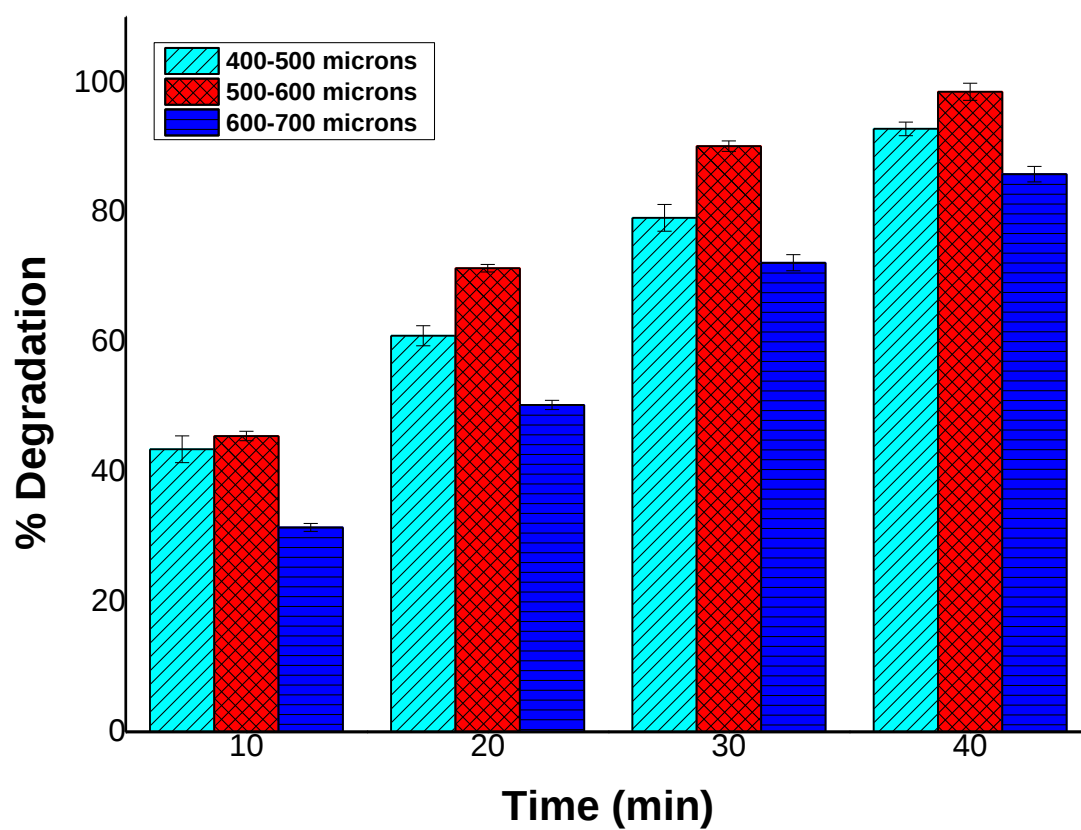


Figure 4.10: Catalytic ozonation degradation of 2×10^{-3} M 4CP using different size ranges of 1.25 wt% β -FeOOH/polyamide



Figure 4.11: Beta-FeOOH/polyamide nanocomposites removed from treated simulated wastewater with an external magnet (Image magnified)

4.3.2 Catalytic ozonation of 4-chlorophenol

The catalytic activity of the synthesized polymeric nanocomposites with different β -FeOOH loading (0.5, 0.75, 1.0 and 1.25 wt%) was evaluated in combination with ozone (Figure 4.12). Data for the optimisation processes are presented in Appendices 7.A – 7.D. There was a steady increase in the catalytic activity of the nanocomposites with increasing nanoparticles loading. The 4CP removal efficiency of 98.52% was obtained for the composite with 1.25 wt% β -FeOOH loading after 40 min, while ozonation alone gave 62.94%. The marked improvement in the removal efficiency can be attributed to the catalytic contributions of the β -FeOOH/polyamide catalyst introduced in the ozonation process.

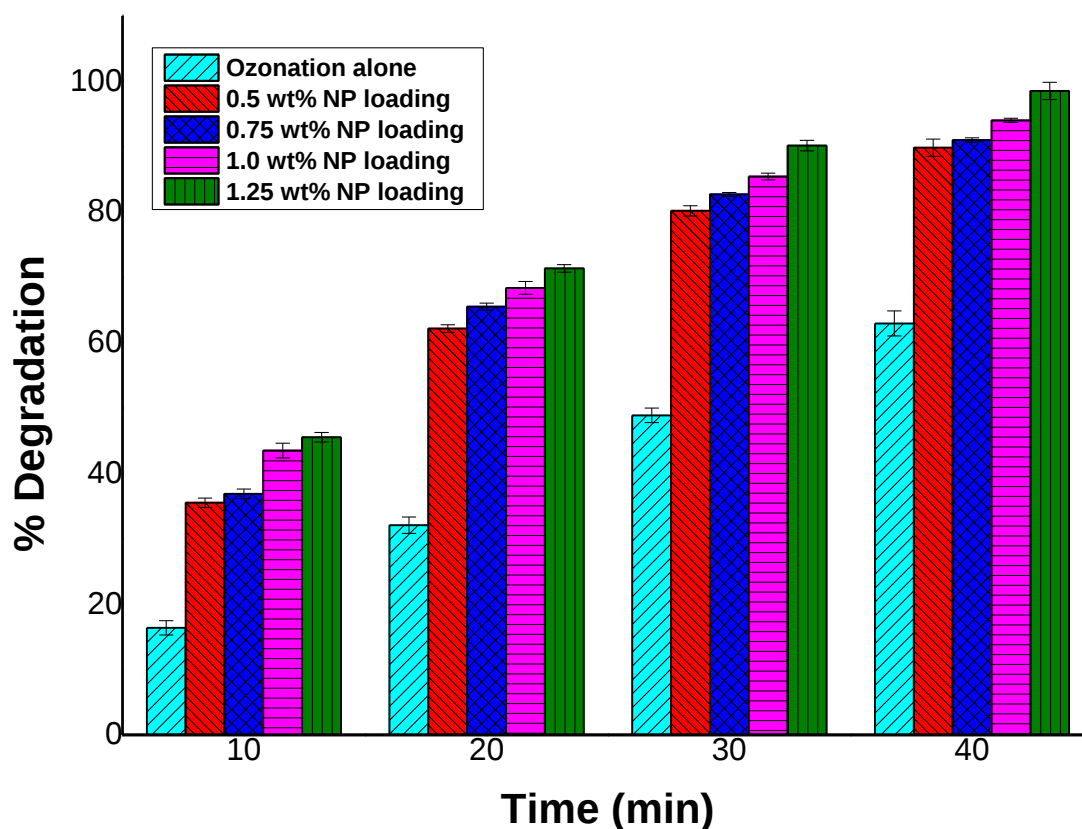
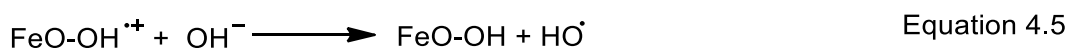
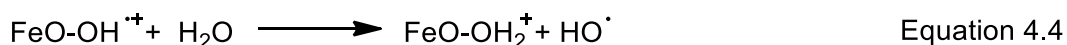
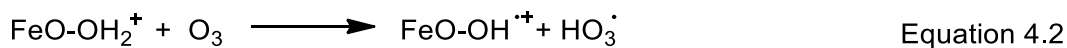
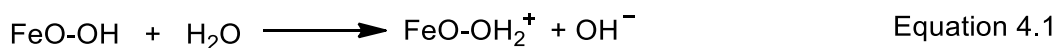


Figure 4.12: Degradation of 2×10^{-3} M 4CP using polymeric nanocomposites with different β -FeOOH loading

The incorporated β -FeOOH in combination with ozone produces HO^* due to surface reactions of the β -FeOOH with ozone (Oputu et al., 2015b). The surface hydroxyl groups present in metal oxides such as β -FeOOH is favourable for ozone decomposition and HO^* generation (Zhao et al., 2009; Kasprzyk-Hordern et al., 2003). Introducing metal oxides into water brings about a strong adsorption of water molecules (Wang et al., 2018a; Yang et al., 2010); making the hydroxyl groups to act like Brønsted acid sites and catalytic centres of the catalyst (Yang et al., 2009). Ozone is unstable in water due to its high reactivity and can undergo electrophilic or nucleophilic reactions, and can also react as a dipole (Kasprzyk-Hordern et al., 2003). This enables the ozone molecules to easily undergo reaction with the Brønsted acid ($-\text{OH}_2^+$) formed by the surface hydroxyl groups present in the β -FeOOH nanoparticles. Therefore, Equation 4.1 – 4.5 is proposed as the probable reaction mechanism for the hydroxyl radical generation in this system. The generated hydroxyl radicals oxidises the 4CP adsorbed on the polymeric nanocomposites or diffuses into the solution to oxidise 4CP moieties present in solution (Sui et al., 2010).



To confirm the involvement of the HO^* in the degradation process of the analyte, methanol a HO^* scavenger with a rate constant high as $9.6 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$ was utilized in a ratio of 1:50 (4CP and methanol). The result obtained as compared to ozonation and the catalysed ozonation process indicate that the 4CP degradation was majorly through the oxidative action of the HO^* . The degradation efficiency of 4CP was significantly reduced to 25.64% as compared to 62.94% and 98.52% for ozonation and the catalysed ozonation reactions, respectively (Figure 4.13). The marked difference is accounted for by considering that most ozone molecules infused into the analyte solution are converted into HO^* in the catalysed reaction, thereby reducing their availability to degrade 4CP directly. More so, the generated HO^* are readily scavenged by the methanol which makes them

unavailable for the degradation of 4CP. In a similar heterogeneous catalytic process reported by Liu et al. (2018), the degradation efficiency was reduced to zero when methanol was added to the FeO(OH)-reduced graphene oxide/H₂O₂/visible light system for 4CP removal.

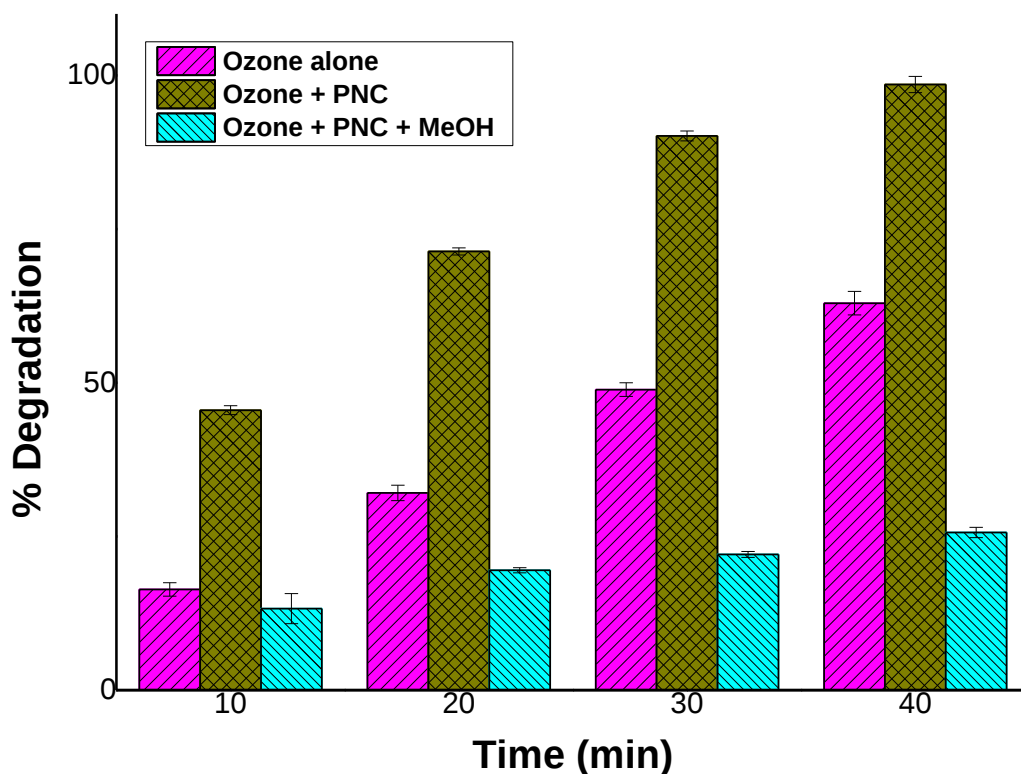


Figure 4.13: Degradation of 2×10^{-3} M 4CP showing the hydroxyl radicals scavenging effects of methanol

Catalyst adsorption capability enhances the degradation efficiency of the contaminant, as their increasing adsorption on the surface of the catalyst gives higher efficiency (Sharma et al., 2015; Ghanem et al., 2014). The nanocomposites, when tested for their adsorption capacity, were able to absorb 21% of the 2×10^{-3} M 4CP in solution after equilibrating for 60 min. Adsorption capacity may be a contributory factor to the high oxidative degradation efficiency recorded during the catalytic ozonation process. FTIR spectrum of the spent polymeric nanocomposites after five cycles of use (Figure 4.14) was essentially the same, except for the changes in the intensities of the polymer characteristic absorption peaks—the amide II bending and stretching hydrogen bonds, the amide doublet band and the amide I bending vibrations. These changes did not significantly affect the catalytic property of the composite as the degradation efficiency only dropped by 0.22% on the sixth reuse

cycle. Furthermore, the solutions obtained from the regeneration of the polymeric nanocomposites between each reuse cycle were analysed to check for the presence of 4CP. The regeneration solutions did not show the presence of 4CP, suggesting that the surface adsorption of 4CP only aided its degradation, and the effective removal was by catalytic oxidation.

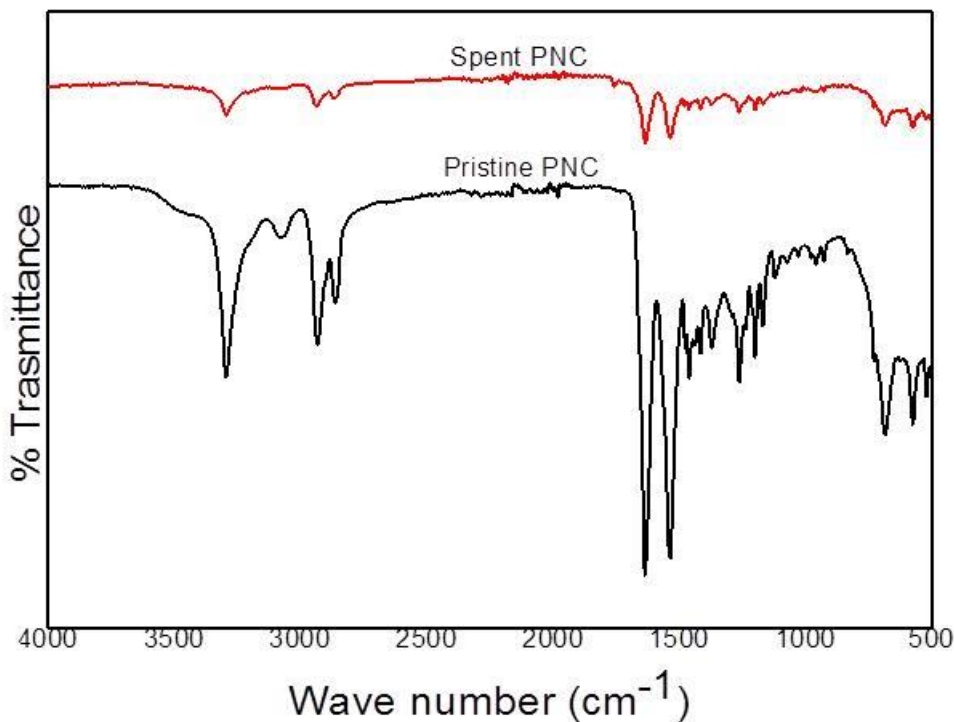


Figure 4.14: FTIR spectra of pristine and spent (after five reuse cycles) polymeric nanocomposites

4.3.3 Catalytic ozonation of 4-nitrophenol

The catalytic activities of the polymeric nanocomposites were utilized to degrade 4NP analyte for comparative studies. Results showed that the polymeric catalysts exhibited good degradation capability for 4NP (Figure 4.15), with the 1.25 wt% β -FeOOH/polyamide composite giving the best result as obtained for 4CP. Comparatively, the polymeric nanocomposites gave better performance for the oxidation of 4CP as shown in Figure 4.16. The percentage degradation of 98.52% was achieved after 40 min for 4CP relative to 89.66% for 4NP. This trend is supported by the extensive AOPs remediation of 4CP and 4NP carried out by Gimeno et al. (2005). In all systems investigated (O_3 , UV-vis, O_3 +UV-vis, TiO_2 +UV-vis, O_3 +UV-vis+ TiO_2 and O_3 + TiO_2), 4CP degradation was more favourable.

The trend was attributed to the chloro-substitution on the phenol molecule which increased the oxidation rate irrespective of its electron-withdrawing character. The nitro-substituent (also electron-withdrawing with a positive Hammett constant) follows the normal step by slowing down the efficiencies. The kinetic study of ozonation of phenol and substituted phenols by Bhosale et al. (2019) also affirmed this trend with the rate constants of $6.71 \times 10^6 \text{ M}^{-1} \text{ S}^{-1}$ and $4.57 \times 10^6 \text{ M}^{-1} \text{ S}^{-1}$ obtained for 4CP and 4NP, respectively.

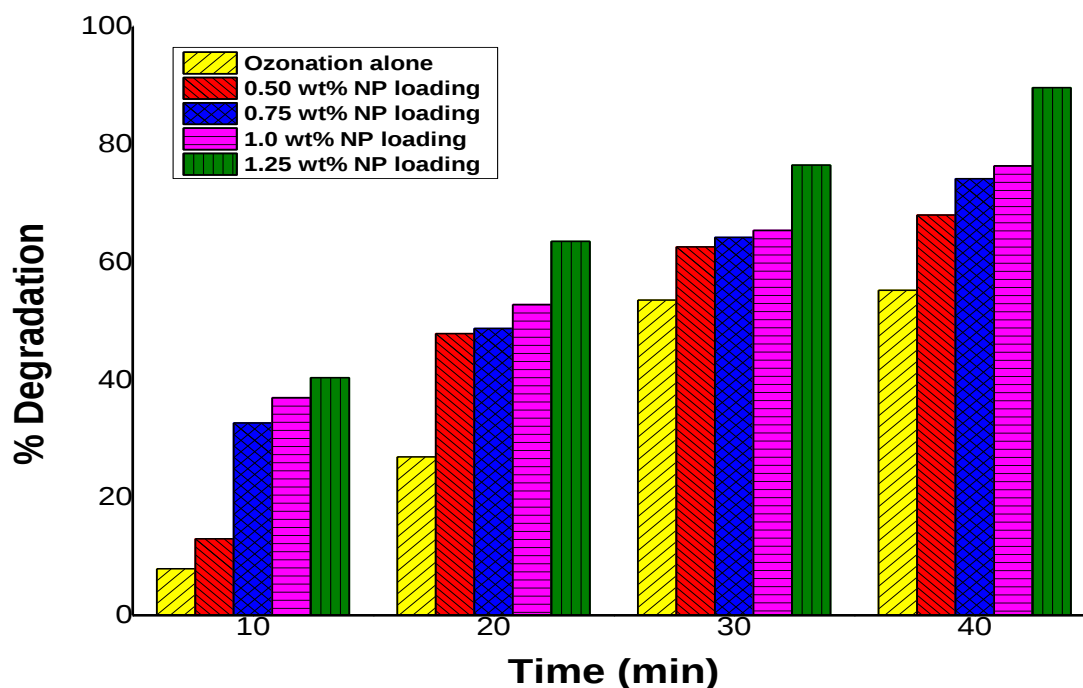


Figure 4.15: Degradation of $2 \times 10^{-3} \text{ M}$ 4NP using polymeric nanocomposites with different $\beta\text{-FeOOH}$ loading

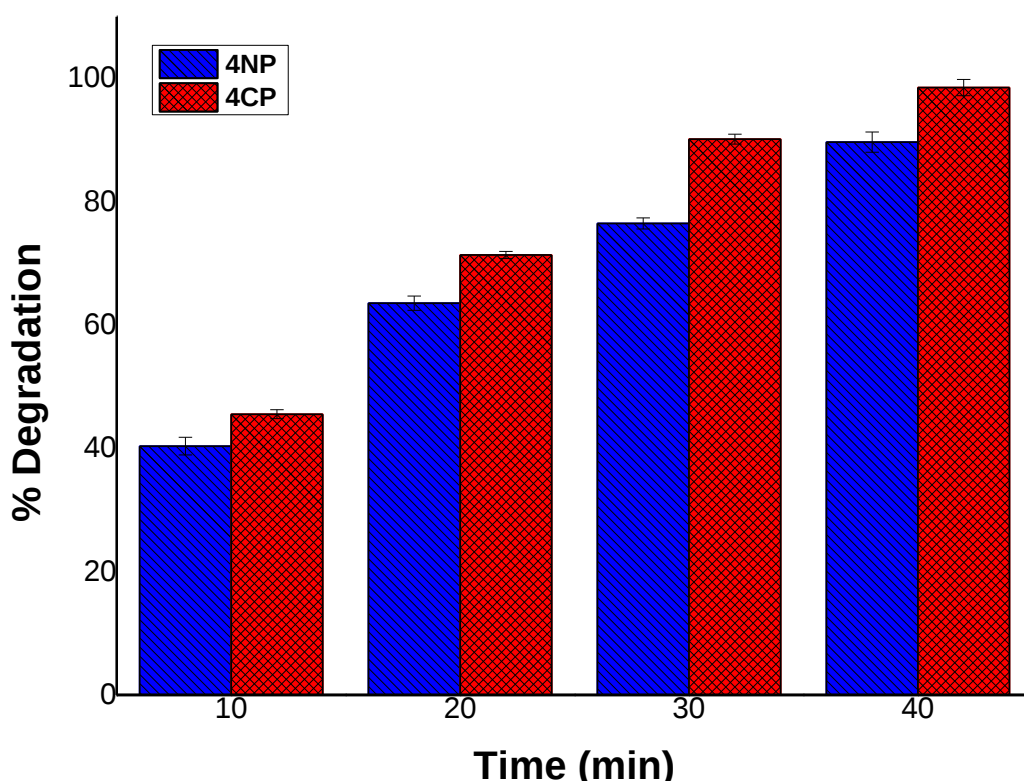
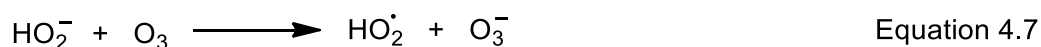


Figure 4.16: 4CP versus 4NP degradation efficiencies using 1.25 wt% β -FeOOH/polyamide composite

4.3.4 Kinetic study and effect of initial pH on the degradation efficiency of 4CP

The pH of wastewaters undergoing remediation plays a critical role in the overall treatment output. In catalytic ozonation processes, higher pH tends to be more favourable for the generation of highly reactive and non-selective hydroxyl radicals as deduced from equations 4.6 - 4.13.





Experimental data obtained from the catalytic ozonation of 2×10^{-3} M 4CP at initial pH of 3, 7 and 10 are presented in Figure 4.17. The overall higher degradation efficiency of the 4CP was recorded at initial pH 10 with 96.01% 4CP removal after 30 min as compared to 90.16% and 83.56% recorded for pH 7 and 3. This trend is well supported by literature as alkaline conditions leads to more efficient removal of 4CP (Hirvonen et al., 2000) due to more $\text{HO}^\bullet$ radicals production in the solutions. Oputu et al. (2015b) reported the same phenomenon in their investigation involving the degradation of 4CP by $\beta\text{-FeOOH}$ catalysed ozonation process. The degradation rate of the 4CP solution with different initial pH values was evaluated using the pseudo-first-order reaction kinetics and the duration limited to 30 min due to the formation of intermediates (organic acids) that lowered the pH of the solutions (García-Molina et al., 2005). The data presented in Figure 4.18 shows that the reaction rate constant (k) increased with the increasing pH values. Values of 0.0645, 0.0665 and 0.1123 were obtained for pH 3, pH 7 and pH 10, respectively.

