Monitoring the behaviour of silver nanoparticles as emerging contaminants in urban wastewaters

By

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Thesis submitted in fulfilment of the requirements for the degree
Master of Engineering: Chemical Engineering
In the Faculty of Engineering and Built Environment
At the Cape Peninsula University of Technology

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Bellville Campus

February 2023

DECLARATION

I, **Moses Ajibade Bisi-Johnson**, declare that the contents of this dissertation represent my own unaided work and that the dissertation has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University ofTechnology.

Signed **Date 16-02-2023**

ABSTRACT

Nanomaterials (NMs) have become a distinctive component in several manufactured commercial, industrial, and domestic products due to the extensive development of nanotechnology over the last decade. As a result, there are some concerns over the intentional and incidental discharges of NMs into the environment due to widespread uncertainty of their roles as emerging contaminants (ECs). As an EC, NMs will find their way into municipal wastewater treatment plants at various stages of their life cycles. If not effectively treated, they will eventually be discharged into the aquatic environment, which serves as the final sink.

Despite advances in the applications of NMs, there is still a lack of knowledge in NM quantification, as well as in their fate, transport and behaviour in the environment. Of all NMs, silver nanoparticles (AgNPs) are the most common and extensively produced and utilized nanoparticles (NPs), found regularly in various nano-products (including personal care products, home appliances, laundry additives, cosmetics, food preservatives, paints, and textiles) mainly due to their unique antifungal, antiviral, and antibacterial attributes. As a result, AgNPs are likely to be released into the aquatic environment as NPs, aggregates or agglomerates, and soluble or insoluble ions, which will be a source of contaminants and could have toxic effects on aquatic organisms.

The fate and behaviour of AgNPs are influenced by intrinsic NP characteristics such as shape, size, structure, coating, morphology, surface area; as well as environmental conditions of the media such as pH, salinity, ionic strength, total dissolved solids (TDS), natural organic matter (NOM), and dissolved organic matter (DOM). In this study, a simulated wastewater treatment plant (SWWTP) was constructed according to the Organization for Economic Cooperation and Development (OECD) guidelines (OECD 303A) to mimic a typical municipal sewage treatment plant. The SWWTP consisted of three units (a control containing no NPs, and two test units (containing 5 mg/L and 10 mg/L, respectively)) run simultaneously. Each unit consisted of an influent holding tank (5 L), aeration chamber (3 L), a settling vessel (1.5 L), and an effluent tank (5 L). The influent and aeration tanks were constantly stirred to keep the wastewater in suspension. The aeration chamber was fed by pumping influent at a rate of 6.33 L/min using a peristaltic pump, with air being constantly supplied using a glass frit at a flow rate of 290 L/min to keep the dissolved oxygen (DO) above 2 mg/L and hydraulic retention time maintained at