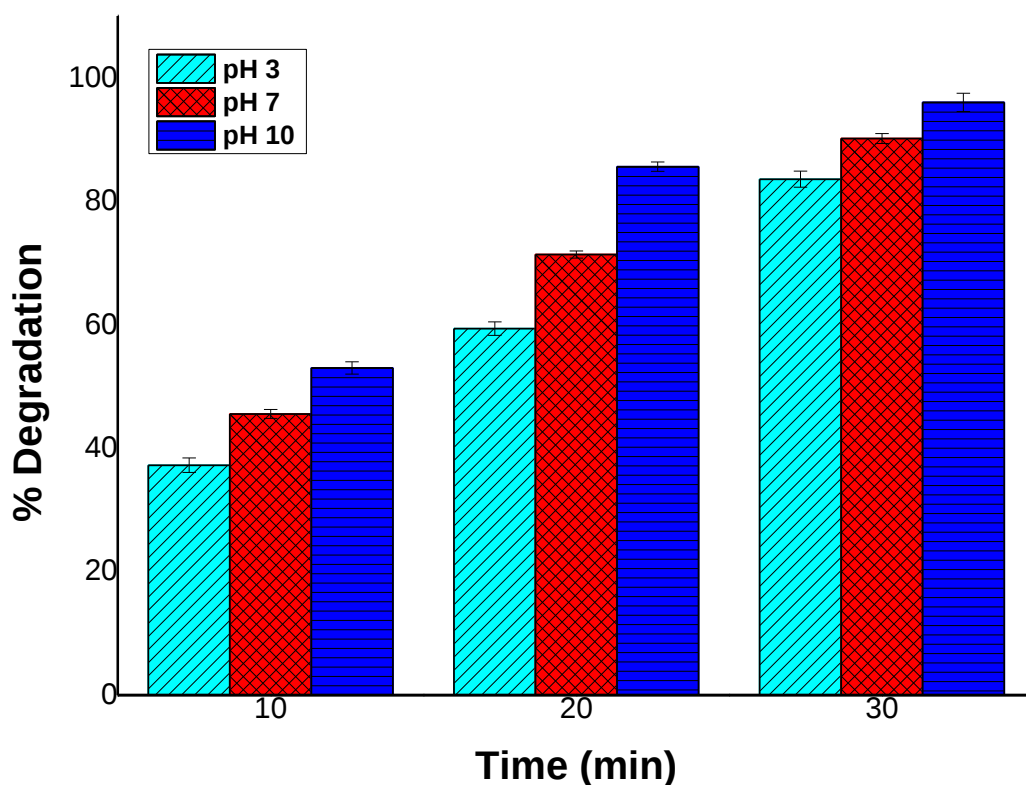


Figure 4.17: Degradation efficiency of 1.25 wt% β -FeOOH/polyamide utilized for the degradation of 2×10^{-3} M 4CP at different initial pH

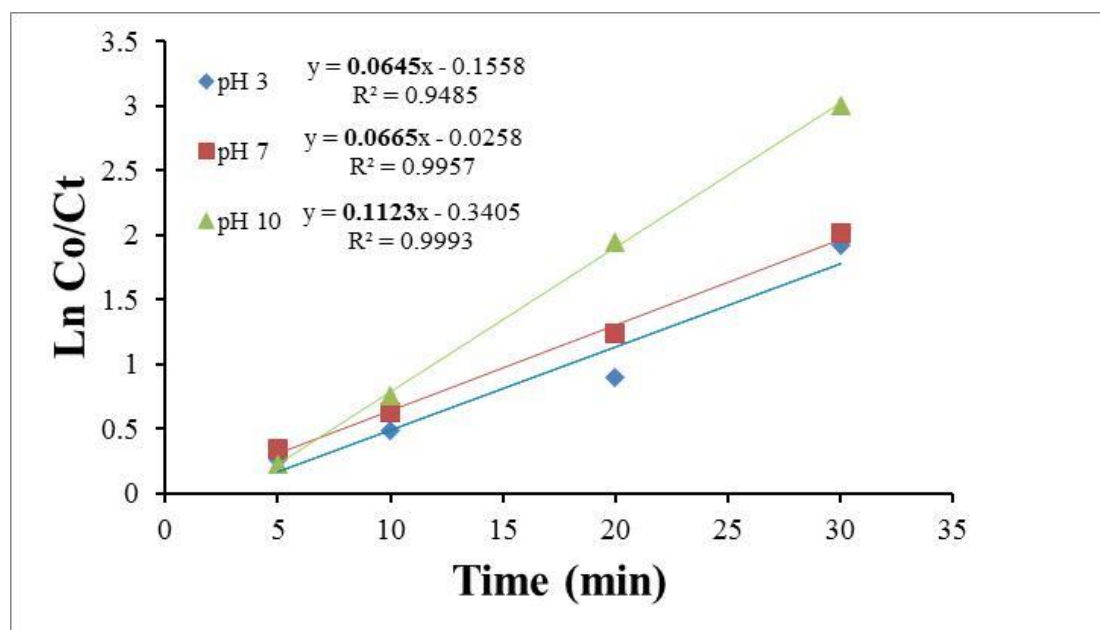


Figure 4.18: Degradation rate of 1.25 wt% β -FeOOH/polyamide utilized in combination with ozone for the degradation of 2×10^{-3} M 4CP at different initial pH

4.4 Intermediates of 4CP and 4NP ozonation

4.4.1 Effects of pH on intermediates

In the oxidation of organic contaminants in wastewaters, the route and nature of the intermediates leading to the final degradation products are usually of interest (Li et al., 2018). This valuable information provides knowledge that may lead to better design and fabrication of treatment solutions to obtain more effective and efficient treatment processes. The pH of water systems plays an important role and may be of immense contribution to the route and nature of the intermediates generated (Cao et al., 2018). It also contributes to the effectiveness of the treatment processes (Doong et al., 2001). The intermediates of 4CP and 4NP were investigated under different initial pH range of 3 - 10. Sample collection was done at different intervals during the ozonation processes over 60 min. The samples were analysed immediately using the LCMS-TOF instrumentation. The intermediates sought by molecular features in the qualitative analysis workflow (QAW) was mined using the algorithm setting of $C \leq 30$, $H \leq 60$, $O \leq 10$, with Cl and N set as ≤ 10 for 4CP and 4NP, respectively. The algorithm employed gave considerations for possible dimer and trimer products and other intermediates. Data obtained include molecular mass, the mass-to-charge ratio (m/z), molecular formula, and retention time. Further scrutiny for identification of intermediates was carried out using the mass spectra (MS) as a veritable tool.

4.4.2 Intermediates of 4-Chlorophenol

Chlorophenols are part of the group of pollutants currently regarded as priority pollutants due to their toxic nature and resistance to biodegradation which makes it difficult to remove them from the environment (Jimenez-Becerril et al., 2013). Classified as a priority pollutant by USEPA, 4CP is suspected to possess carcinogenic and mutagenic properties (Haddadi and Shavandi, 2013; Lim et al., 2013; Nalbur and Alkan, 2007). It is one of the most commercially important chlorophenols and is widely produced as intermediates in the production of insecticides, herbicides, wood preservatives, pharmaceuticals and dyes (Igbinosa et al., 2013).

The degradation of 4CP mostly follows two routes; the 4-chlorocatechol and hydroquinone routes. Both 4-chlorocatechol and hydroquinone lead to the degradation of aliphatic carboxylic acids and the final mineralization to CO_2 and H_2O . The ozonation of 4CP- C_6H_5ClO (Figure 4.19a) yielded 4-chlorocatechol- $C_6H_5ClO_2$ (Figure 4.19b) as one of the

first intermediate products of the degradation process for the analyte solutions at different pH values. The formation of the 4-chlorocatechol intermediate occurs via the hydroxylation of the 4CP at the preferred *ortho* positions; the *meta* positions are characteristically deactivated for electrophilic aromatic substitutions. The mechanism essentially involves the attack of the $\text{OH}^{\bullet}$ on the *ortho* position of the hydroxyl group of the 4CP, followed by the elimination of a hydrogen atom for the recovery of the aromatic ring (Theurich et al., 1996). The diode-array detector (DAD) chromatogram and the confirmation mass spectrum for the 4CP standard are shown in Figure 4.20. The extracted ion count (EIC) spectra and their corresponding mass spectra (Appendices 7.E, 7.F and 7.G) obtained after 10 min confirmed that the hydroxylation step occurred first rather than the dechlorination process (Figure 4.21).

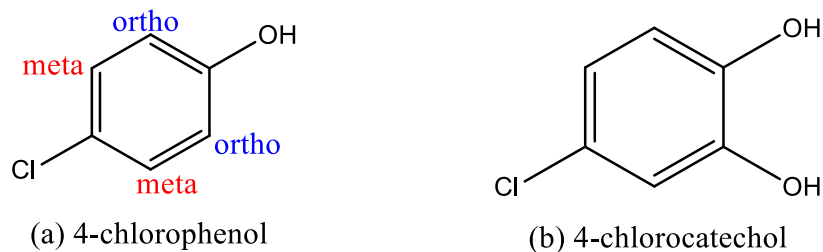


Figure 4.19: Chemical structures of (a) 4-chlorophenol and (b) 4-chlorocatechol

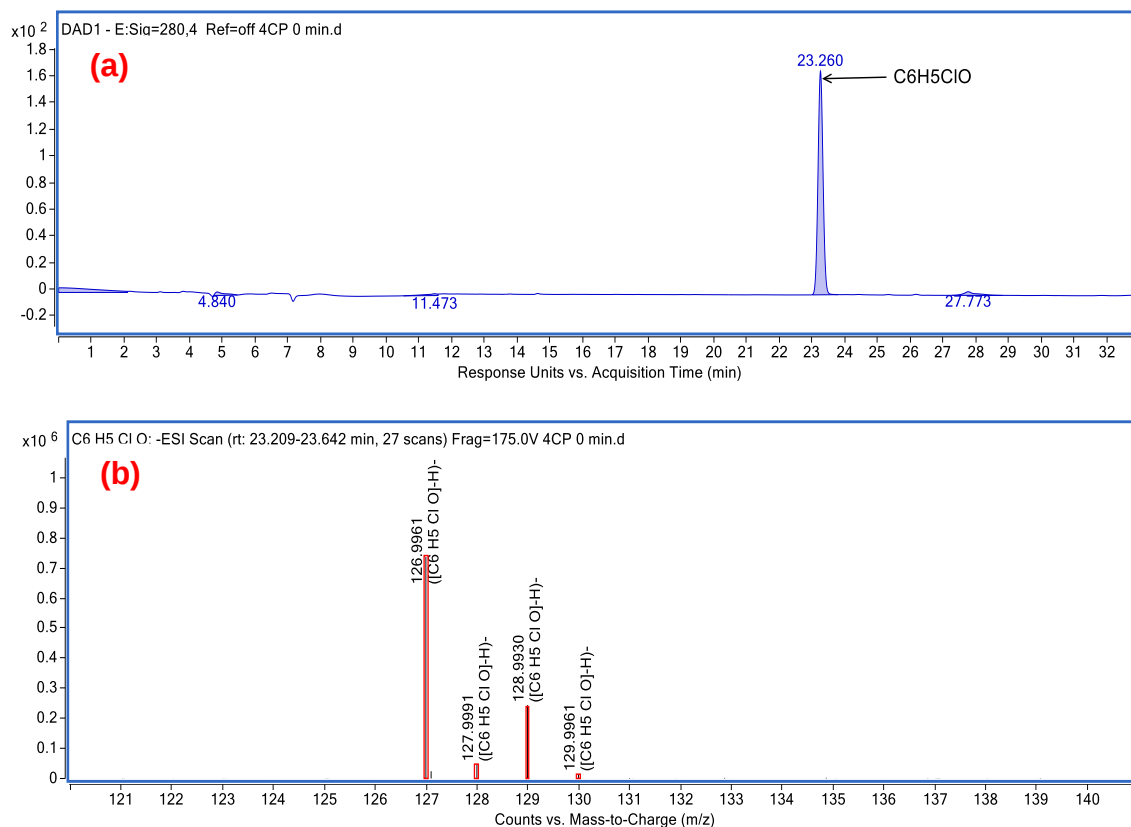


Figure 4.20: DAD chromatogram (a) and mass spectrum of 4-chlorophenol (b)

Several intermediates and breakdown products were identified for the 4CP solutions after 10 min of ozonation. The prominent ones were mainly the hydroxylation and dimer intermediates of the 4CP compound. The time-based intermediates were identified from the compounds list generated from the QAW as presented in Table 4.2. The confirmation of the breakdown compounds was done using the MS tool. The extracted ion chromatogram (EIC) and the MS analysis confirmed 4-chlorocatechol as a prominent intermediate present in all samples taken after 10 min and analysed. These were further confirmed by the QAW data where the correct formula was generated with a mass-to-charge ratio (m/z) of 142.99. The m/z ratio was identical to the value of 143 obtained previously in a study that also used LC-MS instrumentation operated at a negative mode (Huang et al., 2008).

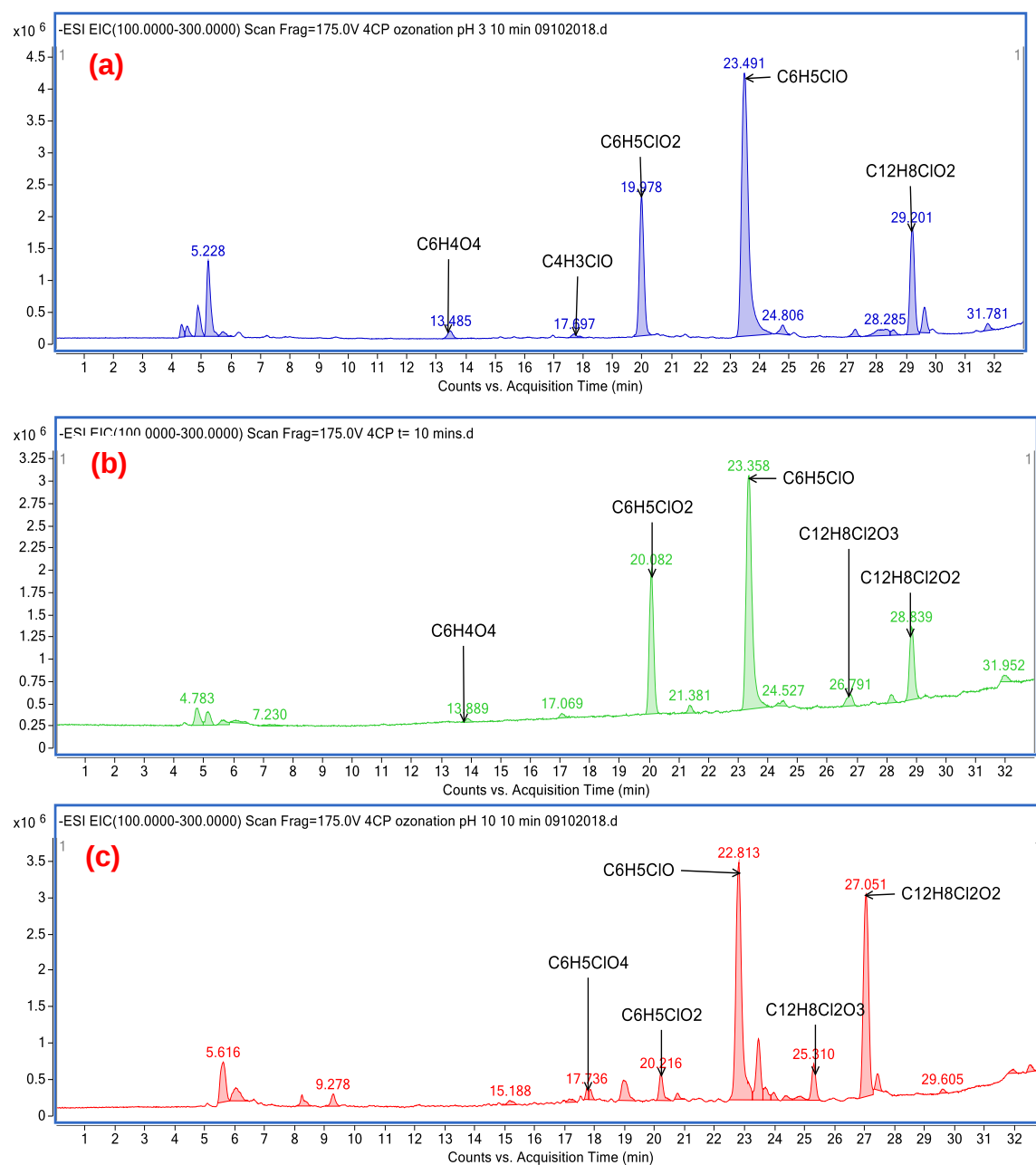


Figure 4.21: EIC spectra for 4CP ozonation at pH 3 (a), pH 7 (b) and pH 10 (c) at 10 min

Table 4.2: Intermediates of 4-chlorophenol ozonation at different pH identified from EIC/TIC chromatogram and mass spectra

Time (min)	Acidic pH (3)			Dissolution pH (7)			Alkaline pH (10)		
	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)
0 min	C ₆ H ₅ ClO	128.0036	23.306	C ₆ H ₅ ClO	128.0038	23.366	C ₆ H ₅ ClO	128.3200	23.235
10 min	C ₄ H ₃ ClO	101.9872	17.696	-	-	-	-	-	-
	C ₅ H ₄ O ₃	112.0158	9.579	-	-	-	-	-	-
	C ₆ H ₄ O ₄	140.0108	13.472	C ₆ H ₄ O ₄	140.0112	13.634	-	-	-
	C ₆ H ₅ ClO	128.003	23.500	C ₆ H ₅ ClO	128.0032	23.263	C ₆ H ₅ ClO	128.0030	22.107
	C ₆ H ₅ ClO ₂	143.9985	19.986	C ₆ H ₅ ClO ₂	143.9982	19.860	C ₆ H ₅ ClO ₂	144.0021	20.107
	-	-	-	-	-	-	*C ₆ H ₅ ClO ₂	143.998	18.939
	C ₁₂ H ₈ Cl ₂ O ₂	253.9807	29.208	C ₁₂ H ₈ Cl ₂ O ₂	253.9838	28.827	C ₁₂ H ₈ Cl ₂ O ₂	253.9838	27.050
	*C ₁₂ H ₈ Cl ₂ O ₂	253.9908	23.456	*C ₁₂ H ₈ Cl ₂ O ₂	253.9906	23.232	*C ₁₂ H ₈ Cl ₂ O ₂	253.9908	22.791
	*C ₁₂ H ₈ Cl ₂ O ₂	253.9908	31.769	-	-	-	*C ₁₂ H ₈ Cl ₂ O ₂	253.9904	29.605
	C ₁₂ H ₈ Cl ₂ O ₃	269.9854	28.579	-	-	-	C ₁₂ H ₈ Cl ₂ O ₃	269.9856	25.309
	*C ₁₂ H ₈ Cl ₂ O ₃	269.9853	24.620	-	-	-	*C ₁₂ H ₈ Cl ₂ O ₃	269.9855	23.889
	*C ₁₂ H ₈ Cl ₂ O ₃	269.9856	27.270	-	-	-	-	-	-
	-	-	-	C ₁₂ H ₇ ClO ₄	250.0036	27.529	-	-	-
20 min	C ₄ H ₃ ClO	101.9874	17.990	-	-	-	-	-	-
	C ₆ H ₄ O ₄	140.0101	14.210	C ₆ H ₄ O ₄	140.0109	13.993	-	-	-
	C ₆ H ₅ ClO	128.0040	23.139	C ₆ H ₅ ClO	128.0034	23.377	C ₆ H ₅ ClO	128.0041	22.608
	*C ₆ H ₅ ClO	128.0028	15.511	-	-	-	*C ₆ H ₅ ClO	128.0028	16.829
	C ₆ H ₅ ClO ₂	144.0008	20.035	C ₆ H ₅ ClO ₂	143.9994	20.095	C ₆ H ₅ ClO ₂	143.9979	19.050
	*C ₆ H ₅ ClO ₂	143.9979	17.692	*C ₆ H ₅ ClO ₂	143.9980	17.725	*C ₆ H ₅ ClO ₂	143.9979	17.003

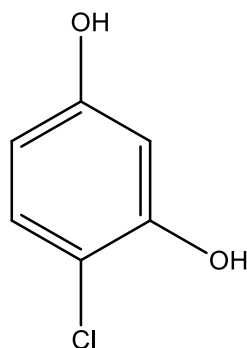
Time (min)	Acidic pH (3)			Dissolution pH (7)			Alkaline pH (10)		
	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)
	C ₆ H ₅ ClO ₄	175.9871	17.148	-	-	-	-	-	-
	C ₁₂ H ₈ Cl ₂ O ₂	253.9897	28.265	C ₁₂ H ₈ Cl ₂ O ₂	253.9909	28.865	C ₁₂ H ₈ Cl ₂ O ₂	253.9910	26.861
	*C ₁₂ H ₈ Cl ₂ O ₂	253.9906	23.089	*C ₁₂ H ₈ Cl ₂ O ₂	253.9906	23.364	*C ₁₂ H ₈ Cl ₂ O ₂	253.9908	22.601
	*C ₁₂ H ₈ Cl ₂ O ₂	253.9907	31.355	-	-	-	*C ₁₂ H ₈ Cl ₂ O ₂	253.9903	29.109
	C ₁₂ H ₈ Cl ₂ O ₃	269.9856	26.291	-	-	-	C ₁₂ H ₈ Cl ₂ O ₃	269.9857	25.131
	*C ₁₂ H ₈ Cl ₂ O ₃	269.9848	23.220	-	-	-	*C ₁₂ H ₈ Cl ₂ O ₃	269.9856	23.71
	C ₁₂ H ₉ ClO ₃	236.0239	21.233	-	-	-	C ₁₂ H ₉ ClO ₃	236.0240	20.865
	-	-	-	-	-	-	*C ₁₂ H ₉ ClO ₃	236.0237	21.463
	-	-	-	-	-	-	*C ₁₂ H ₉ ClO ₃	236.0234	21.911
	-	-	-	-	-	-	C ₁₂ H ₈ Cl ₂ O ₄	285.9797	27.643
	-	-	-	C ₁₂ H ₇ ClO ₄	250.0036	27.572	-	-	-
30 min	C ₄ H ₃ ClO	101.9874	18.364	-	-	-	-	-	-
	C ₅ H ₄ O ₃	112.0155	11.012	-	-	-	-	-	-
	C ₅ H ₄ O ₄	128.0110	8.797	-	-	-	C ₅ H ₄ O ₄	128.0110	8.825
	*C ₅ H ₄ O ₄	128.0104	7.968	-	-	-	*C ₅ H ₄ O ₄	128.0110	8.073
	C ₅ H ₆ O ₄	130.0252	7.541	-	-	-	-	-	-
	*C ₅ H ₆ O ₄	130.262	6.382	-	-	-	-	-	-
	C ₆ H ₄ O ₄	140.0101	14.384	C ₆ H ₄ O ₄	140.0112	13.951	C ₆ H ₄ O ₄	140.0112	13.790
	C ₆ H ₄ O ₄	140.0107	12.478	*C ₆ H ₄ O ₄	140.0114	6.990	*C ₆ H ₄ O ₄	140.0110	6.830
	C ₆ H ₅ ClO	128.0034	23.621	C ₆ H ₅ ClO	128.0030	23.393	C ₆ H ₅ ClO	128.0030	23.186
	C ₆ H ₅ ClO (Isomer in	128.0029	15.670	*C ₆ H ₅ ClO	128.0030	15.407	C ₆ H ₅ ClO (Isomer in EIC)	128.0030	15.407

Time (min)	Acidic pH (3)			Dissolution pH (7)			Alkaline pH (10)		
	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)
	EIC)								
	C ₆ H ₅ ClO ₂	143.9983	20.569	C ₆ H ₅ ClO ₂	143.9986	20.103	C ₆ H ₅ ClO ₂	143.9998	20.032
	C ₆ H ₅ ClO ₄	175.9873	17.420	-	-	-	-	-	-
	C ₁₂ H ₈ Cl ₂ O ₂	253.9911	27.313	C ₁₂ H ₈ Cl ₂ O ₂	253.9908	28.859	C ₁₂ H ₈ Cl ₂ O ₂	253.9906	28.566
	C ₁₂ H ₉ ClO ₃	236.0242	21.8390	-	-	-	-	-	-
	C ₁₂ H ₈ Cl ₂ O ₃	269.9855	25.829	C ₁₂ H ₈ Cl ₂ O ₃	269.9851	26.325	C ₁₂ H ₈ Cl ₂ O ₃	269.0238	26.586
	C ₁₂ H ₉ Cl ₂ O ₇	300.0040	16.480	-	-	-	-	-	-
	-	-	-	-	-	-	C ₁₂ H ₈ Cl ₂ O ₄	285.9802	29.397
40 min	C ₄ H ₃ ClO	101.9874	17.773	C ₄ H ₃ ClO	101.9875	17.754	-	-	-
	-	-	-	C ₅ H ₃ ClO ₅	177.9670	7.365	C ₅ H ₃ ClO ₅	177.9671	7.853
	C ₅ H ₄ O ₄	128.0112	8.460	C ₅ H ₄ O ₄	128.112	8.681	C ₅ H ₄ O ₄	128.0110	9.025
	C ₅ H ₄ O ₃	112.0155	10.278	C ₅ H ₄ O ₃	112.0160	10.874	-	-	-
	C ₆ H ₄ O ₄	140.0101	13.746	C ₆ H ₄ O ₄	140.0111	14.074	C ₆ H ₄ O ₄	140.0110	14.638
	C ₆ H ₄ O ₄	140.0109	6.467						
	C ₆ H ₅ ClO (Isomer in EIC)	128.0026	15.326	*C ₆ H ₅ ClO	128.0030	15.425	C ₆ H ₅ ClO (Isomer in EIC)	128.0030	15.829
	C ₆ H ₅ ClO	128.0033	23.289	C ₆ H ₅ ClO	128.0033	23.271	*C ₆ H ₅ ClO (Main compound but no longer seen in EIC)	128.0030	23.055
	C ₆ H ₅ ClO ₂	143.9982	19.989	C ₆ H ₅ ClO ₂	143.9986	19.916	C ₆ H ₅ ClO ₂ (Main product)	143.9987	19.757
	*C ₆ H ₅ ClO ₂	143.9979	17.597	*C ₆ H ₅ ClO ₂	143.9980	17.506	C ₆ H ₅ ClO ₂ (Isomer)	143.9982	17.33

Time (min)	Acidic pH (3)			Dissolution pH (7)			Alkaline pH (10)		
	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)
	C ₆ H ₅ ClO ₄	175.9843	17.012	-	-	-	-	-	-
	C ₁₂ H ₈ Cl ₂ O ₃	269.9781	26.682	C ₁₂ H ₈ Cl ₂ O ₃	269.9854	26.772	C ₁₂ H ₈ Cl ₂ O ₃	269.9856	26.205
	-	-	-	-	-	-	C ₁₂ H ₈ Cl ₂ O ₄	285.9802	28.719
	C ₁₂ H ₉ ClO ₃	236.0241	21.371	C ₁₂ H ₉ ClO ₃	236.0240	21.282	-	-	-
	C ₁₂ H ₈ Cl ₂ O ₂	253.9908	28.697	C ₁₂ H ₈ Cl ₂ O ₂	253.9981	28.836	-	-	-

Intermediates/compounds in asterisk (*) were only found in the qualitative analysis workflow data.

A probable isomer of 4-chlorocatechol- $C_6H_5ClO_2$ was identified from the qualitative analysis workflow data at 10 min for pH 10. Its presence was further confirmed at 20 min for the various solutions for pH 3, 7 and 10. This compound has been previously reported as 4-chloro-1,3-dihydroxybenzene (Figure 4.22) from 4CP ozonation studies (Sauleda and Brillas, 2001). The researchers reported that the unique intermediate was generated by the action of O_3 itself on the deactivated *meta* position of the 4CP analyte rather than the selective attack of the OH^* on the more favourable *ortho* position. This unfavourable route of formation can be adduced for its transient nature and low concentration that made it unreadable in EIC, TIC or DAD spectra. However, at 40 min an identifiable peak was obtained for 4-chloro-1,3-dihydroxybenzene on the TIC spectrum of the pH 10 4CP solution and confirmed with the extracted mass spectrum (Appendix 7.H). This could be due to the reduced concentrations of 4CP and other major intermediates visible in reduced peaks (Figure 4.23) that were almost completely oxidized. Hence, the peak became intense relative to others present.



4-chloro-1,3-dihydroxybenzene

Figure 4.22: Chemical structure of 4-chloro-1,3-dihydroxybenzene

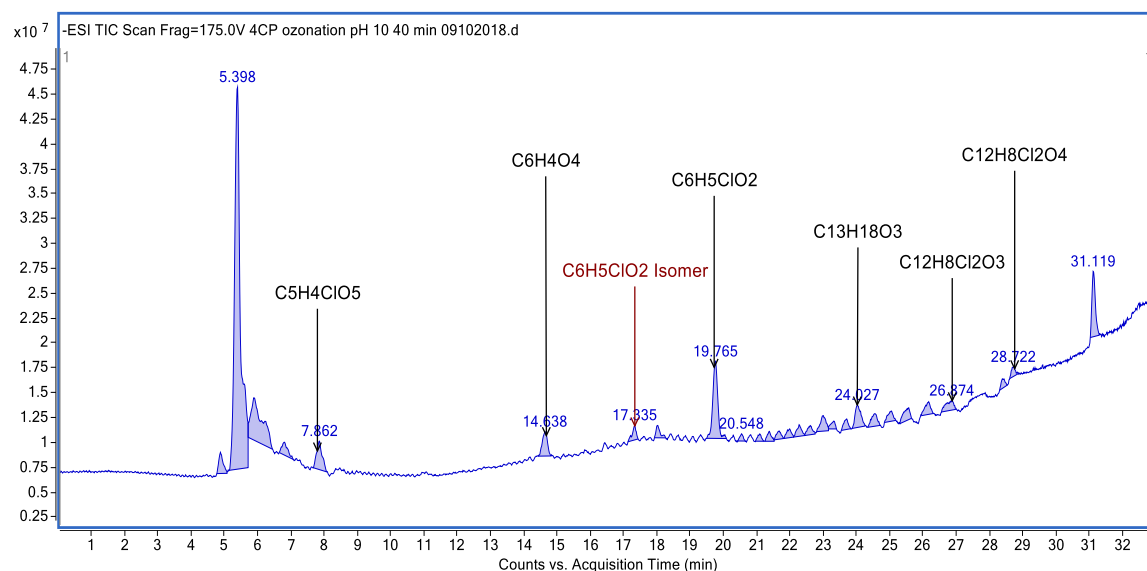
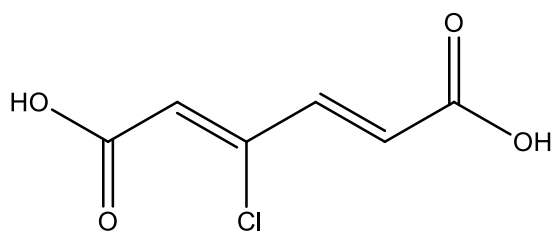


Figure 4.23: TIC chromatogram of 4CP solution (pH 10) at 40 min

Another intermediate $C_6H_5ClO_4$; 175.9871 with a retention time of 17.75 min (MS: Appendix 7.1) was identified after 20 min for 4CP standard solution (pH 3) only. Li et al. (1999) previously identified this compound as a ring-opening product of 4-chlorocatechol; the formation is favoured by the presence of superoxides (O_2^-) and in acidic conditions. The ubiquitous 4-chlorocatechol and the superoxides generated in the ozonation oxidation process (Oputu et al., 2015b) resulted in the formation of the 3-chloro-trans,trans-muconic acid ($C_6H_5ClO_4$) intermediate (Figure 4.23) in the 4CP solution with pH 3. similarly, Myilsamy et al. (2016) and Thomas et al. (2016) both identified 3-chloro-trans,trans-muconic acid as a degradation product of the catalytic processes of 4CP with TiO_2 -based catalysts.



3-chloro-trans, trans-muconic acid

Figure 4.24: Chemical structure of 3-chloro-trans, trans-muconic acid

A six-carbon ring compound $C_6H_4O_4$; 140.0112, RT= 13.63 min was observed in the EIC spectrum of the pH 7 4CP solution at 10 min (MS: Appendix 7.J). This was later identified at 20 min for pH 3 solution at RT= 14.21 min and after 30 min for pH 10 at RT= 13.79 min. Theurich et al. (1996) in a photodegradation study of 4CP posited that the intermediate 2-hydroxybenzoquinone; $C_6H_4O_3$ (Figure 4.25a) might be the last aromatic compound before the ring-opening step leading to the final mineralization of 4CP. However, Oputu et al. (2015a) identified the intermediate $C_6H_4O_4$, in an ozonation based degradation process using similar LCMS-TOF instrumentation as employed in this study. Li et al. (1999) had previously observed the compounds 4-chloro-3,6-dihydroxyphenol, 4-chloro-2,3-dihydroxyphenol, 5-chloro-2-hydroxybenzoquinone and 2,4,5-trihydroxyphenol (Figure 4.25b, c, d and e) as intermediates of 4CP degradation leading to ring-opening products. These compounds can undergo oxidation (2-hydroxybenzoquinone and 2,4,5-trihydroxyphenol), or dechlorination/oxidation (4-chloro-3,6-dihydroxyphenol, 4-chloro-2,3-dihydroxyphenol and 5-chloro-2-hydroxybenzoquinone) to give the intermediate $C_6H_4O_4$. It is pertinent to state that structure 2-hydroxybenzoquinone was ubiquitous in all the samples analysed in this investigation, with 4-chloro-3,6-dihydroxyphenol and 4-chloro-2,3-dihydroxyphenol equally identified in the QAW generated compound list. The dechlorination of 4-chloro-3,6-dihydroxyphenol yields 2,5-dihydroxyphenol (Figure 4.25f), which was also identified alongside it at a retention time of 20.04 min. The transient nature, low concentration and fast conversion of the aforementioned intermediates to the $C_6H_4O_4$ can be adduced as the reason they are not detected in the EIC or TIC scans.

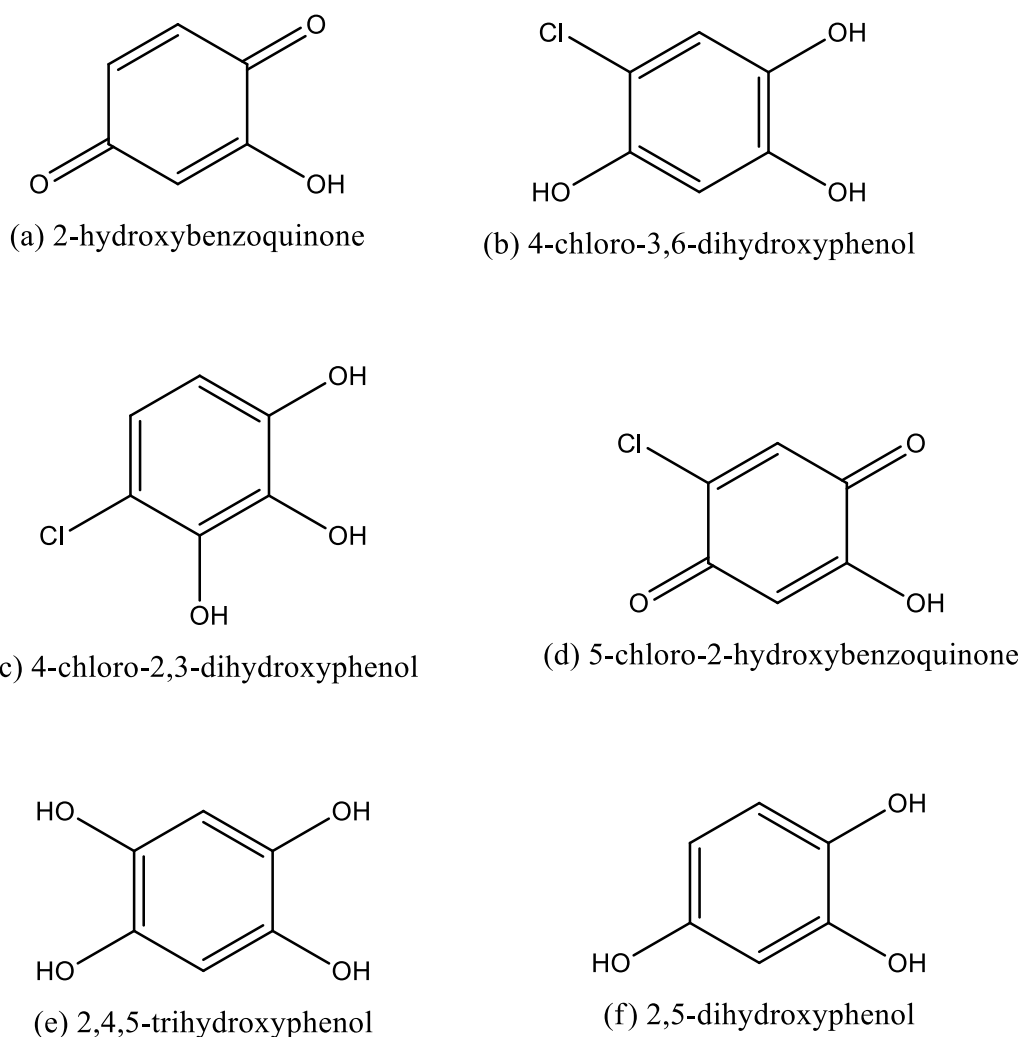
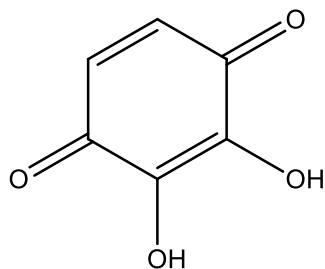


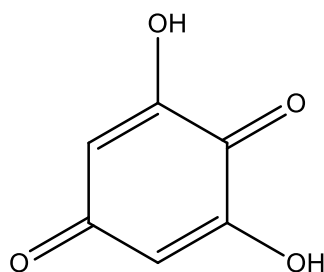
Figure 4.25: Chemical structures of (a) 2-hydroxybenzoquinone, (a) 4-chloro-3,6-dihydroxyphenol, (c) 4-chloro-2,3-dihydroxyphenol, (d) 5-chloro-2-hydroxybenzoquinone, (e) 2,4,5-trihydroxyphenol and (f) 2,5-dihydroxyphenol

Subsequently, the possible isomers for the $C_6H_4O_4$ intermediate are presented as 2,3-dihydroxybenzoquinone, 2,6-dihydroxybenzoquinone, 2,5-dihydroxybenzoquinone, 4,5-dihydroxy-1,2-benzoquinone and 3,6-dihydroxy-1,2-benzoquinone (Figure 4.26a-e). Amongst these isomers, the ortho-hydroxylation product 2,6-dihydroxybenzoquinone (Figure 4.26b) supports the main isomer for the $C_6H_4O_4$ intermediate based on the favoured route of formation. A possible isomer with the same molecular formula $C_6H_4O_4$ was identified at 30 min for all the 4CP solutions occurring at the retention times of 6.72 min, 6.99 min and 6.83 min for pH 3, 7 and 10, respectively. The isomer was only found in the EIC spectrum obtained at pH 3. It was generated as part of the compound lists of the

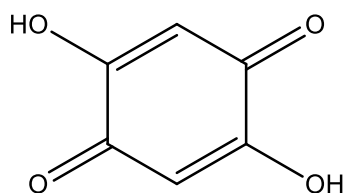
QAW data for pH 7 and 10. This isomer may be any of the structures represented as Figure 4.26a, c, d and e.



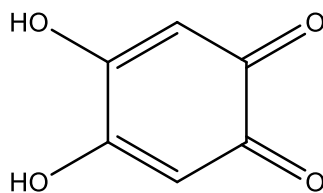
(a) 2,3-dihydroxybenzoquinone



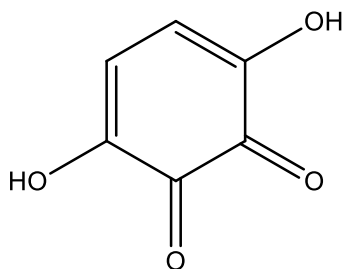
(b) 2,6-dihydroxybenzoquinone



(c) 2,5-dihydroxybenzoquinone



(d) 4,5-dihydroxy-1,2-benzoquinone



(e) 3,6-dihydroxy-1,2-benzoquinone

Figure 4.26: Chemical structures of (a) 2,3-dihydroxybenzoquinone, (b) 2,6-dihydroxybenzo-quinone, (c) 2,5-dihydroxybenzoquinone, (d) 4,5-dihydroxy-1,2-benzoquinone and (e) 3,6-dihydroxy-1,2-benzoquinone

Two isomers of the $C_6H_6O_2$; 110.0365 were identified in the mined data generated for pH 10 4CP solution with retention times of 8.93 min and 13.35 min, respectively. From literature, these compounds could be either hydroquinone (Figure 4.27a) or catechol (Figure 4.27b) formed by the preferred attack by O_3/OH^* on the *ortho* or *para* positions of phenol ring. Their formation is aided by the fact that the substituent hydroxyl group present in the phenol compound is an electron density-enhancing one whose inductive and conjugative effects give rise to *ortho* and/or *para* substituents (Xu et al., 2005). Hence, the

phenol is rapidly converted to either of the compounds above. In this case, the product hydroquinone (MS: Appendix 7.K) seems to be the intermediate formed at the retention time of 8.93 min, while catechol (MS: Appendix 7.L) was obtained at the retention time of 13.35 min as confirmed against pure standards of both compounds shown in Figure 4.19. Several researchers have reported instances where both 4-chlorocatechol and hydroquinone intermediates were identified in the degradation processes of 4CP (Myilsamy et al., 2016; Theurich et al., 1996). However, only one of the routes is usually the main products while the other intermediate is often transient and in low concentration, if identified. Besides the 4-chlorocatechol and hydroquinone intermediates, Theurich et al. (1996) identified phenol (the precursor to catechol) as one of the minor intermediates in the photocatalytic degradation of 4CP in an aerated aqueous titanium dioxide suspension.

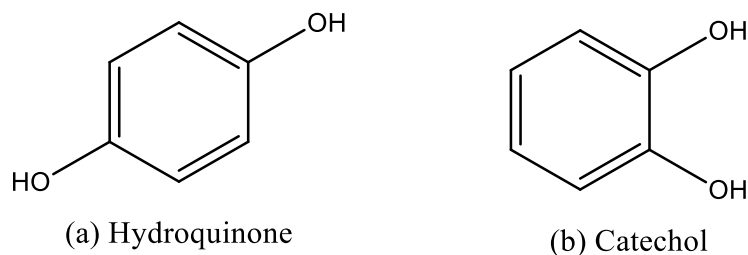


Figure 4.27: Chemical structures of (a) hydroquinone and (b) catechol

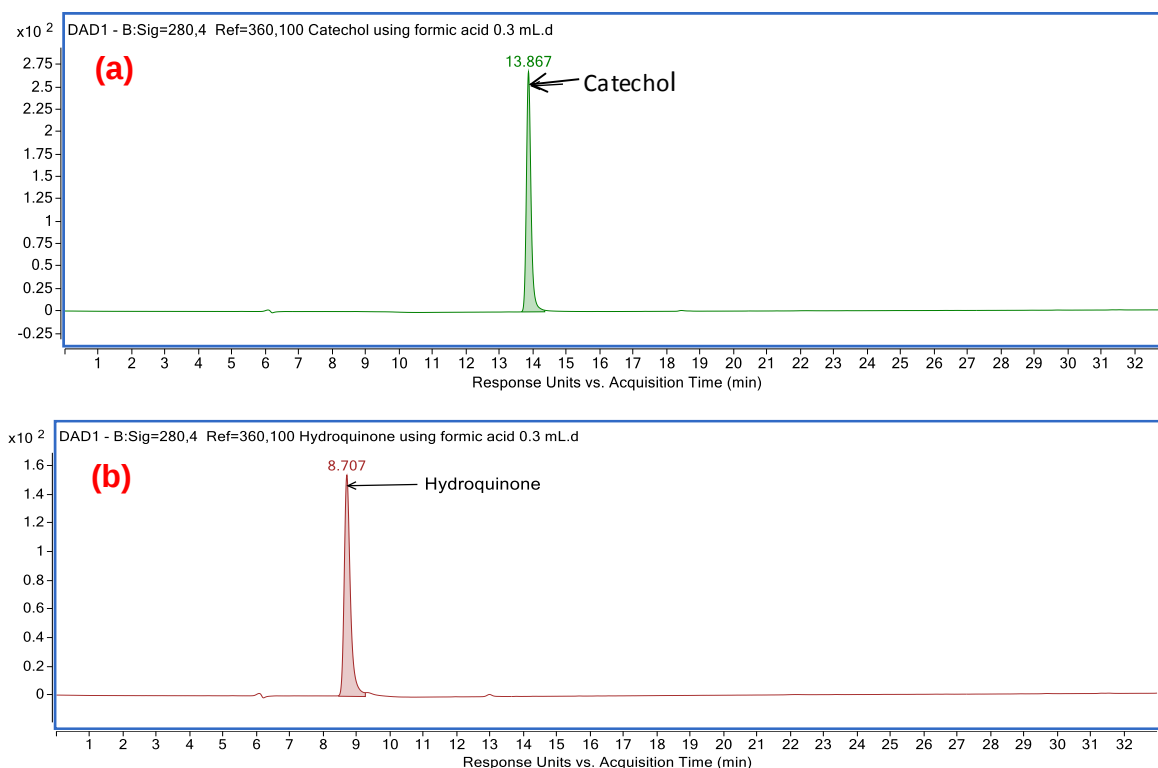
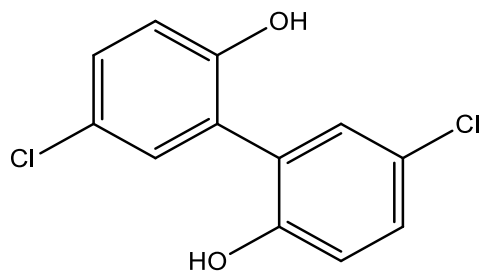


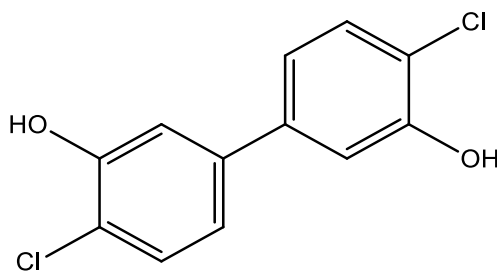
Figure 4.28: DAD spectra for catechol (a) and hydroquinone (b)

A major dimer intermediate identified in this study is $C_{12}H_8Cl_2O_2$; 253.9906, RT= 27.05 min. It was the dominant intermediate for the pH 10 solution with a prominent peak in the EIC spectrum and confirmed from the mass spectrum (MS: Appendix 7M.). However, with the progression of time, the peak became less intense, while the 4-chlorocatechol intermediate became more prominent. The intermediate was present in all the samples collected at the different time interval and analysed, except for the pH 10 sample drawn at 40 min due to its complete degradation or conversion to 4CP at this point. The formation of the $C_{12}H_8Cl_2O_2$ compound tends to be more favoured in alkaline conditions as indicative of its prominent peak at pH 10, due to the ease of ionization of the 4CP molecules and subsequent dimerization. The chemical structures shown in Figure 4.29a-c were picked as the possible representation for the compound from a list of 119 isomers obtained from the ChemSpider database (search made on 2nd January 2019). Based on the symmetry and *ortho*-position favoured hydroxylation product of 4CP, the structure in Figure 4.29a was assigned as the main isomer of $C_{12}H_8Cl_2O_2$. The chemical structure in Figure 4.29b is formed from the dimerization of the *meta*-hydroxylated 4CP. Also, the structure in Figure 4.29c is formed from two *meta*-hydroxylated 4CP but with the link occurring at the hydroxyl-positioned substituent and the main phenolic hydroxyl group of the other *meta*-hydroxylated 4CP ring. These compounds (4,4'-dichloro-3,3'-biphenyldiol and 4,6'-dichloro-

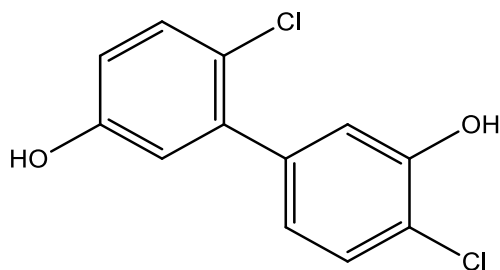
3,3'-biphenyldiol) are the likely isomers observed at retention time 22.79 min and 29.61 min. In a previous report, Oputu et al. (2015a) also identified the major isomer as a dimer product of 4CP.



(a) 5,5'-dichloro-2,2'-biphenyldiol



(b) 4,4'-dichloro-3,3'-biphenyldiol



(c) 4,6'-dichloro-3,3'-biphenyldiol

Figure 4.29: Chemical structures of (a) 5,5'-dichloro-2,2'-biphenyldiol, (b) 4,4'-dichloro-3,3'-biphenyldiol and (c) 4,6'-dichloro-3,3'-biphenyldiol

The compound $C_{12}H_8Cl_2O_3$; 269.9955, RT= 25.31 min (MS: Appendix 7.N) was identified alongside the $C_{12}H_8Cl_2O_2$ in most of the samples analysed. Its formation is by the oxidation of the 4CP dimer $C_{12}H_8Cl_2O_2$ to a higher oxidation product. Like its precursor, an isomer present only in the qualitative analysis workflow data was identified for it at the retention time of 23.89 min. Further oxidation product $C_{12}H_8Cl_2O_4$; 285.9797, RT= 27.64 min was observed after 20 min for the pH 10 solution only. Other dimer intermediates identified in this study were $C_{12}H_9ClO_3$; 236.0239 (RT= 27.53 min), $C_{12}H_7ClO_4$; 250.0036 (RT= 21.23

min) and $C_{12}H_9Cl_2O_7$; 300.0040 (RT= 16.48 min). These dimer compounds are considered novel since they have not been previously reported in any similar studies. Their confirmation mass spectra are presented in Figures 4.30 and 4.31.

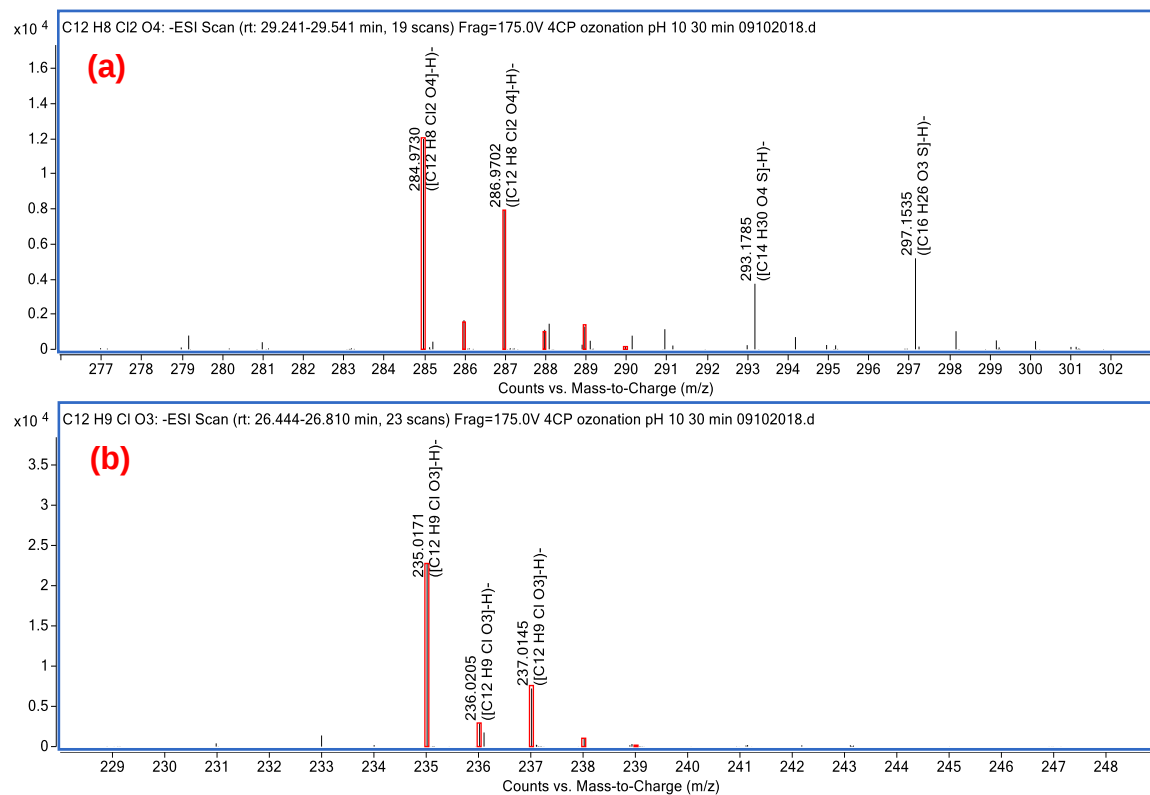


Figure 4.30: Mass spectra for the intermediates $C_{12}H_8Cl_2O_4$ (a) and $C_{12}H_9ClO_3$ (b)

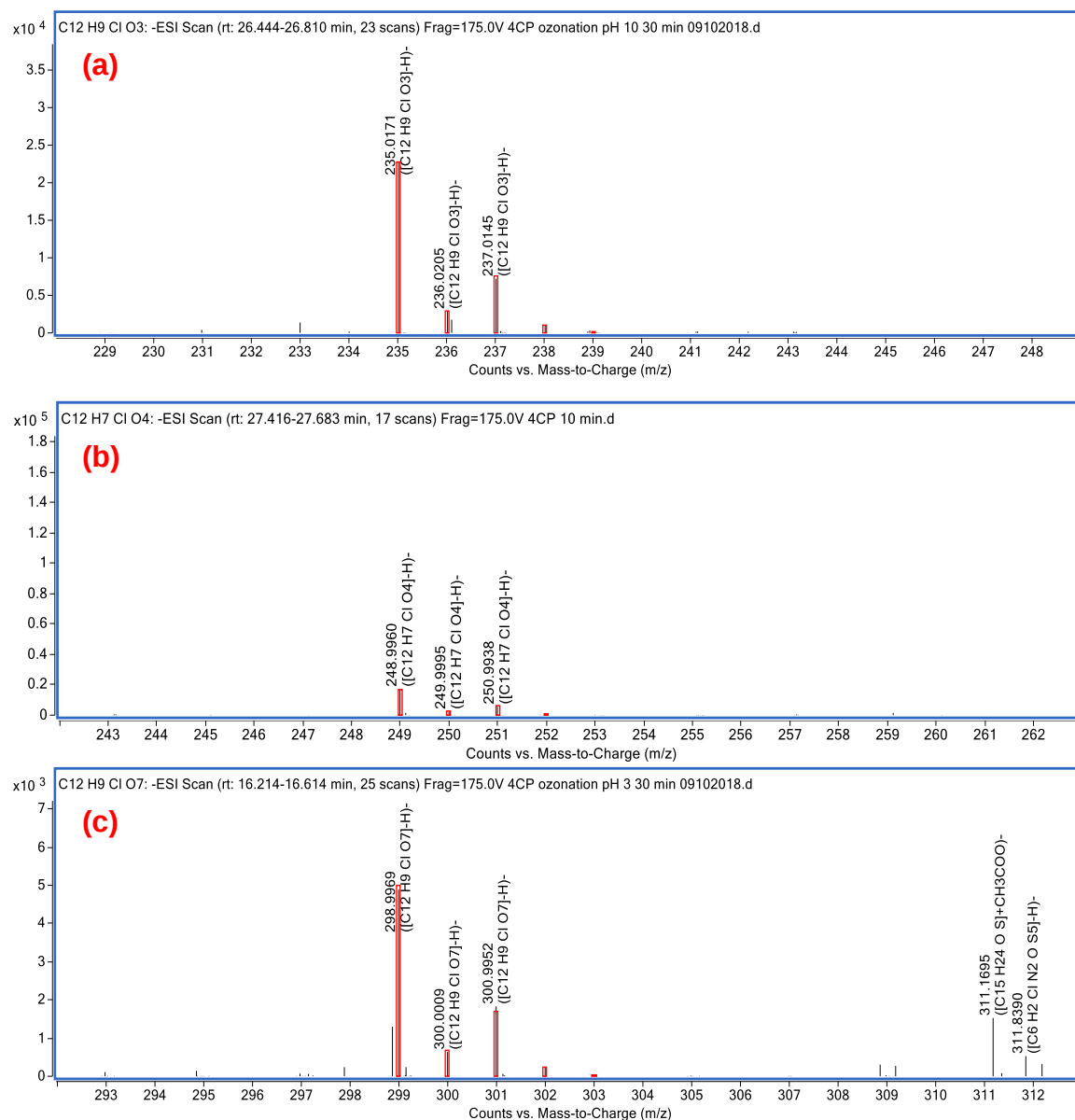


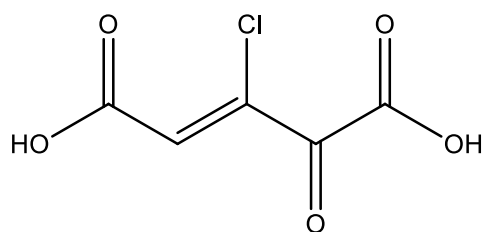
Figure 4.31: Mass spectra for the intermediates $C_{12}H_9ClO_3$ (a), $C_{12}H_7ClO_4$ (b) and $C_{12}H_9ClO_7$ (c)

4.4.2.1 Residual five-carbon (C5) compounds

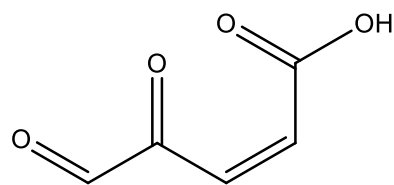
Four C5 compounds were identified as major intermediates during the degradation process of the 4CP. They are the probable breakdown products of the previously identified ring-opening intermediate 3-chloro-trans,trans-muconic acid. Their formation follows a series of oxidation, decarboxylation/dechlorination and further oxidation as the case may be. The first in line amongst these C5 compounds is $C_5H_3ClO_5$; 177.9671, RT= 7.37 min obtained at 40 min for both pH 7 and 10 (MS: Appendix 7O.). As stated above, its

formation may come from the oxidation of the 3-chloro-trans,trans-muconic acid, followed by decarboxylation and oxidation again. The previous report from 4CP degradation by Li et al. (1999) supports this route for its formation, and the intermediate was identified as 3-chloro-2-oxopent-3-enedioic acid (Figure 4.32a). The formation of $C_5H_4O_4$; 128.0110, RT= 8.80 min (MS: Appendix 7.P) stems from the dechlorination step after the initial oxidation, carboxylation/oxidation of 3-chloro-trans,trans-muconic acid. The intermediate was identified as (z)-4,5-dioxopent-2-enoic acid (Figure 4.32b) based on stereochemistry. The C5 intermediate $C_5H_6O_4$; 130.0252, RT= 7.54 min (MS: Appendix 7.Q) was found in pH 3 solution only after 30 min, showing that its formation is likely favoured by the acidic condition. The acidic condition prevalent in pH 3 was rife with H^+ ions which readily attack the double bond present in the intermediate (z)-4,5-dioxopent-2-enoic acid leading to the formation of 4,5-dioxopentanoic acid assigned the structure in Figure 4.32c.

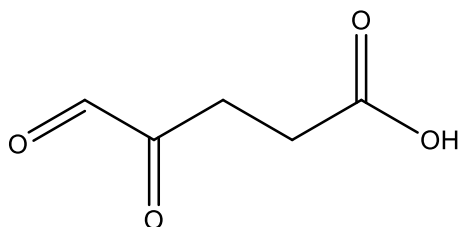
Furthermore, the intermediate $C_5H_4O_3$; 112.0158, RT= 9.58 min, occurred at 10 min sampling time in the pH 3 solution only and was later observed in the pH 7 solution after 40 min as confirmed from the mass spectra in each case (MS: Appendix 7.R). For the pH 10 solution, the residual intermediate was only generated as part of the compound list in the mined data. From ChemSpider search, only one structure 2-furoic acid (Figure 4.32d) was found for the chemical formula $C_5H_4O_3$. Hence, this was adduced as the structure for it. This intermediate is also one of the compounds most likely formed from 3-chloro-trans,trans-muconic acid and possibly obtained by the ring formation of (z)-4,5-dioxopent-2-enoic acid due to rearrangement and subsequent loss of an oxygen atom. Again, this intermediate has not been reported in any previous ozonation investigation.



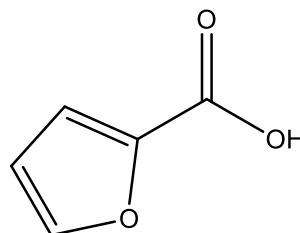
(a) 3-chloro-2-oxopent-3-enedioic acid



(b) (z)-4,5-dioxopent-2-enoic acid



(c) 4,5-dioxopentanoic acid



(d) 2-furoic acid

Figure 4.32: Chemical structures of (a) 3-chloro-2-oxopent-3-enedioic, (b) (z)-4,5-dioxopent-2-enoic acid, (c) 4,5-dioxopentanoic acid and (d) 2-furoic acid

4.4.2.2 Residual four carbon (C4) compounds

The intermediate C_4H_3ClO ; 101.9872, $RT = 17.70$ min was the prominent C4 compound identified in this study. It was observed for all the samples drawn for the pH 3 4CP solution (MS: Appendix 7.S) and only became evident in the EIC spectrum at 40 min for pH 7 (MS: Appendix 7.T). This trend shows that its formation is aided by acidic conditions as the pH 7 analyte solution itself became acidic with $pH \approx 3$ at this time. The intermediate may be a product for the likely cleavage of 4-chlorocatechol at the 1,5-position to yield an open-chain product which immediately undergoes rearrangement to form a stable compound. A search for the probable structure in Chemspider gave two of the isomers 2-chlorofuran (Figure 4.33a) and 3-chlorofuran (Figure 4.33b). Both are the rearrangement products after the initial 1,5-ring cleavage. However, based on the position of the chlorine substituent as retained from the precursor, 3-chlorofuran was chosen as the intermediate. From literature, Oputu et al. (2015a) reported the presence of this intermediate in their ozonation of 4CP, while it is scarce in many related works.



Figure 4.33: Chemical structure of (a) 2-chlorofuran and (b) 3-chlorofuran

The residual intermediate $C_4H_4O_4$ was observed in all samples at the later stage of the ozonation processes. Two isomers with retention time 6.16 min and 9.12 min were found, representing the fumaric acid (Figure 4.34a) and maleic acid Figure 4.34b isomers reported in many literatures (Wang et al., 2016b; Coteiro and De Andrade, 2007; Wang and Wang, 2007; Xu et al., 2005; Sauleda and Brillas, 2001). Also, further oxidation of $C_4H_4O_4$ intermediate yields $C_4H_4O_6$, 150.0139, and this compound was equally found among the compound list generated by the qualitative analysis workflow at a retention time of 5.37 min. Coteiro and De Andrade (2007) previously identified the intermediate as succinic acid (Figure 4.34c).

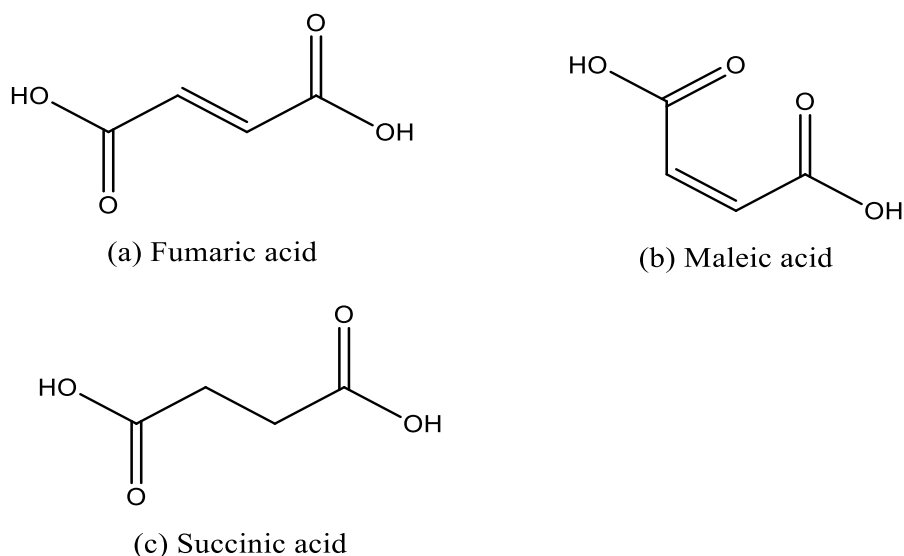
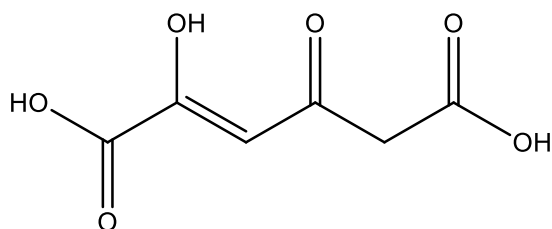


Figure 4.34: Chemical structure of (a) fumaric acid, (b) maleic acid and (c) succinic acid

Possible formation of the $C_4H_4O_4$ isomers may have occurred via two routes. Firstly, the dechlorination and oxidation of the C4 compound C_4H_3ClO (3-chlorofuran) can likely lead to the $C_4H_4O_4$ intermediates. Also, its formation may occur through the ring-opening reaction of the previously identified $C_6H_4O_4$ (2,6-dihydroxybenzoquinone) to form an open-chain compound- (z)-2-hydroxy-4-oxohex-2-enedioic acid ($C_6H_6O_6$) shown in Figure 4.35.

This intermediate $C_6H_6O_6$; 174.0143 was one of the residual intermediates present in the generated data with a retention time of 6.04 min which arguably falls in the region most of the carboxylic acids were identified.

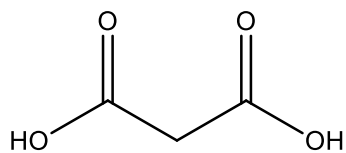


(z)-2-hydroxy-4-oxohex-2-enedioic acid

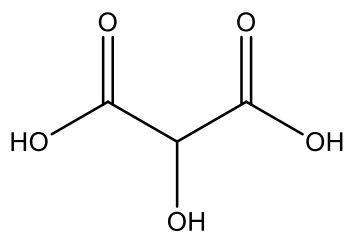
Figure 4.35: Chemical structure of (z)-2-hydroxy-4-oxohex-2-enedioic acid

4.4.2.3 Residual three carbon (C3) compounds

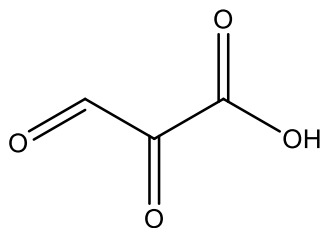
The C3 intermediates identified in this investigation were only evident in the QAW generated data. Their low concentrations in solution which likely results from their immediate mineralization once formed may be responsible for this trend. The intermediate $C_3H_4O_4$; 104.0110, RT= 5.48 min was mostly observed after 30 min in the drawn samples and has been previously identified as malonic acid (Figure 4.36a) by several researchers (Wang et al., 2016b; Coteiro and De Andrade, 2007; Wang and Wang, 2007). Further oxidation of malonic acid gives the intermediate $C_3H_4O_5$; 120.0034 with the retention time of 5.56 min. The compound was identified as hydroxyl malonic acid (Figure 4.36b) based on literature guidance (Thomas et al., 2016; Wang et al., 2016b). Another C3 compound identified in this investigation is $C_3H_2O_4$; 101.9952, RT= 5.35 min, an intermediate which was also reported as part of the breakdown product of 4-chlorocatechol by Li et al. (1999) as 2,3-dioxopropanoic acid (Figure 4.36c). Further oxidation of the 2,3-dioxopropanoic acid intermediate yields 2-oxopropan-1,3-dioic acid ($C_3H_2O_5$) identified at the retention time of 5.39 min (Figure 4.36d). This intermediate is scarce in literature for the degradation of 4CP. Based on the elucidation of the intermediates as discussed above, the proposed degradation pathway for 4-chlorophenol in this study is as presented in Figure 4.37, and further breakdown products of some major intermediates are presented in Figure 4.38.



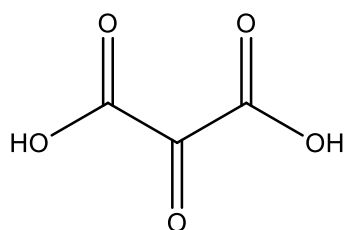
(a) Malonic acid



(b) Hydroxyl malonic acid



(c) 2,3-dioxopropanoic acid



(d) 2-oxopropan-1,3-dioic acid

Figure 4.36: Chemical structure of (a) malonic acid, (b) hydroxyl malonic acid, (c) 2,3-dioxopropanoic acid and (d) 2-oxopropan-1,3-dioic acid

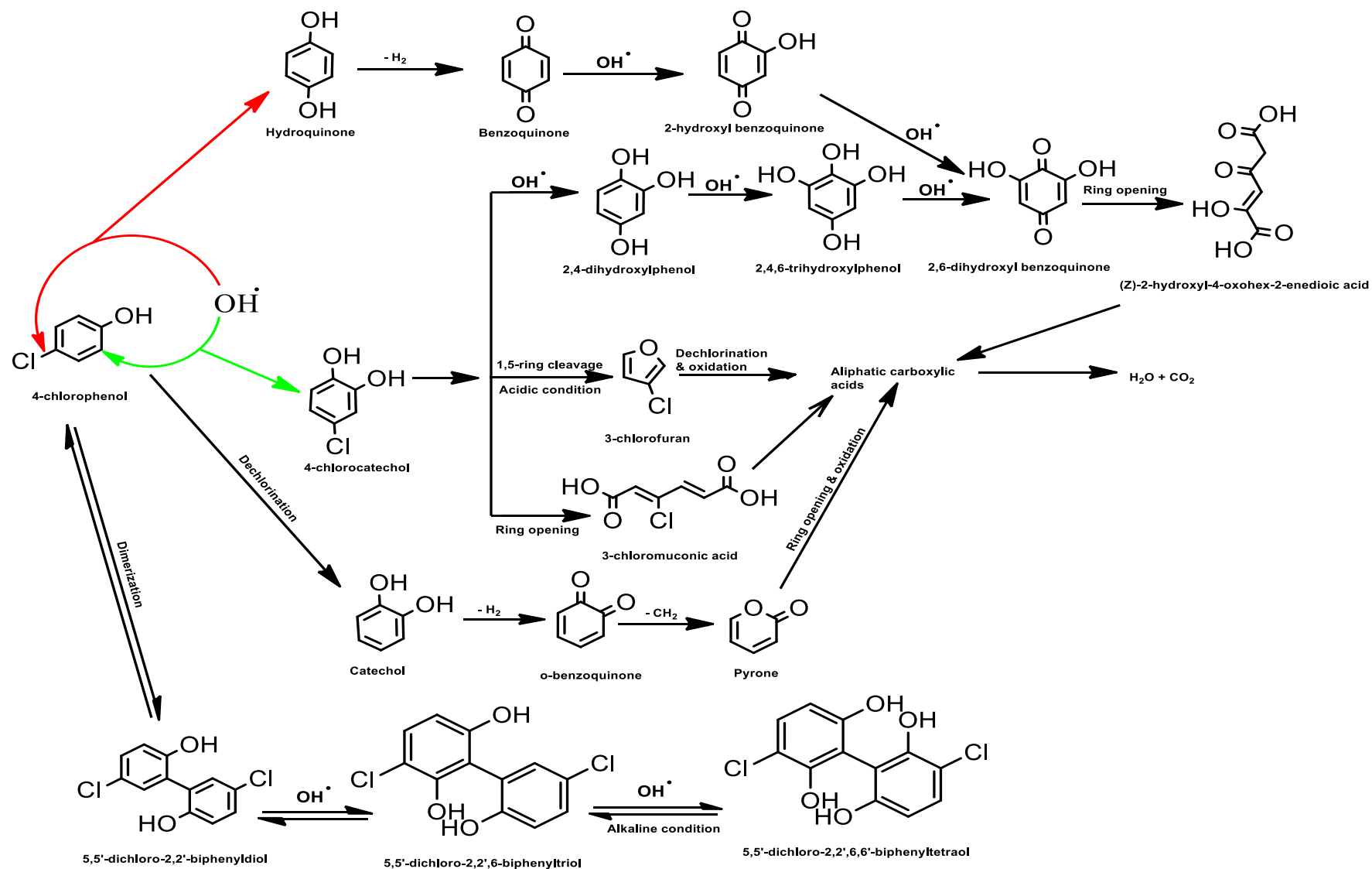


Figure 4.37: Proposed degradation pathways for 4-chlorophenol based on this study

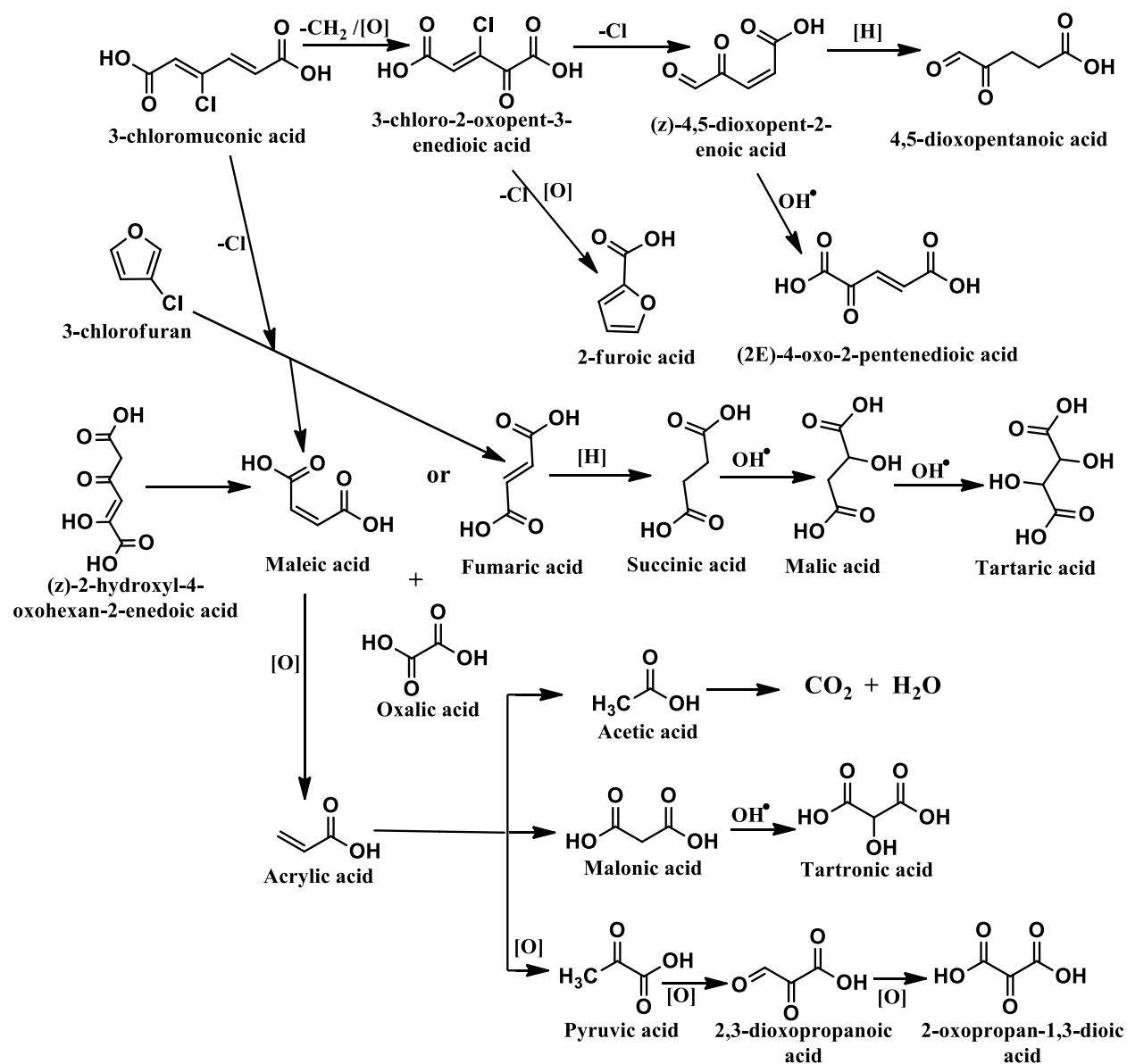


Figure 4.38: Degradation routes of some major intermediates to 5C, 4C, 3C and 2C compounds

4.4.3 Intermediates of 4-nitrophenol

The chemical 4-nitrophenol (4-NP) is an important member of nitroaromatic compounds and part of the phenolics classified as priority pollutants. As part of the mononitrophenols, it is produced in the highest quantities worldwide, possesses the highest toxicity and also most water-soluble among them (Ahmaruzzaman and Gayatri, 2010). The toxic effect of 4-NP can cause damage to the central nervous system, liver, kidney and blood of humans and animals; coupled with the fact that it is resistant to traditional water treatment techniques (Zhang et al., 2007). Typically, 4-NP is found in many industrial effluents arising from the production of drugs, dyes, explosives, phosphor-organic insecticides, pesticides, and leather colouring (Tomei et al., 2008). The xenobiotic tendencies of 4-NP and its prevalent presence in environmental matrices (especially aquatic) make it a major pollutant of interest to researchers in the global scientific community.

The degradation of 4NP; $C_6H_5NO_3$ (Figure 4.39a) has been identified in several studies to follow the 4-nitrocatechol and hydroquinone routes like its 4CP counterpart. They both follow a similar reaction mechanism in this first step to attain these intermediate products. In the degradation of 4NP, several reports abound which suggest that both the 4-nitrocatechol and hydroquinone intermediates were generated as the first products and showing that the breakdown processes can follow both routes simultaneously (Pan et al., 2015; Khatamian et al., 2012; Daneshvar et al., 2007; Marais et al., 2007; Quiroz et al., 2005). Also, literature has shown instances where either the 4-nitrocatechol (Xiong et al., 2015) or the hydroquinone route (Khavar and Jafarisani, 2017) were only followed in the degradation processes. In this study, 4-nitrocatechol ($C_6H_5NO_4$) presented in Figure 4.39b was the primary intermediate firstly identified. The 4-nitrocatechol intermediate was observed in all the samples analysed for the 4NP analyte solution with different initial pH 4NP as shown in Table 4.3.

The 4-nitrocatechol; 155.0226 was identified at the retention times of 17.95 min, 17.97 min and 18.01 min for initial pH 3, 7 and 10 solutions respectively at 10 min. The formation of the 4-nitrocatechol proceeds via the preferential *ortho*-position (to the -OH) attack by the electrophilic OH^* on the 4NP ring. The EIC chromatograms and the mass spectra confirmation for each of the different initial pH solutions are presented in Figure 4.40 - 4.42. As observed for 4CP, another 4-nitrocatechol isomer was identified only in the QAW

data after 20 min in both the initial pH 7 and 10 4NP solutions. This shows the possible formation of the *meta*-position hydroxylation 4NP intermediate as observed for 4CP.

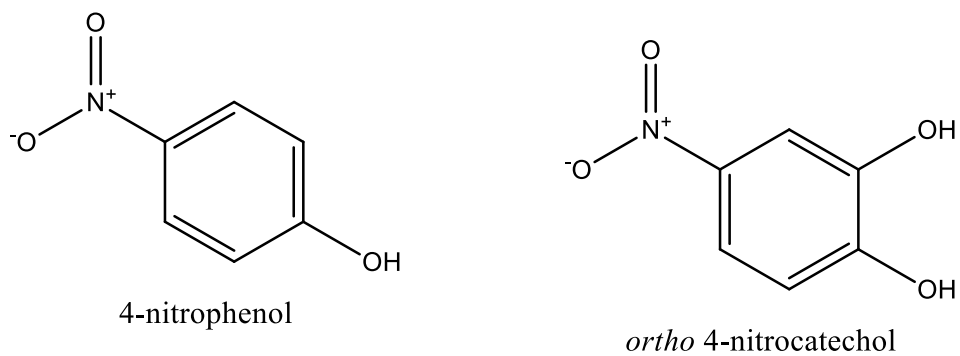


Figure 4.39: Chemical structure of (a) 4-nitrophenol and (b) *ortho* 4-nitrocatechol

Table 4.3: Intermediates of 4-nitrophenol ozonation at different pH identified from EIC/TIC chromatogram and mass spectra

Time (min)	Acidic pH (3)			Dissolution pH (7)			Alkaline pH (10)		
	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)
0 min	C ₆ H ₅ NO ₃	139.0274	20.758	C ₆ H ₅ NO ₃	139.0268	20.846	C ₆ H ₅ NO ₃	139.0273	20.669
10 min	C ₆ H ₅ NO ₃	139.0274	20.782	C ₆ H ₅ NO ₃	139.0267	20.796	C ₆ H ₅ NO ₃	139.0274	20.863
	C ₆ H ₅ NO ₄	155.0226	17.953	C ₆ H ₅ NO ₄	155.0217	17.972	C ₆ H ₅ NO ₄	155.0180	18.0102
20 min							C ₃ H ₅ NO ₅	135.0170	7.468
							*C ₆ H ₆ O ₂	110.0363	14.310
	C ₆ H ₅ NO ₃	139.0273	20.900	C ₆ H ₅ NO ₃	139.0270	20.829	C ₆ H ₅ NO ₃	139.0274	20.818
	C ₆ H ₅ NO ₄	155.0227	17.936	C ₆ H ₅ NO ₄	155.0213	17.952	C ₆ H ₅ NO ₄	155.0222	17.550
				*C ₆ H ₅ NO ₄	155.0219	15.950	*C ₆ H ₅ NO ₄	155.0219	14.894
							C ₆ H ₄ N ₂ O ₅	184.0127	22.817
30 min				C ₄ H ₆ O ₃	102.0307	6.743	C ₄ H ₆ O ₃	102.0318	7.711
							C ₆ H ₅ O ₃	125.0239	17.852
	C ₆ H ₅ NO ₃	139.0274	21.0880	C ₆ H ₅ NO ₃	139.0270	20.829	C ₆ H ₅ NO ₃	139.0274	20.818
							*C ₆ H ₅ NO ₃	139.0273	18.120

Time (min)	Acidic pH (3)			Dissolution pH (7)			Alkaline pH (10)		
	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)	Formula	Mass	Retention time (min)
40 min	C ₆ H ₅ NO ₄	155.0226	17.929	C ₆ H ₅ NO ₄	155.0213	17.952	C ₆ H ₅ NO ₄	155.0222	17.852
				*C ₆ H ₅ NO ₄	155.0219	15.950	*C ₆ H ₅ NO ₄	155.0218	14.625
							C ₆ H ₅ NO ₅	171.0172	14.470
							C ₆ H ₄ N ₂ O ₅	184.0128	22.975
							C ₄ H ₆ O ₃	102.0314	7.239
				C ₄ H ₃ N ₄ O ₆	203.0043	6.714			
							C ₆ H ₅ O ₃	125.0239	19.036
	C ₆ H ₅ NO ₃	139.0275	20.802	C ₆ H ₅ NO ₃	139.0268	20.867	C ₆ H ₅ NO ₃	139.0273	21.421
							*C ₆ H ₅ NO ₃	139.0273	19.207
	C ₆ H ₅ NO ₄	155.0226	17.912	C ₆ H ₅ NO ₄	155.0215	17.955	C ₆ H ₅ NO ₄	155.0223	19.035
							C ₆ H ₅ NO ₅	171.0172	16.288
							*C ₆ H ₅ NO ₅	171.172	17.713
							C ₆ H ₄ N ₂ O ₅	184.0127	23.057
							*C ₆ H ₄ N ₂ O ₅	184.0128	20.607

Intermediates/compounds in asterisk (*) were only found in the qualitative analysis workflow data.

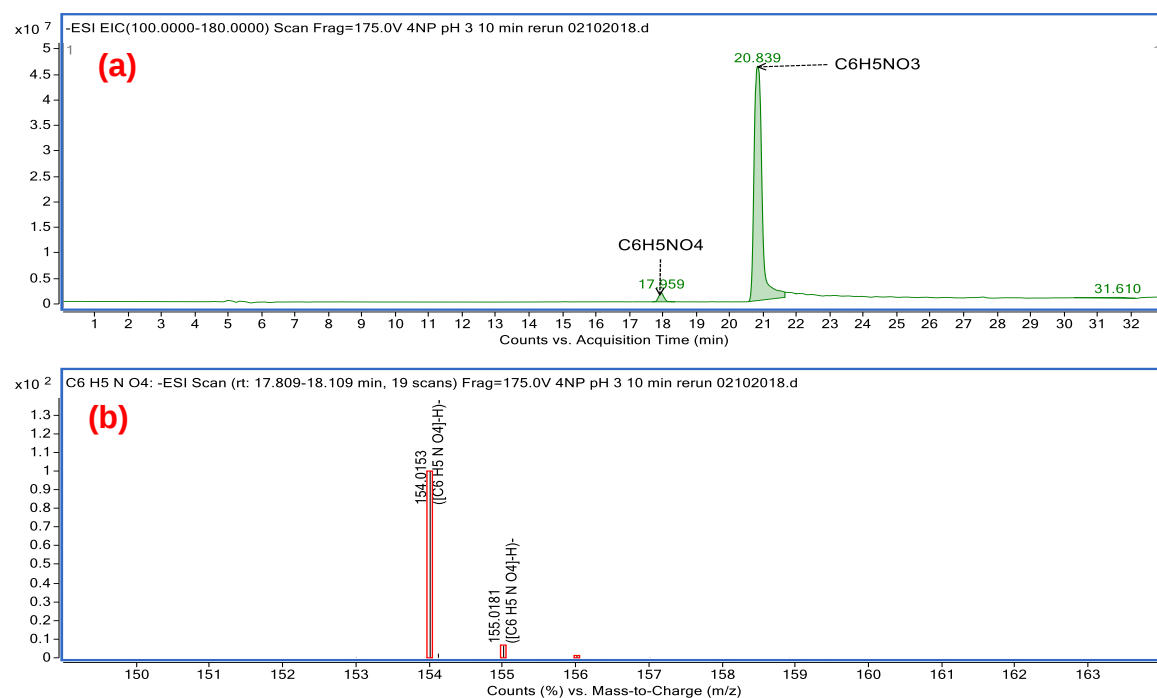


Figure 4.40: The EIC chromatogram (a) and confirmation mass spectrum (b) of 4-nitro catechol for pH 3 initial 4NP solution

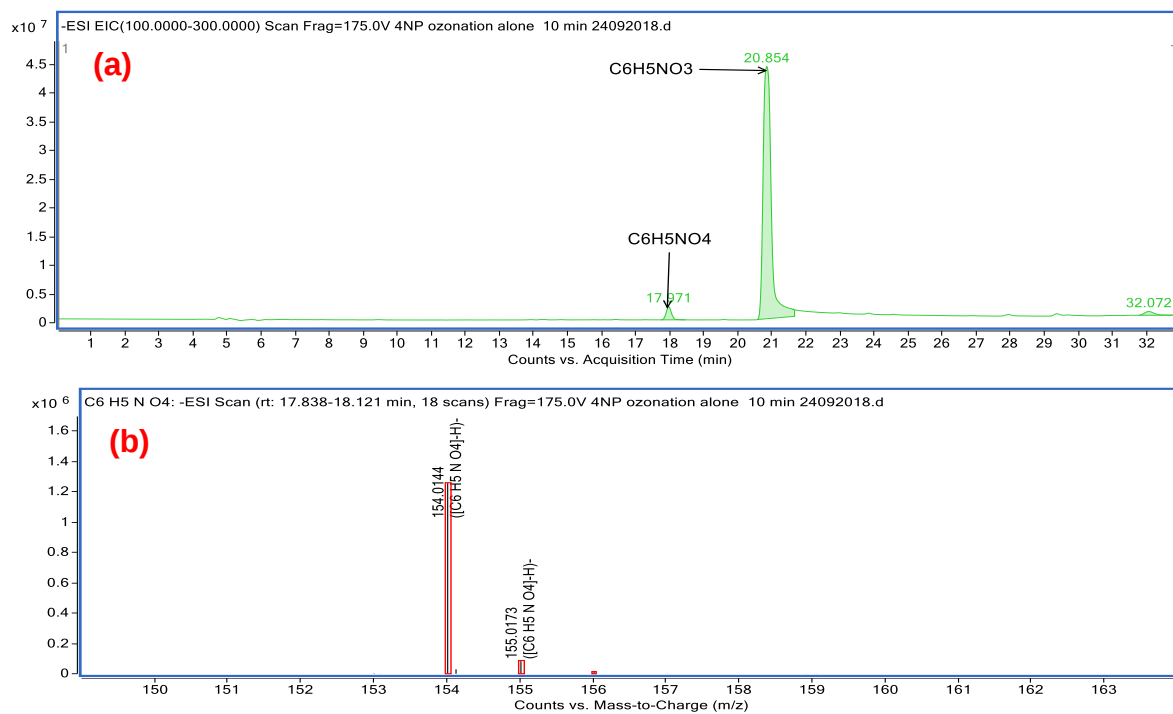


Figure 4.41: The EIC chromatogram (a) and confirmation mass spectrum (b) of 4-nitro catechol for pH 7 initial 4NP solution

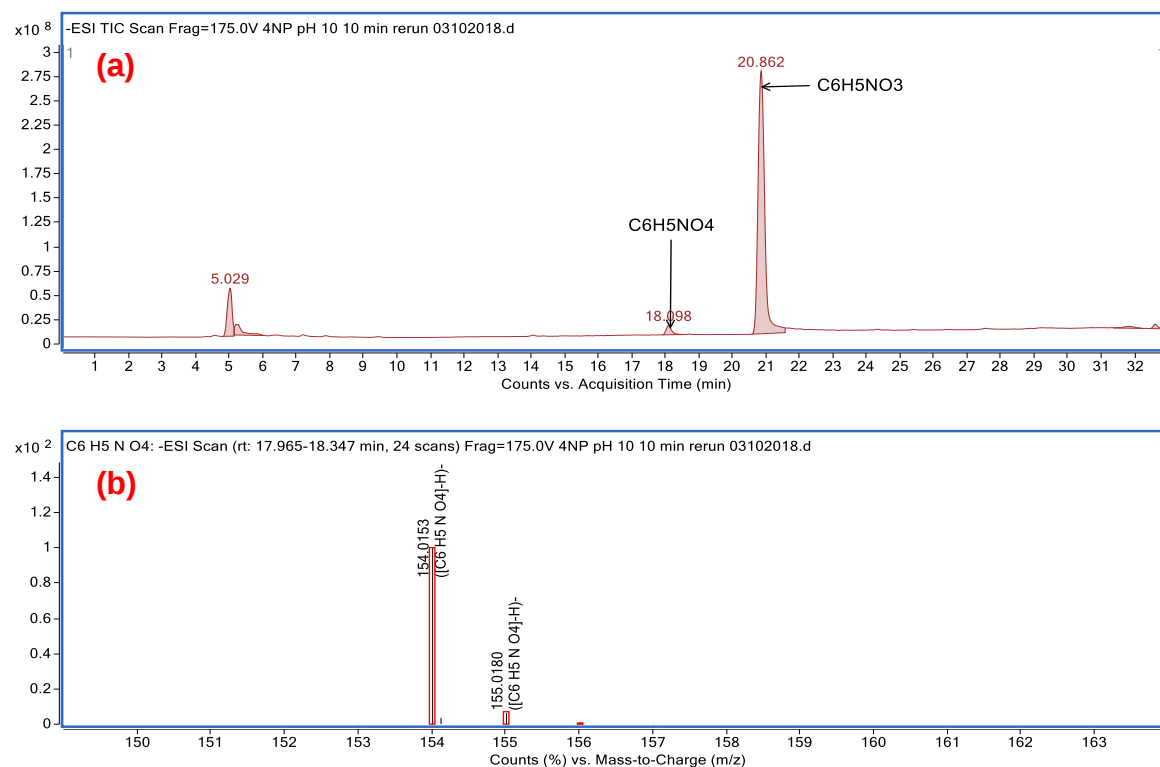


Figure 4.42: The EIC chromatogram (a) and confirmation mass spectrum (b) of 4-nitrocatechol for pH 10 initial 4NP solution

The intermediate $C_6H_4N_2O_5$; 184.0217, RT= 22.82 min (MS: Appendix 7.Q) was identified at 20 min and other samples drawn after it for only the initial pH 10 solution. Its presence in the initial alkaline 4CP solution alone suggests that its formation was favoured by such conditions. This novel intermediate seems absent from numerous literature searches involving ozone-based degradation, however, Carlos et al. (2008) identified it as a possible intermediate in the degradation of nitrobenzene. The formation of the $C_6H_4N_2O_5$ compound may be due to the attack of a pristine 4NP by a NO_2^* in solution which probably cleaved from another 4NP that has been degraded or converted to an intermediate bereft of the $-NO_2$ group. Two possible isomers were identified from ChemSpider search. The *ortho*-intermediate 2,4-dinitrophenol (Figure 4.43a) was chosen as the main isomer that was identified in the EIC spectrum, while the *meta*-intermediate 3,4-dinitrophenol (Figure 4.43b) represents the isomer observed in the QAW data at 30 min with a retention time of 20.607.

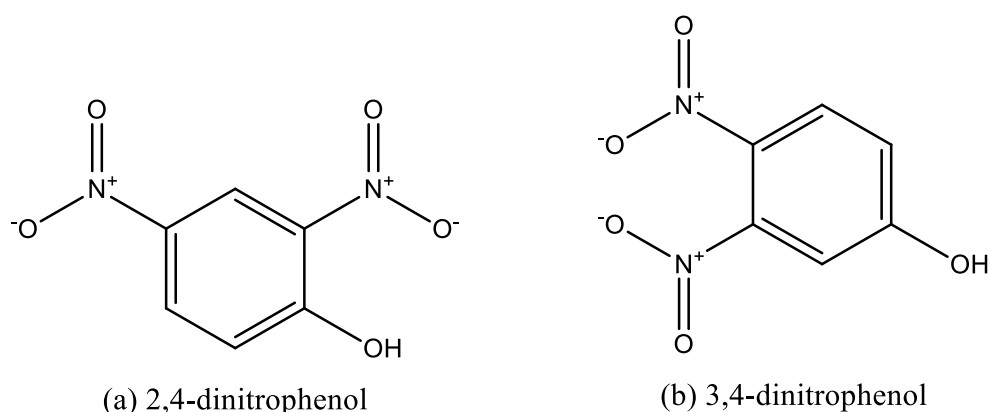


Figure 4.43: Chemical structure of (a) 2,4-dinitrophenol and (b) 3, 4-dinitrophenol

Another compound $C_6H_5NO_5$; 171.0172, RT= 14.47 min (MS: Appendix 7.V) was observed for the initial alkaline solution from 30 min. The intermediate is a further hydroxylation product after the formation of 4-nitrocatechol. As may be expected, two isomers were observed for the intermediate with only one visibly identified in the TIC spectrum while the other one was present in the compound list generated from the QAW. The intermediates have been previously reported by Xiong et al. (2015) in their investigation involving the degradation of 4NP using advanced Fenton process followed by analysis with LC-MS/MS instrumentation. They identified the main isomer as *p*-nitropyrogallol or rather 4-nitro-1,2,6-benzenetriol (Figure 4.44a), while 4-nitropyrogallol or 4-nitro-1,2,3-benzenetriol (Figure 4.44b) was assigned the minor isomer. The intermediate $C_6H_5O_3$; 125.0239 (MS: Appendix 7.W) was identified at a retention time of 19.04 min for the initial alkaline solution alone after 30 min. From literature search, Meijide et al. (2017) highlighted the compound as a possible intermediate in their proposed pathway for the degradation of 4NP by the electro-Fenton process followed by identification using GC-MS and ion-exclusion instrumentation. The intermediate is a likely product from the denitration of intermediates 4-nitro-1,2,6-benzenetriol and 4-nitro-1,2,3-benzenetriol, followed by oxidation to yield 2,6-dihydroxycyclohexa-2,5-dienone (Figure 4.44c) and 2,3-dihydroxycyclohexa-2,5-dienone (Figure 4.44d), respectively.

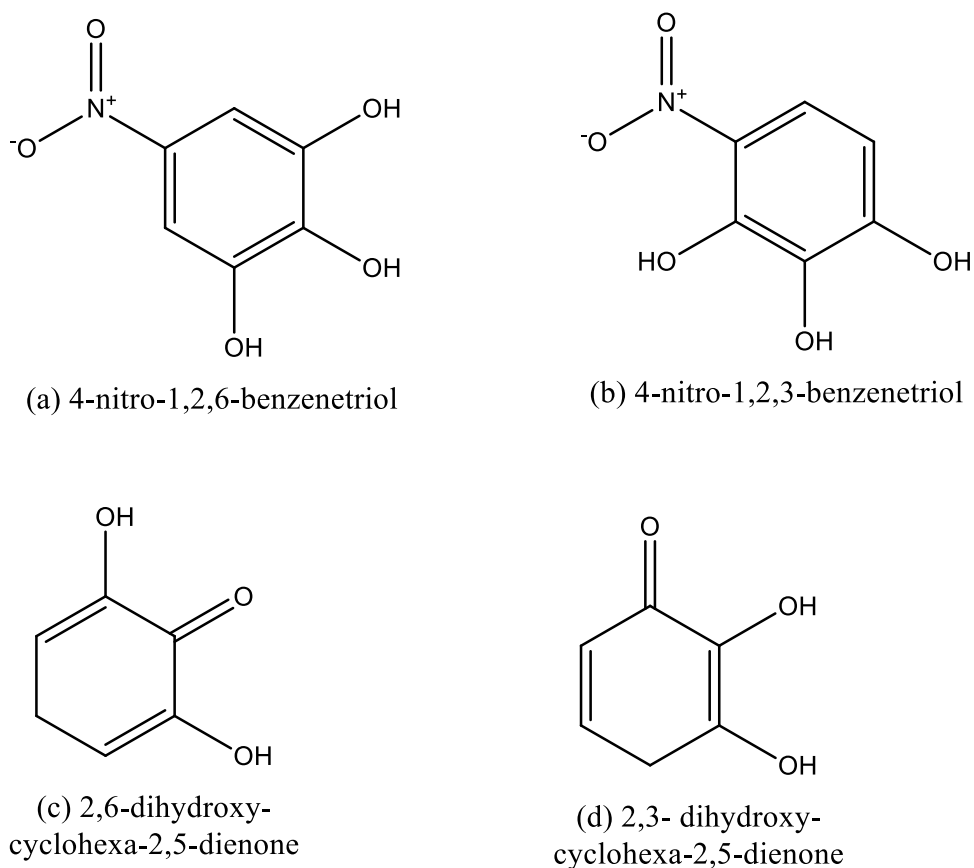


Figure 4.44: Chemical structure of (a) 4-nitro-1,2,6-benzenetriol, (b) 4-nitro-1,2,3-benzenetriol, (c) 2,6-dihydroxycyclohexa-2,5-dienone and (d) 2,3-dihydroxycyclohexa-2,5-dienone

The compound $C_6H_6O_2$; 110.0361 was found in the pH 10 analyte solutions only for the samples drawn at 20 min and 30 min. However, unlike in the case of 4CP, only one isomer was identified which could be either hydroquinone or catechol. The retention time observed for the intermediate was more aligned to the retention time of 13.35 min obtained for the pure catechol analyte as against 8.93 min obtained for hydroquinone. There is the possibility that the degradation of 4NP in this investigation did not go through the hydroquinone route.

Also, the dimer product ($C_{12}H_8N_2O_6$) of 4NP was generated as part of the mined compounds. Its absence in the TIC or EIC spectra, however, connotes that the concentration may be very low. The $C_{12}H_8N_2O_6$; 276.0337 with a retention time of 26.91 min was assigned the structure in Figure 4.45 based on the reasons adduced for the 4CP analogous dimer product. Also, a further hydroxylation product $C_{12}H_8N_2O_7$; 292.0333, RT= 24.95 min was identified in the generated data for all the pH 10 samples only.

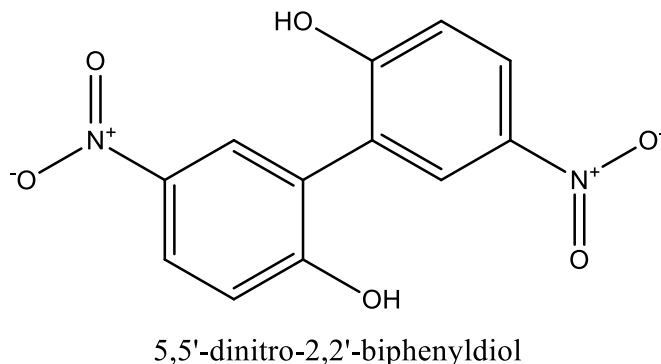


Figure 4.45: Chemical structure of 5,5'-dinitro-2,2'-biphenyldiol

As observed for 4CP, a plethora of C3, C4, C5 and C6 intermediates were identified for the 4NP analyte during the ozonation process. Many of the breakdown products are the same for both analytes and their mechanism of formation possibly followed the same route. The summary of these compounds as observed for 4NP is presented in Figure 4.46, and the proposed degradation pathway is presented in Figure 4.47. Comparatively, the oxidation of 4CP and 4NP occurs via the 4-chloro- and 4-nitrocatechol degradation route via the *ortho*-hydroxylation reaction. The formation of coupling compounds occurs in both cases, favoured by alkaline conditions. However, hydroquinone identified as a transient intermediate for 4CP was not detected throughout the 4NP ozonation period, but rather the 2,4-dinitrophenol intermediate was observed leading to the formation of more nitro-aliphatic carboxylic compounds as compared to 4CP. The observed difference in some of the intermediates and degradation pathways despite both substituents being electron-withdrawing groups may be due to the effect of their activity on the benzene ring-independent of the main hydroxyl substituent. Typically, the chloro-group has a positive activating potential on the benzene ring, while the nitro-group deactivates the ring. The much higher electron-withdrawing power of the nitro-group coupled with its deactivation potential makes it less reactive towards electrophilic attack (Politzer et al., 1984).

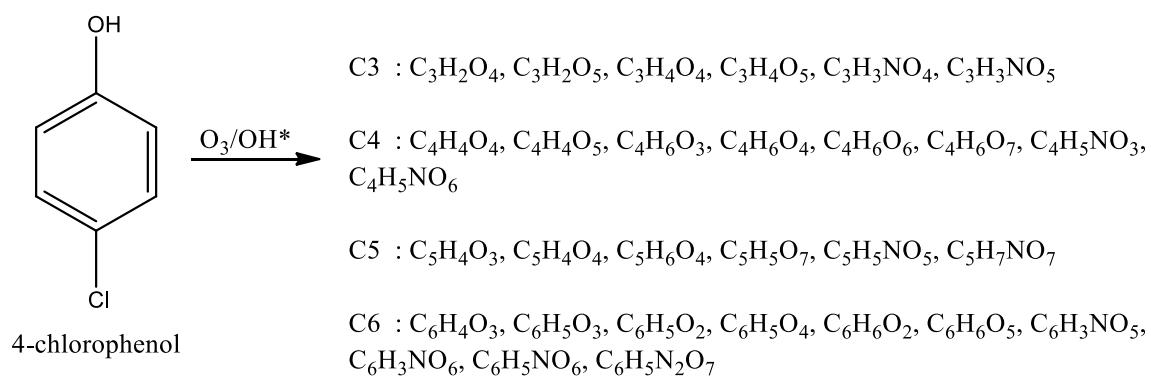


Figure 4.46: Residual intermediates of 4-nitrophenol degradation

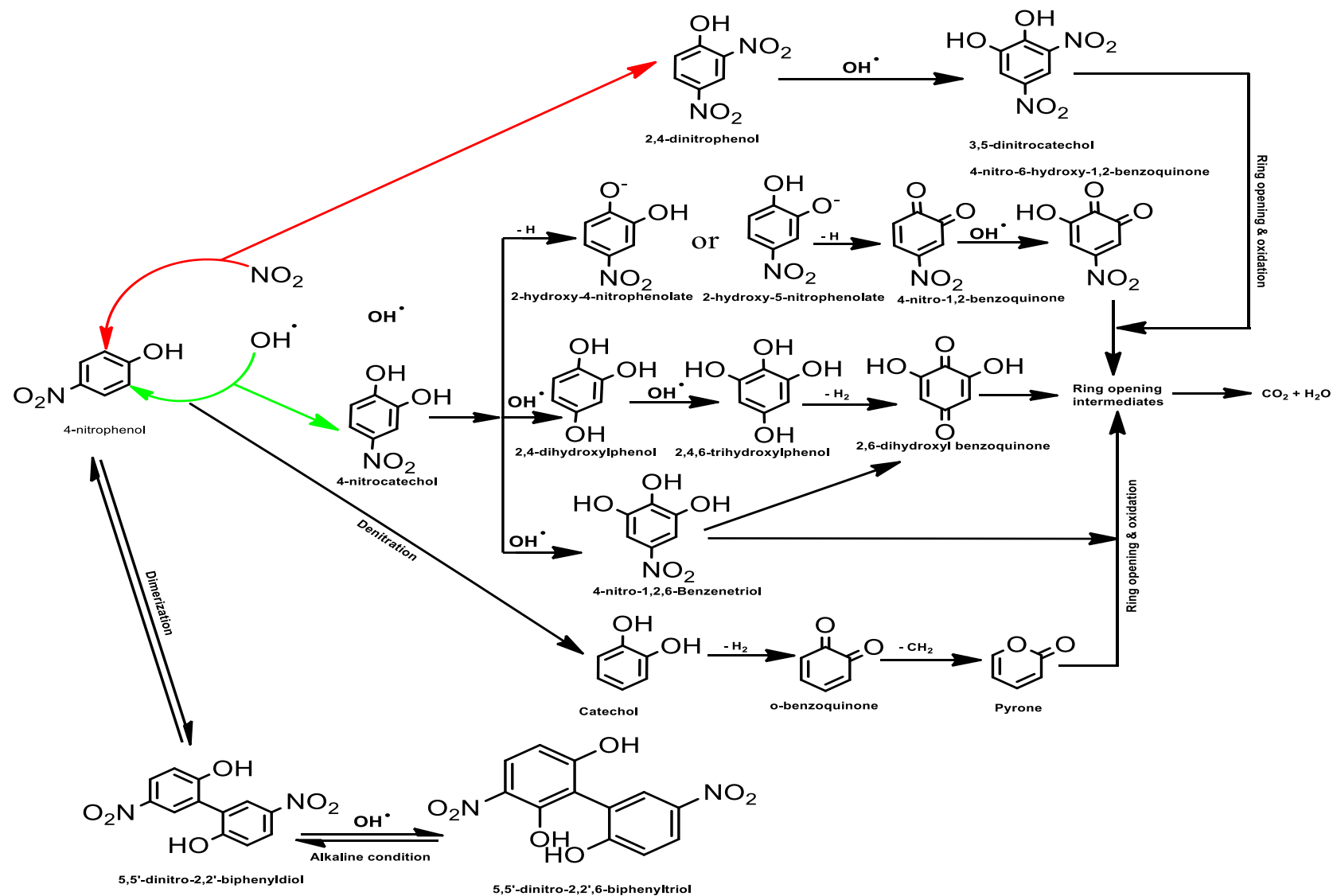


Figure 4.47: Proposed degradation pathways for 4-nitrophenol based on this study

4.5 Regeneration and reuse studies

The economic cost of any treatment method determines to a large extent its scale of application and sustainability. The ability to use polymeric nanocomposites over several application cycles without a drastic decline in their efficiencies may lead to a viable alternative treatment option. In this study, the β -FeOOH/polyamide composites were used over six cycles without a significant decline in its degradation ability. Complete degradation (100%) was obtained after 60 min when the pristine composite was applied for the degradation of 2×10^{-3} M 4CP via the catalytic ozonation process (Figure 4.48). Subsequent reuse after the regeneration cycle gave 99.73% efficiency for the 6th reuse. The regeneration process contributed to the reactivation of the active sites possibly due to weak interacting bonds (physisorption) which existed between the β -FeOOH/PA and the contaminant or its degradation products. These superficial bonds were easily broken by the action of the hot water and the active sites regenerated.

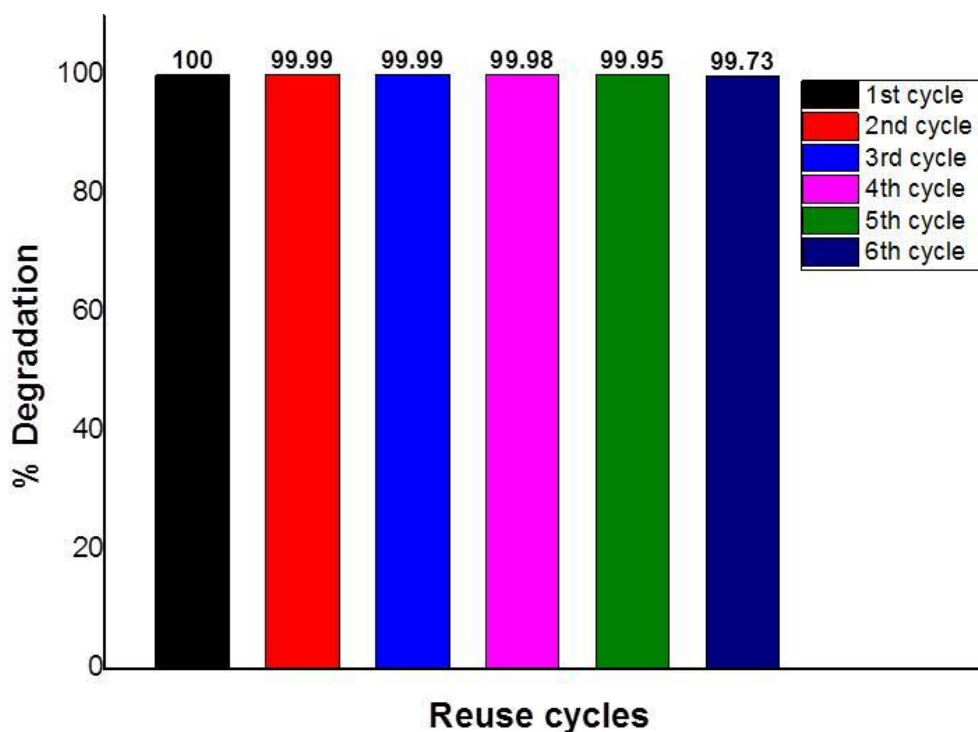


Figure 4.48: Regeneration and reuse cycles of 1.25 wt% β -FeOOH/polyamide utilized for the degradation of 2×10^{-3} M 4CP after 60 minutes

4.6 Leaching studies

A core objective of this research was to address the challenge of reductive dissolution of the β -FeOOH as reported by Oputu et al. (2015b). The polyamide matrix provided adequate support for the β -FeOOH nanoparticles and the leaching of iron eliminated. The *in situ* preparation route for the polymeric nanocomposite might have provided a well-blended composite with the nanoparticles embedded into the polyamide matrix with little chances of leaching. Generally, *in situ* methods provides a uniform dispersion of nanoparticles in polymer matrices through enhanced interpenetrative networks leading to higher compatibility between the constituents, and stronger interfacial interactions (Kango et al., 2013). Iron leaching was not observed for nanocomposites rinsed prior to usage, and those regenerated for reuse over six cycles. However, minimal Fe level of 0.2296 and 0.0476 (Figure 4.49) were obtained at pH 3 and 7 when the β -FeOOH/polyamide composites were utilized without prior rinsing (with Milli-Q) before use. This suggested the presence of a few superficial β -FeOOH nanoparticles exposed after the composite post-polymerization size grading. As required for other water treatment materials such as activated carbon and ion exchange resins, the polymeric nanocomposites need to be rinsed before usage. Additionally, the trend in the iron levels obtained for the 'un-rinsed' nanocomposites is consistent with the report of more reductive dissolution and Fe leaching at acidic pH (Oputu et al., 2015b).

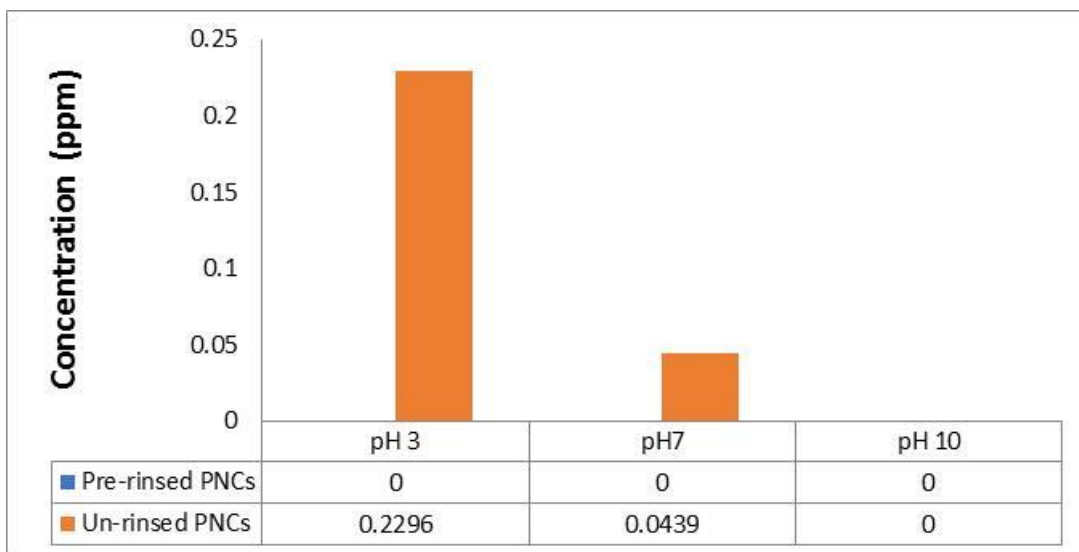


Figure 4.49: Fe levels for the pre-rinsed and un-rinsed PNCs at different pH conditions

4.7 Remediation of organics in real wastewater

The 1.25 wt% polymeric nanocomposite was used for the remediation of real wastewaters. Experiments were conducted to ascertain the potential of the β -FeOOH/polyamide composite for the degradation of organics in real wastewater. Onsite measurement of physicochemical parameters of the influent and effluent samples from the Stellenbosch WWTP Western Cape, South Africa is presented in Table 4.4. Influent samples were treated with ozone alone, and ozone in combination with the synthesized PNC.

The COD and TOC values of the influent sample (wastewater) determined in the laboratory were 628 mg L^{-1} and 102 mg L^{-1} , respectively. The catalytic ozonation process effectively reduced the COD and TOC values of the water to 285 mg L^{-1} (54.62% removal) and 11 mg L^{-1} (89.22% removal), respectively after 60 min. Corresponding values were 415 mg L^{-1} (33.92 % removal) and 54 mg L^{-1} (47.06% removal) when only ozone was used (Figures 4.50 and 4.51). The higher removal efficiency obtained from the catalysed ozonation process highlighted the potential of the β -FeOOH/polyamide composite for its application for wastewater remediation.

Table 4.4: Onsite influent and effluent water quality parameters (mean $\pm$ SD; n=3)

Parameters	Influent	Effluent
pH	7.40 $\pm$ 0.28	7.12 $\pm$ 0.33
DO (mg L^{-1})	1.53 $\pm$ 0.12	2.20 $\pm$ 0.22
Temperature ($^{\circ}\text{C}$)	22.50 $\pm$ 1.08	22.83 $\pm$ 0.90
Conductivity (μs)	1103 $\pm$ 42.10	621 $\pm$ 10.87
ORP (mV)	-254 $\pm$ 31.32	230 $\pm$ 7.59

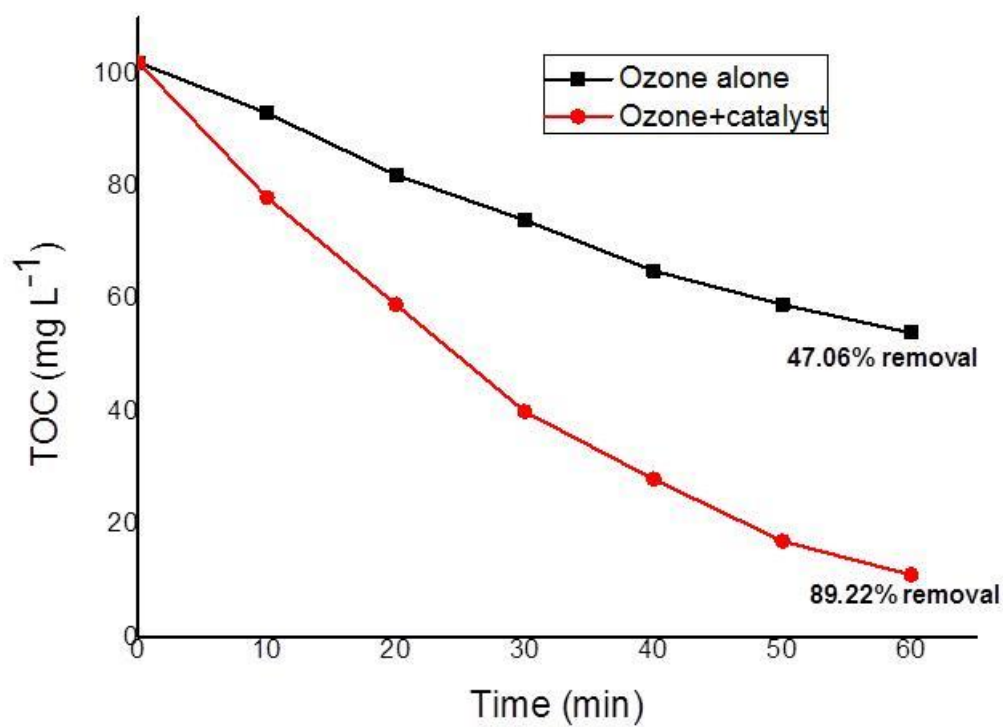


Figure 4.50: TOC removal from wastewater using ozonation and catalytic ozonation

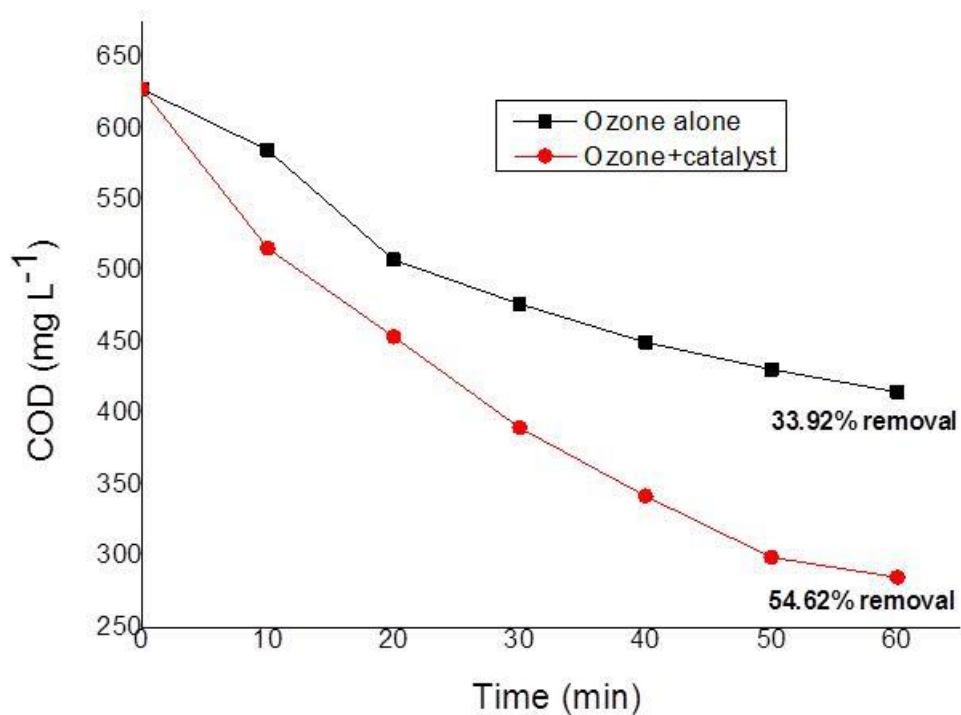


Figure 4.51: COD removal from wastewater using ozonation and catalytic ozonation

4.8 Toxicity assay results

Toxicity assays are highly sensitive analytical tools to assess the environmental implications of pollutants and prove complementary to chemical assays in assessing water quality (Valitalo et al. 2017; Hernando et al. 2005). Toxicity data in literature often suggest that most wastewater treatment processes might not effectively eliminate the toxicological effect patterns or compositions of wastewaters (Valitalo et al. 2017; Zhang et al. 2013). The results of *Daphnia* acute toxicity testing are presented in Table 4.5. The results obtained using the probit analysis shows a general increase in the effective concentration values, from LC_{10} to LC_{50} for both the 24 h and 48 h exposures, except in few instances where no data was returned for the analysis.

LOEC and NOEC are key indicators for accessing water quality (Green et al., 2013). The toxicity detection capacity in terms of the LOEC and NOEC gave a clear picture of the quality of the various water samples analysed. The 4CP contaminated water produced the most toxic effect against the test organisms with LOEC and NOEC values of > 6.250 and ≥ 6.250 percentile for 24 h and 48 h, respectively. From the chemical analysis, 4CP was completely degraded at 1 h of the catalysed ozonation process and the degradation led to a reduction of the solution pH to ≈ 3 due to the breakdown of the analyte to carboxylic acid intermediates. Hence, the treated water at 1 h without pH adjustment was toxic to *D. magna* due to the acidic nature of the solution. The LOEC and NOEC values were both 6.250. Comparatively, the treated water at 1 h with adjusted pH (≈ 7) reduced mortality of the daphnids the exposure period with the LOEC values of 50% and 12.5% observed for 24 h and 48 h exposures. The NOEC values were 100% and 25% for 24 h and 48 h, respectively.

Extension of the catalytic ozonation period for treatment efficiency comparison purposes was carried out at 1.5 h, 2 h and 3 h, respectively. The LOEC and NOEC values at 1.5 h were $> 100\%$ and $\geq 100\%$ for 24 and 48 h, respectively, indicating better water quality than the treatment carried out for 1 h. Conversely, the 2 h treatment period produced a decline in water quality. The LOEC value for the water sample was 100 and 25 percentiles for 24 h and 48 h, with NOEC values of 50 and 12.5 for 24 h and 48 h, respectively. Also, at the 3 h treatment duration, the LOEC further reduced to 25 and 12.5, while the NOEC was 12.5 and 6.250 for 24 h and 48 h, respectively. The indicative decline in the water quality after 1.5 h is suggestively through the presence of excess ozone in the solution. Dehghani et al. (2016) gave this assertion in a similar nanocatalysed process where increased toxicity was

observed with time. The excessive hydrogen peroxide in solution at the extended time intervals was the adduced reason for the trend. The presence of excess ozone in water systems is a potential risk to aquatic organism, especially the microorganisms (Gonçalves and Gagnon, 2011). Graphical representations of the immobilization of the *D. magna* for the different dilution percentile at 24 h and 48 h are given in Figures 4.52 and 4.53. The acute immobilization analysis supports the trend discussed above for LOEC and NOEC. Also, the cumulative immobility data are shown for 24 h and 48 h in Figure 4.54 and Figure 4.55 equally gave corresponding results. The results confirmed the presence of toxic intermediates despite the complete degradation of the 4CP in the 1 h treated samples. After the complete degradation of the parent analyte, the treatment period should be extended for complete removal of intermediates formed. Toxicity assays are therefore important complementary tools with chemical analyses of water and wastewaters.

Table 4.5: Toxicity results for 4CP contaminated water and treated wastewater samples using *D. magna*

Water samples	Assay duration	LC ₁₀	LC ₂₀	LC ₅₀	NOEC	LOEC
Treated wastewater at 1 h (pH = 7)	24 h	10.733	48.293	ND	100.0	50.0
	48 h	7.055	17.674	102.409	25.0	12.5
Treated wastewater at 1 h (unadjusted pH)	24 h	9.530	10.034	11.072	12.500	6.250
	48 h	8.206	8.425	8.861	12.500	6.250
Treated wastewater at 1.5 h (pH = 7)	24 h	ND	ND	ND	≥ 100.0	> 100.0
	48 h	37.387	ND	ND	≥ 100.0	> 100.0
Treated wastewater at 2 h (pH = 7)	24 h	22.999	40.367	118.417	50.0	100.0
	48 h	8.334	14.852	44.860	12.5	25.0
Treated wastewater at 3 h (pH = 7)	24 h	8.811	19.839	93.720	12.5	25.0
	48 h	ND	3.749	24.273	6.250	12.5
4CP contaminated water (0.002 M)	24 h	4.319	4.633	5.298	< 6.250	≤ 6.250
	48 h	3.561	3.875	4.556	< 6.250	≤ 6.250

LOEC: Lowest observed effect concentration; NOEC: No observed effect concentration; LC: Effective concentration for xx% reduction; 95%-CL: 95% Confidence limits; ND: not determined due to mathematical reasons or inappropriate data

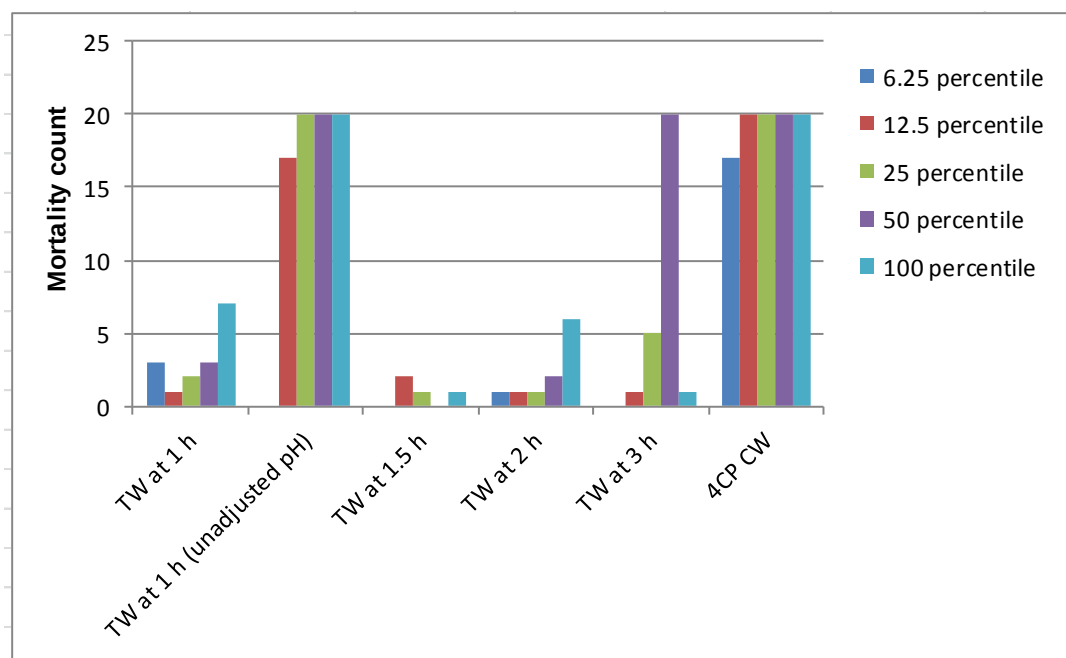


Figure 4.52: Mortality of *D. magna* for 4CP contaminated water and the wastewater treated at different durations for 24 h

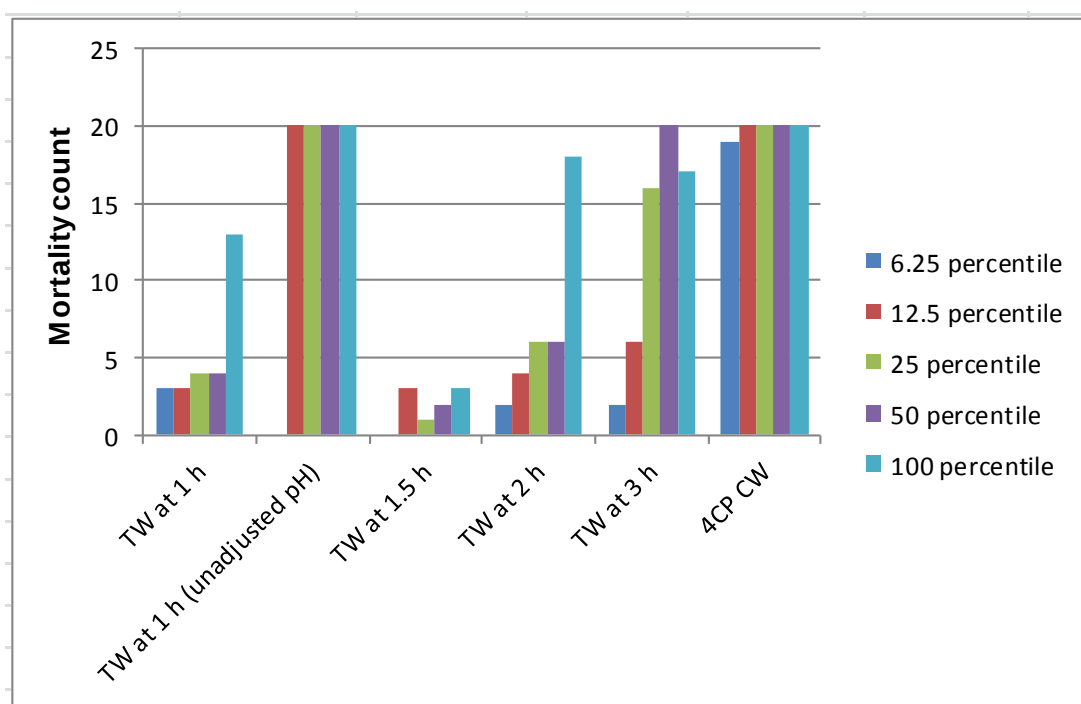


Figure 4.53: Mortality of *D. magna* for 4CP contaminated water and the wastewater treated at different durations for 48 h

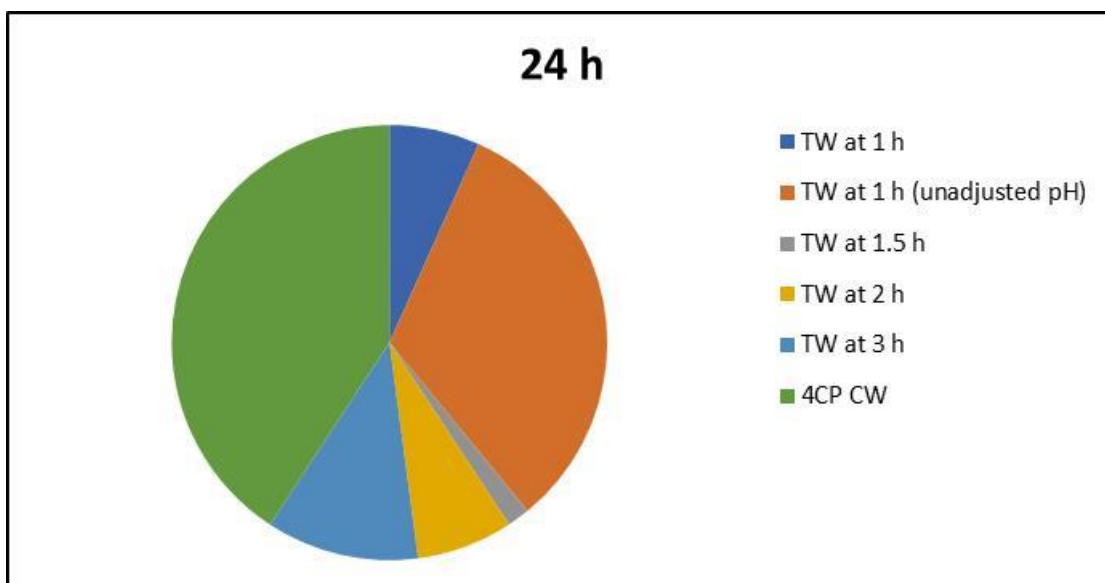


Figure 4.54: Cumulative mortality count of the *D. magna* for the different water samples at 24 h

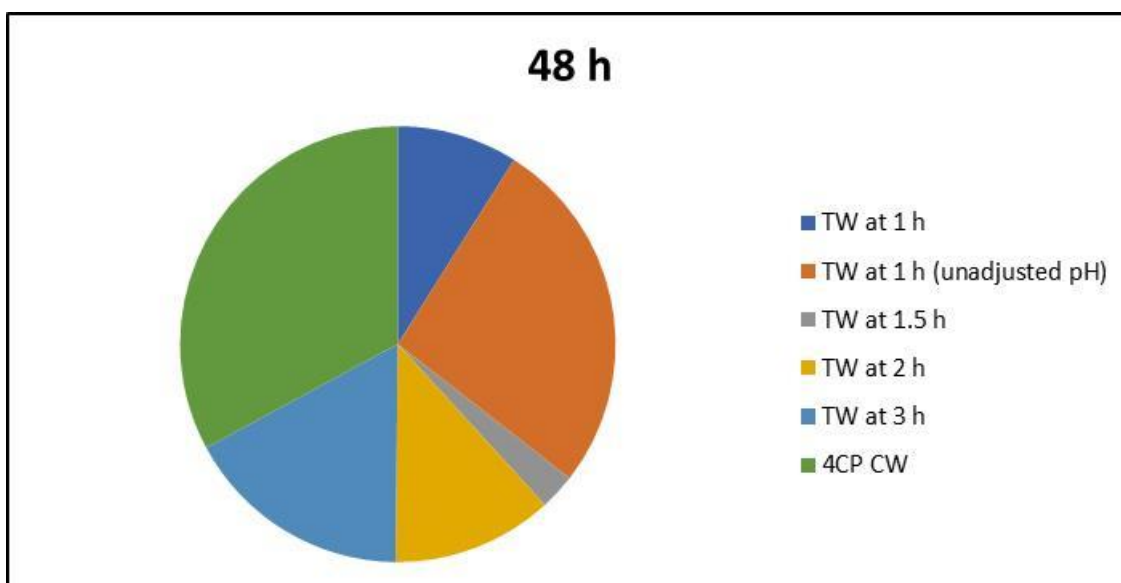


Figure 4.55: Cumulative mortality count of the *D. magna* for the different water samples at 48 h

Chapter: 5 Conclusion and recommendation**5.1 Conclusion**

This research was designed to provide knowledge on the safe application of the β -FeOOH nanoparticles by utilizing polyamide as a support material for their immobilization. The investigation affirmed that polyamide can act as good support for β -FeOOH nanoparticles. The TEM image and XRD micrographs confirmed the incorporation of the nanoparticles in the polyamide matrix.

An insight into the degradation pathways and intermediates formed by the analytes (4CP and 4NP) during ozonation were investigated. There were several pathways for the degradation of 4CP and 4NP with multiple primary intermediates at equilibrium. Generally, only one of the primary intermediate tends to be dominant. Irrespective of the primary intermediates observed, the cyclic intermediates all underwent ring-opening and were degraded to aliphatic carboxylic acids prior to final mineralization into water and carbon dioxide. Comparatively, the 4CP and 4NP both followed the 4-chloro-/4-nitrocatechol and catechol degradation pathways forming several similar intermediates. Hydroquinone was identified as a transient intermediate of 4CP. Hydroxylative denitration to give hydroquinone did not occur for 4NP, rather the 2,4-dinitrophenol intermediate was observed. Hence, the aliphatic carboxylic acids and other ring-opening intermediates formed from the 4NP degradation contained more intermediates bearing the nitro-group attached to them. Dimer products were formed by both analytes under favourable pH conditions (alkaline) with the 4CP showing more versatility in this regard. The initial pH of the analytes solution played a critical role in the generation of certain intermediates. The time-based ozonation followed by LC-MS-TOF instrumentation gave insight into the ozone degradation intermediates and pathways, with some novel intermediates identified.

The β -FeOOH/polyamide nanocomposites exhibited increasing degradation capability with an increase in the nanoparticles loading. Significant increments in degradation percentages were observed in the catalytic ozonation of 4CP and 4NP in comparison to only ozonation. The polymeric nanocomposites were more effective for the removal of 4CP as compared to 4NP. This could be due to chlorine being a better “leaving group” as ascertained from the degradation intermediates study. The chloro-substitution on the phenol molecule increased the oxidation rate regardless of its electron-withdrawing character; in contrast to the nitro-substituent which follows the more logical route by slowing down the efficiencies

Catalytic ozonation was optimal at pH 10 due to the increased generation of the hydroxyl radicals responsible for the 4CP and 4NP breakdown in the solution. This was established with the observed highest degradation efficiency value, and the corresponding rate constant. The kinetic model fitted into the pseudo-first-order reaction model. The process efficiency for the remediation of real wastewater measured using COD and TOC gave excellent results. The catalytic ozonation experiments were more effective relative to ozonation only. The generation of hydroxyl radicals with a higher oxidation potential from ozone is responsible for the faster degradation of the analytes in the catalysed treatments. The involvement of hydroxyl radicals in the breakdown of the phenols/organics was confirmed by using methanol as a scavenger. Introduction of methanol into the reaction systems retarded the degradation process by its hydroxyl radical scavenging actions. Furthermore, the composite exhibited excellent reuse potential with a minimal decrease in its degradation ability over six cycles. No leaching of iron was observed for the pre-rinsed PNCs when applied in acidic, neutral and alkaline conditions.

The toxicity assay provided insight into the treated contaminated water quality. It was used to establish the optimal treatment duration for the 4CP contaminated water. At the treatment duration of 1 h when the 4CP was fully degraded as confirmed using the LCMS-TOF instrumentation, the treated water exhibited a significant level of toxicity to the daphnids. The 4CP contaminated water treated for 1.5 h had better quality. Toxic intermediates persisted in the solution even though the parent analyte was completely degraded. This is quite significant and reiterates the importance of toxicity assays as complementary tools to standard chemical analytical methods. The pH adjustment of the treated water reduced the mortality of *D. magna*.

The novel polymeric nanocomposites gave promising remediation ability and were effective for the removal of 4CP and 4NP from aqueous solutions. The hybrid composites had some operational advantages such as prevention of nanoparticles loss, ease of recovery and regeneration for reuse, and the subsequent safeguarding of our environment and the biota therein.

5.2 Recommendation

This is the first investigation on the incorporation of the β -FeOOH nanoparticles in a polymer matrix and the subsequent utilization in a catalytic ozonation process. The potential of the nanoparticles as an effective catalyst has been further reinforced in this study. The use of polymer matrices as support materials may possibly open a floodgate for its large-scale application in water treatment operations. Other polymers should be investigated for their support potential and synergistic effects on the β -FeOOH nanoparticles in order to ascertain the best-suited matrix or matrices. Although real wastewater samples were used in laboratory experiments, possible pilot medium or large-scale applications should be considered in future studies.

6.0 References

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7.0 Appendices

Appendix 7.A: Optimization results for the catalytic ozonation of 2×10^{-3} M 4CP using 1.25 wt% β -FeOOH/polyamide

Sampling Time	1.25 wt% β -FeOOH/polyamide				
	1 st run Degradation (%)	2 nd run Degradation (%)	3 rd run Degradation (%)	Average Degradation (%)	Standard Deviation
0 min	0	0	0	0	0
10 min	46.56	45.74	44.31	45.54	0.93
20 min	71.19	71.46	71.45	71.37	0.12
30 min	86.54	87.33	96.61	90.16	4.57
40 min	98	97.79	99.77	98.52	0.89

Appendix 7.B: Optimization results for the catalytic ozonation of 2×10^{-3} M 4CP using 1.0 wt% β -FeOOH/polyamide

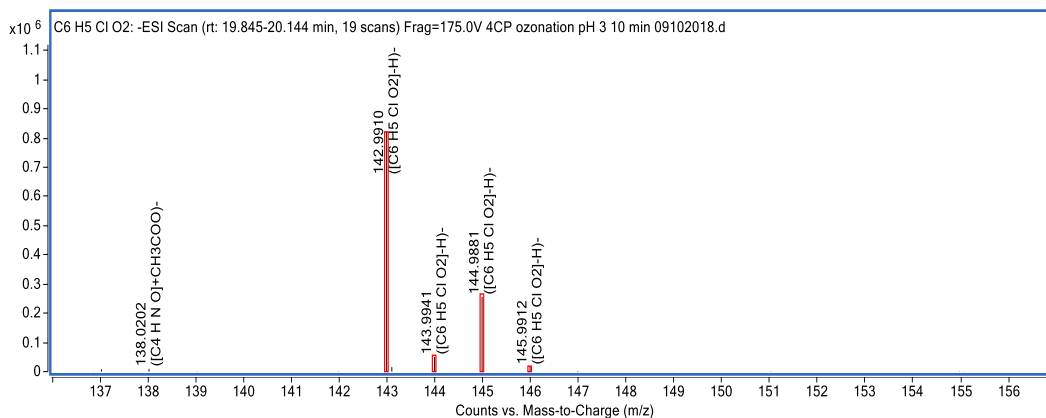
Sampling Time	1.0 wt% β -FeOOH/polyamide				
	1 st run Degradation (%)	2 nd run Degradation (%)	3 rd run Degradation (%)	Average Degradation (%)	Standard Deviation
0 min	0	0	0	0	0
10 min	44.88	42.1	43.52	43.5	1.14
20 min	69.67	67.33	68.15	68.38	0.97
30 min	85.5	84.76	86.01	85.42	0.51
40 min	94.19	93.56	94.27	94.01	0.32

Appendix 7.C: Optimization results for the catalytic ozonation of 2×10^{-3} M 4CP using 0.75 wt% β -FeOOH/polyamide

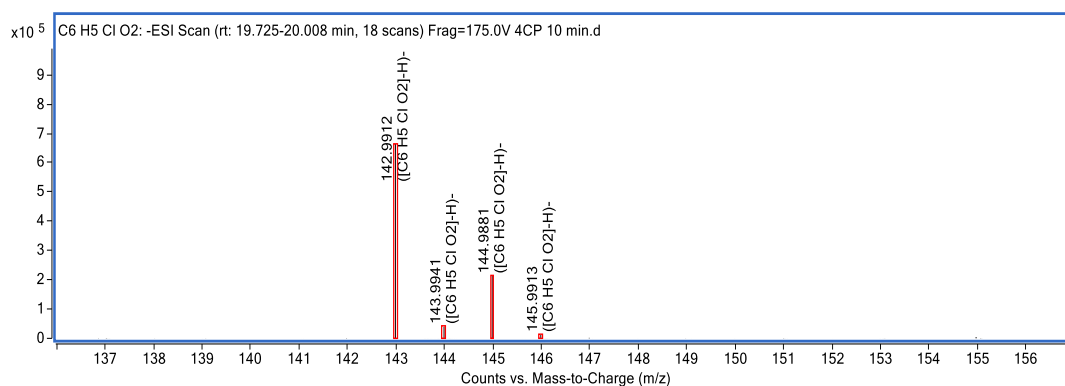
Sampling Time	0.75 wt% β -FeOOH/polyamide				
	1 st run Degradation (%)	2 nd run Degradation (%)	3 rd run Degradation (%)	Average Degradation (%)	Standard Deviation
0 min	0	0	0	0	0
10 min	37.8	36.8	36.03	36.88	0.72
20 min	66.14	65.57	64.84	65.52	0.53
30 min	82.34	82.57	83.11	82.67	0.32
40 min	91.42	90.56	91.03	91.00	0.35

Appendix 7.D: Optimization results for the catalytic ozonation of 2×10^{-3} M 4CP using 0.50 wt% β -FeOOH/polyamide

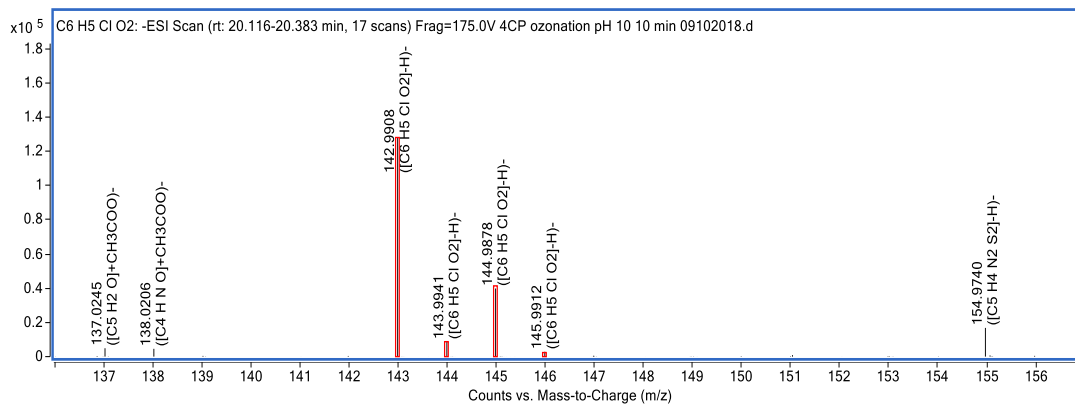
Sampling Time	0.50 wt% β -FeOOH/polyamide				
	1 st run Degradation (%)	2 nd run Degradation (%)	3 rd run Degradation (%)	Average Degradation (%)	Standard Deviation
0 min	0	0	0	0	0
10 min	36.37	34.64	35.17	35.39	0.72
20 min	62.93	62.01	61.55	62.16	0.57
30 min	81.86	80.55	79.92	80.78	0.81
40 min	91.33	90.07	88.11	89.84	1.32



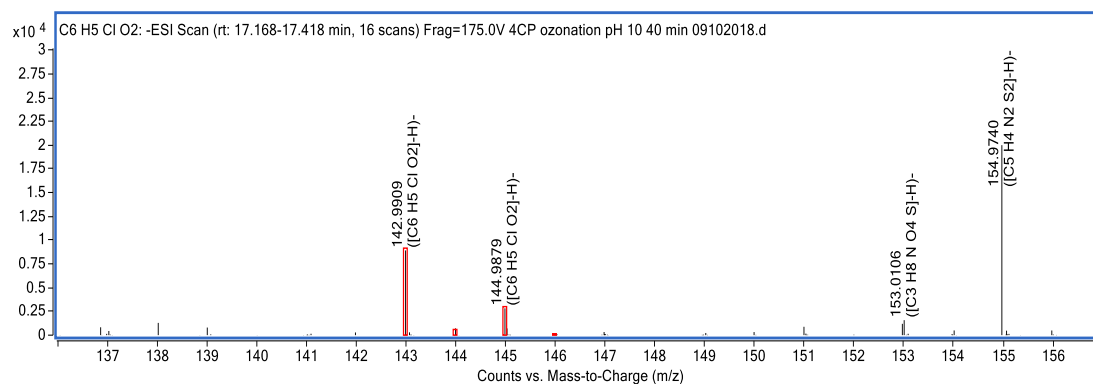
Appendix 7.E: Mass spectrum of single hydroxylation intermediate (C₆H₅ClO₂) of 4CP for pH 3 at 10 min



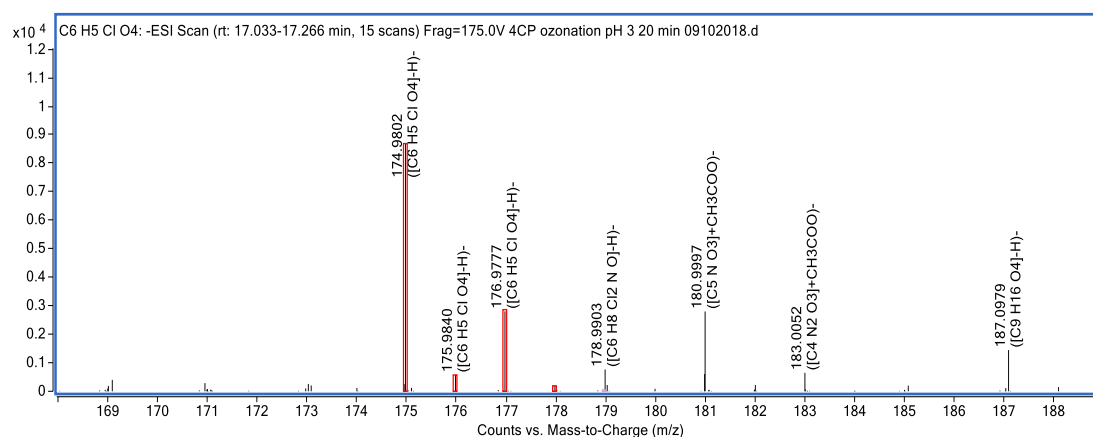
Appendix 7.F: Mass spectrum of single hydroxylation intermediate (C₆H₅ClO₂) of 4CP for pH 7 at 10 min



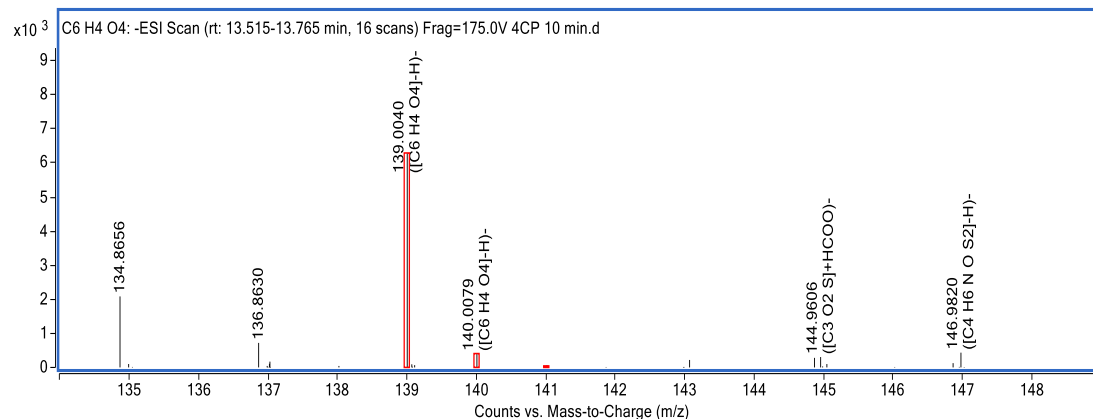
Appendix 7.G: Mass spectrum of single hydroxylation intermediate (C₆H₅ClO₂) of 4CP for pH 10 at 10 min



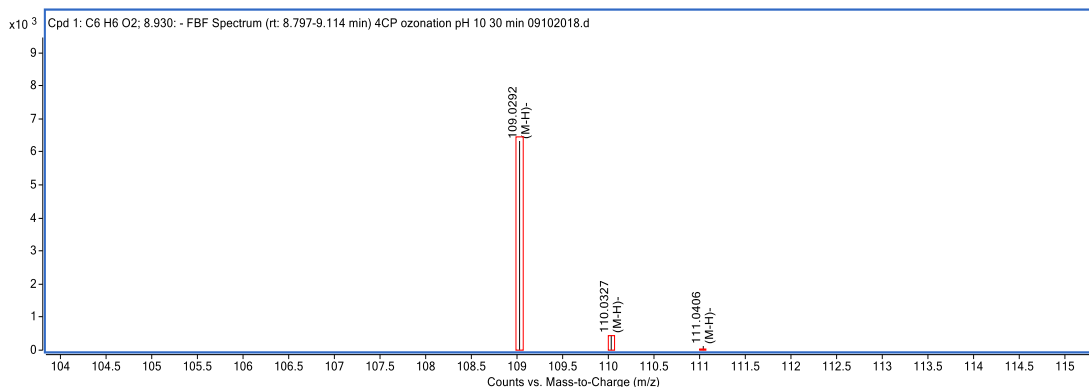
Appendix 7.H: Mass spectrum for the identified isomer of single hydroxylation intermediate ($C_6H_5ClO_2$) of 4CP for pH 10 at 40 min



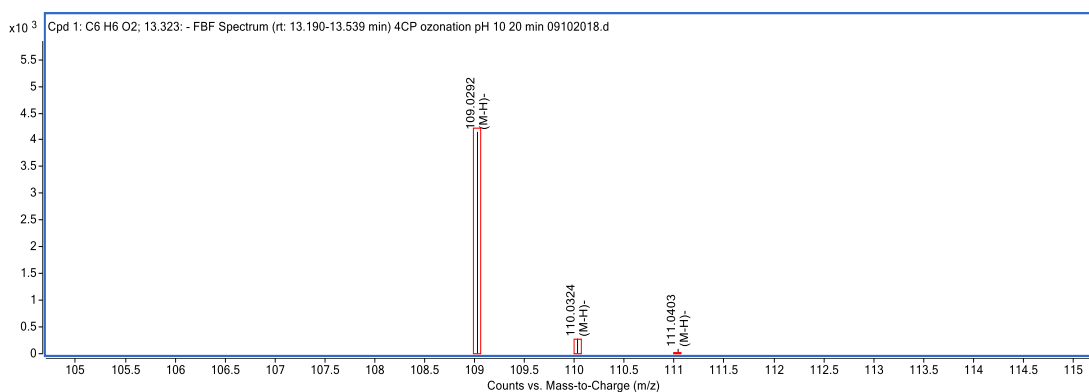
Appendix 7.I: Mass spectrum for the intermediate $C_6H_5ClO_4$ (3-chloro-trans, trans-muconic acid) of 4CP for pH 3 at 20 min



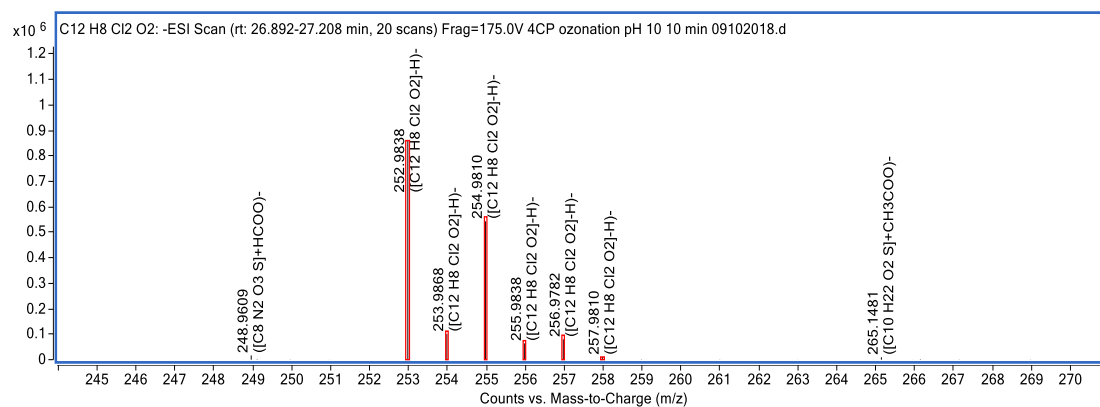
Appendix 7.J: Mass spectrum for the intermediate $C_6H_4O_4$ (2,6-dihydroxybenzoquinone) of 4CP for pH 7 at 10 min



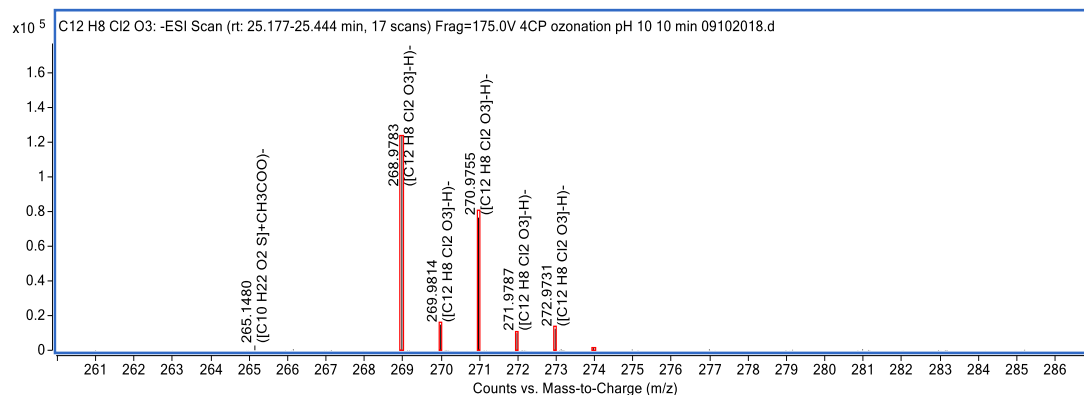
Appendix 7.K: Mass spectrum for the intermediate C₆H₆O₂ (hydroquinone) of 4CP for pH 10 at 30 min



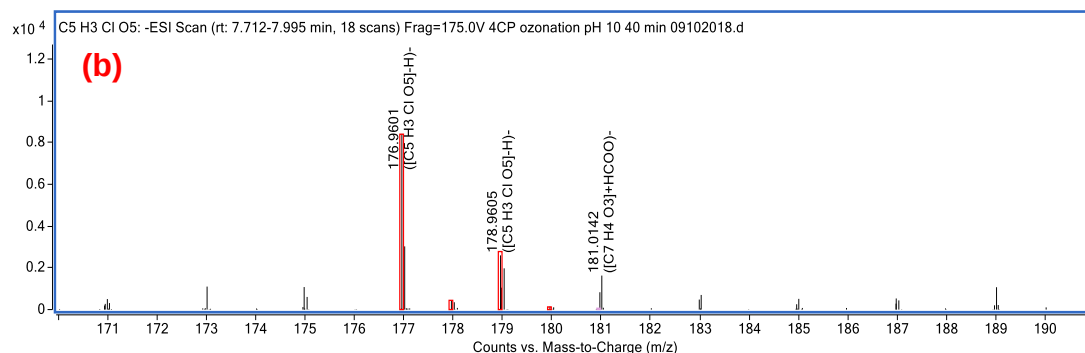
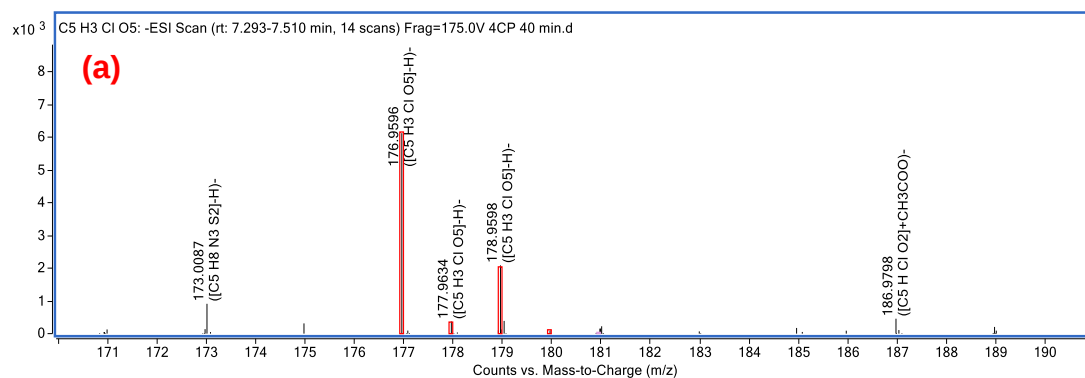
Appendix 7.L: Mass spectrum for the intermediate C₆H₆O₂ (catechol) of 4CP for pH 10 at 20 min



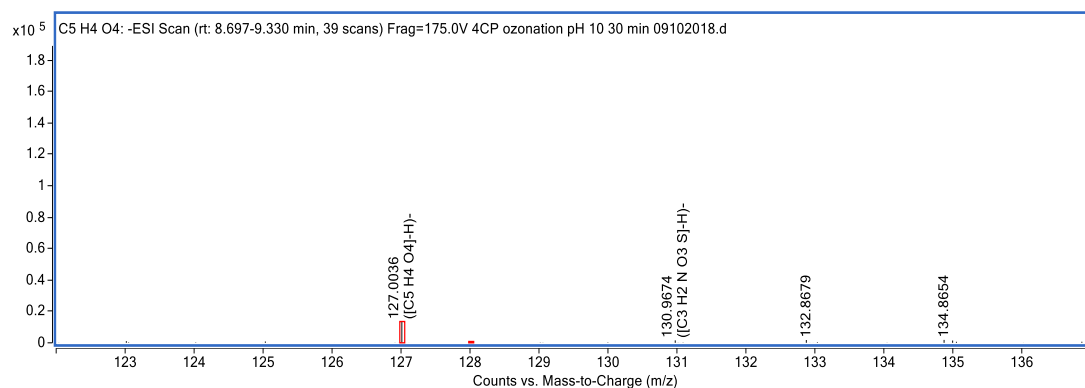
Appendix 7.M: Mass spectrum for the intermediate $C_{12}H_8Cl_2O_2$ (5,5'-dichloro-2,2'-biphenyldiol) of 4CP for pH 10 at 10 min



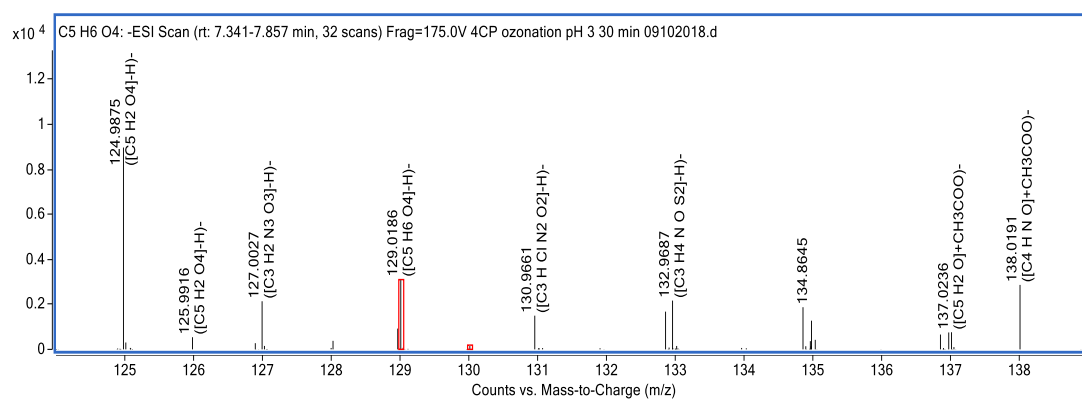
Appendix 7.N: Mass spectrum for the intermediate $C_{12}H_8Cl_2O_3$ of 4CP for pH 10 at 10 min



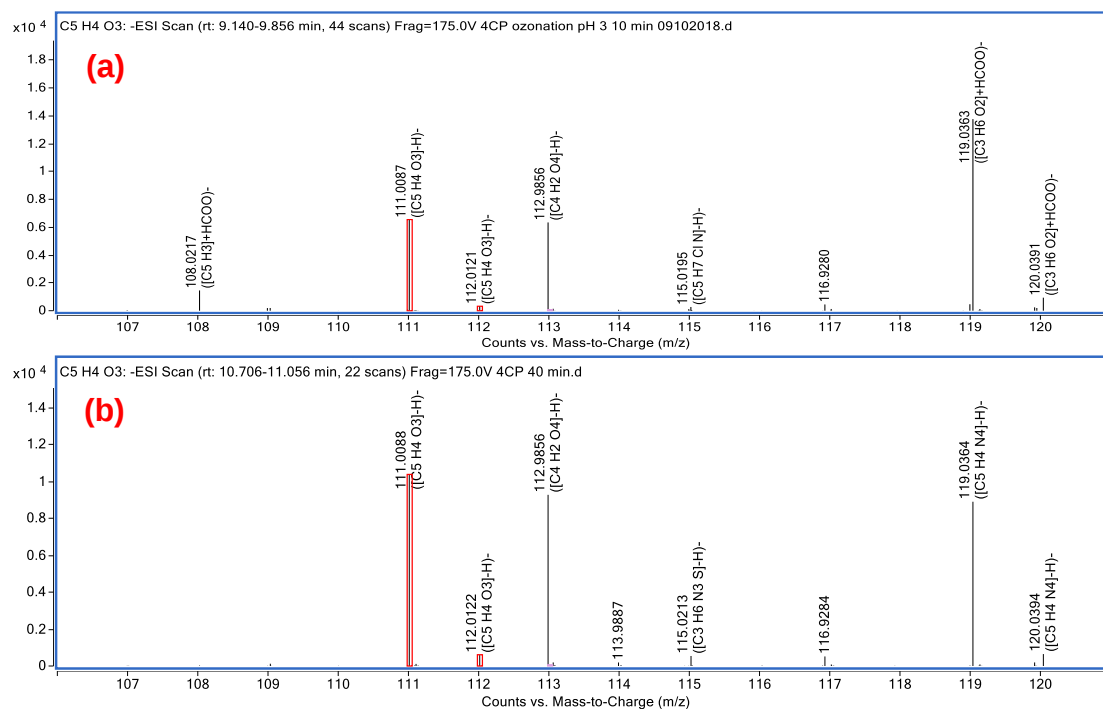
Appendix 7.O: Mass spectrum for the intermediate $C_5H_3ClO_5$ of 4CP for pH 7 (a) and pH 10 (b) at 40 min



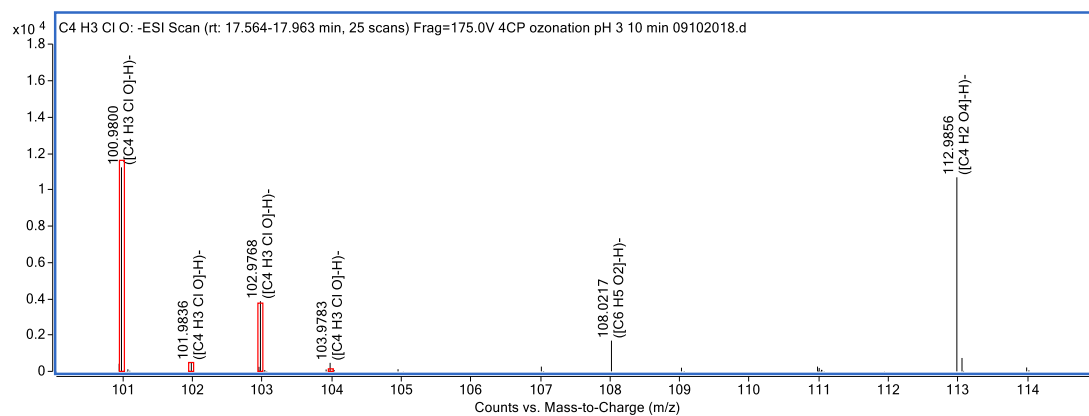
Appendix 7.P: Mass spectrum for the intermediate $C_5H_4O_4$ of 4CP for pH 7 pH 10 at 30 min



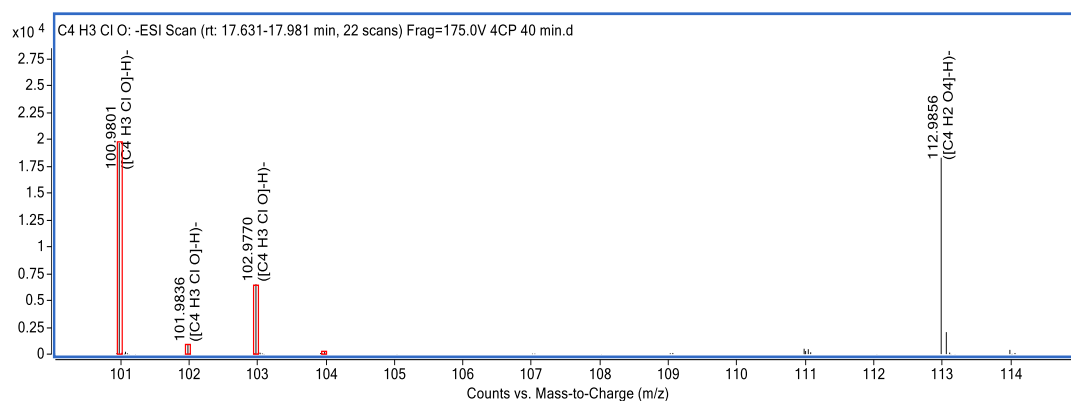
Appendix 7.Q: Mass spectrum for the intermediate C₅H₆O₄ of 4CP for pH 3 at 30 min



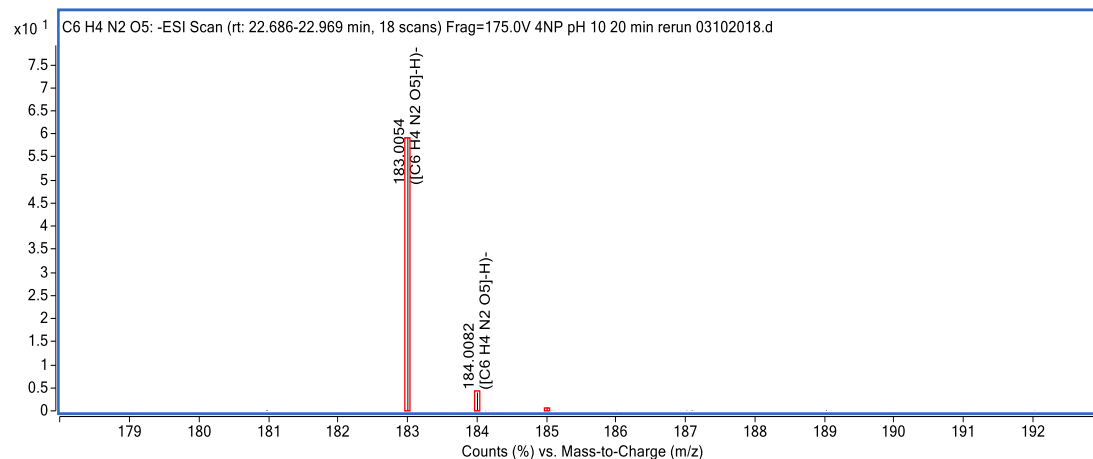
Appendix 7.R: Mass spectrum for the intermediate C₅H₄O₃ of 4CP for pH 3 at 10 min (a) and pH 7 at 40 min (b)



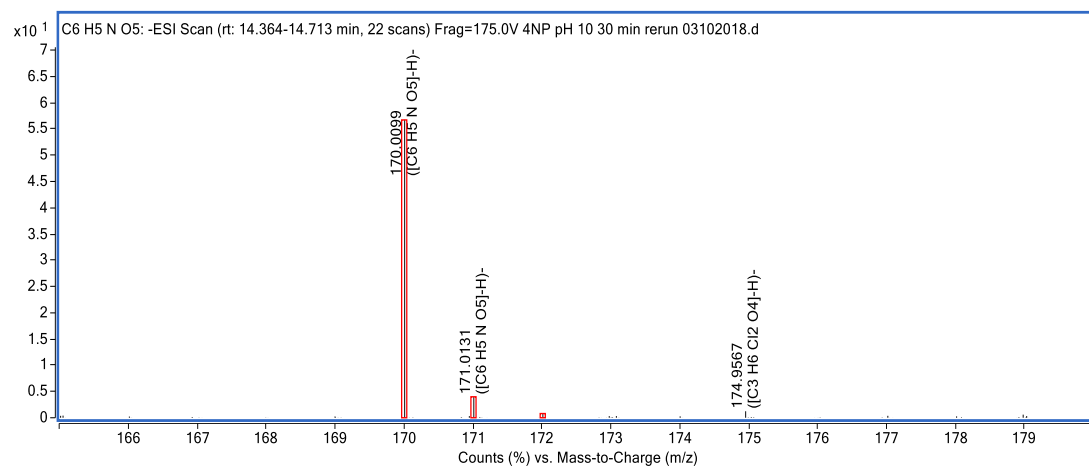
Appendix 7.S: Mass spectrum for the intermediate C₄H₃ClO of 4CP for pH 3 at 10 min



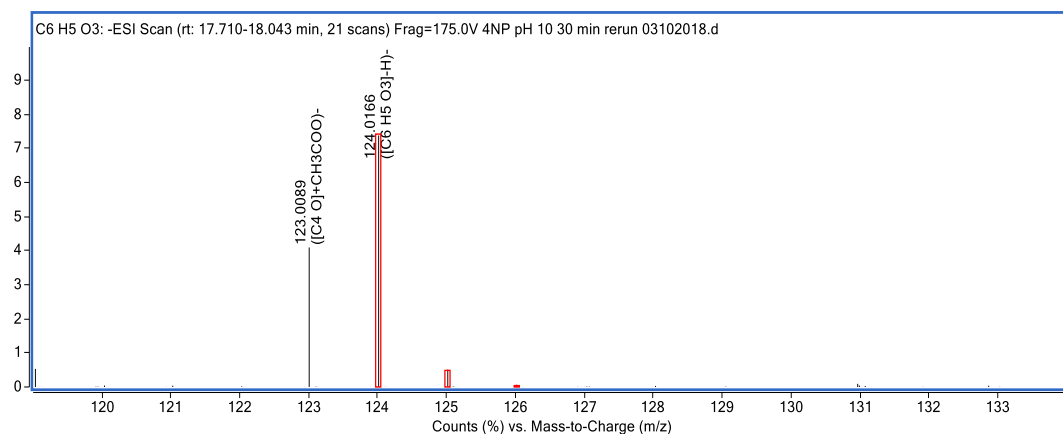
Appendix 7.T: Mass spectrum for the intermediate C₄H₃ClO of 4CP for pH 7 at 40 min



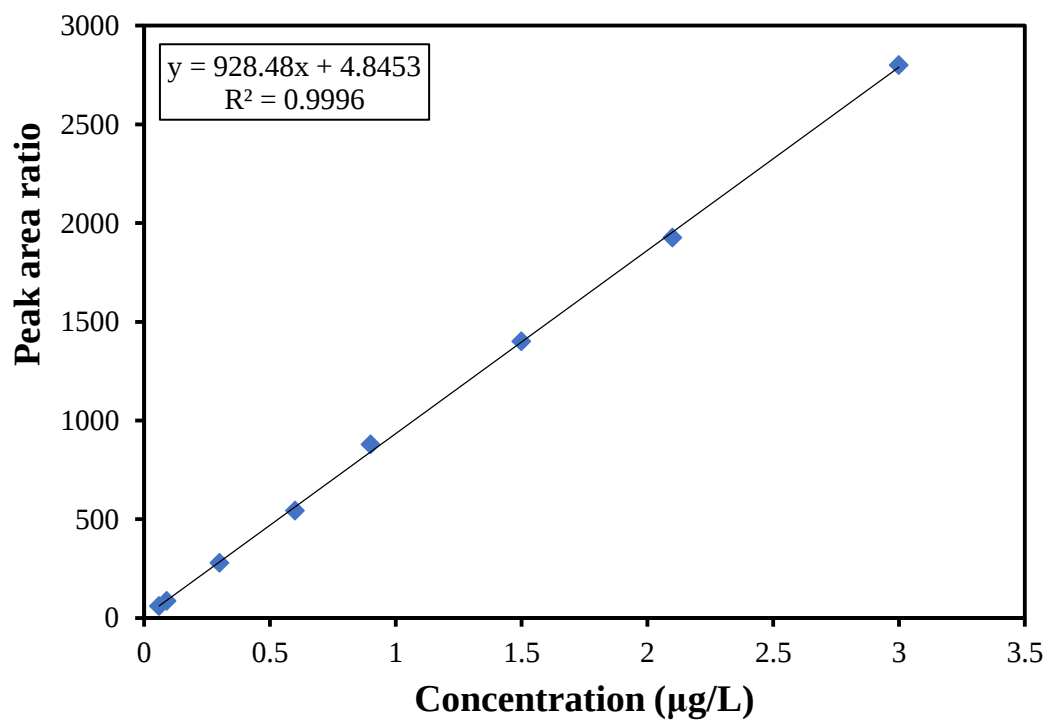
Appendix 7.U: Mass spectrum for the intermediate C₆H₄N₂O₅ of 4NP for pH 10 at 20 min



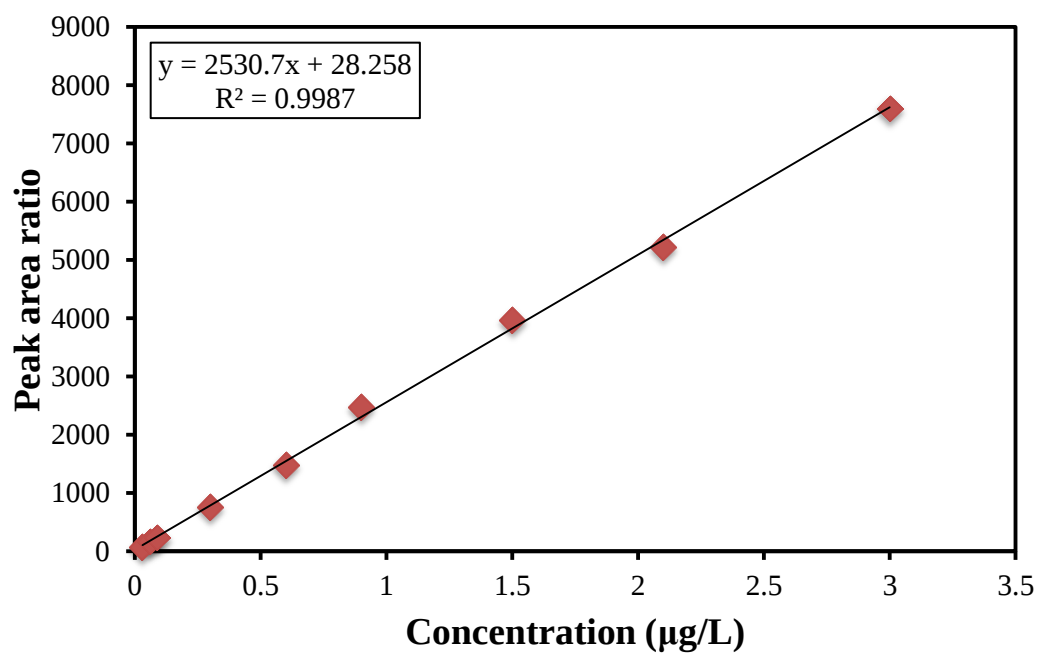
Appendix 7.V: Mass spectrum for the intermediate $C_6H_5NO_5$ of 4NP for pH 10 at 30 min



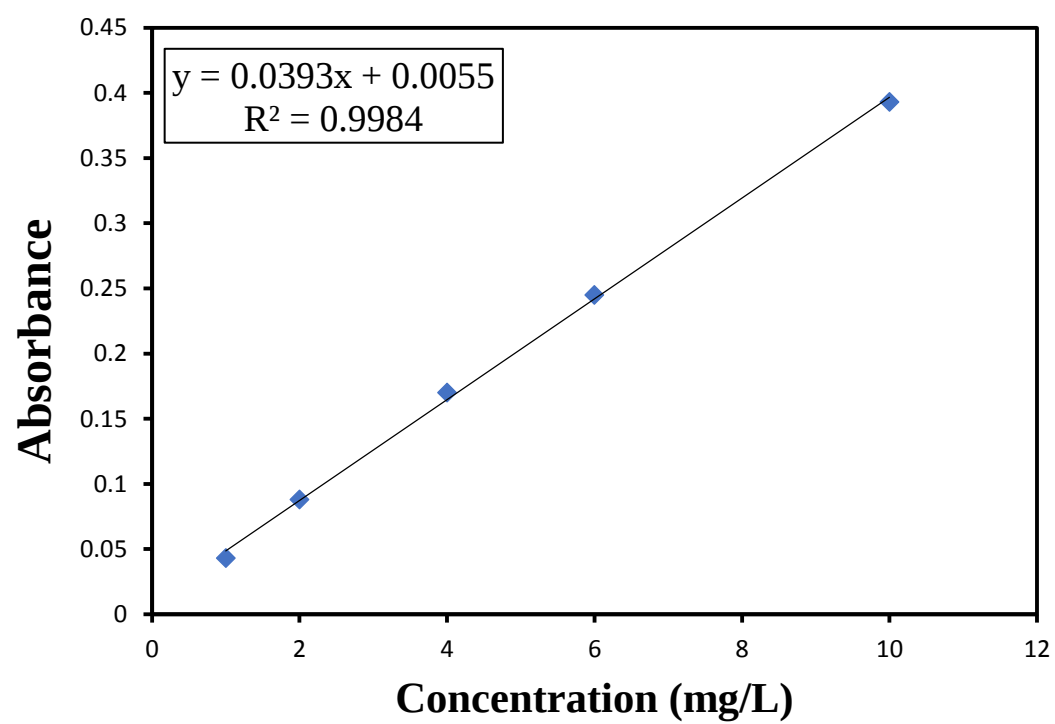
Appendix 7.W: Mass spectrum for the intermediate $C_6H_5O_3$ of 4NP for pH 10 at 30 min



Appendix 7.X: LCMS-TOF calibration curve for 4CP



Appendix 7.Y: LCMS-TOF calibration curve for 4NP



Appendix 7.Z: Fe calibration curve for the leaching studies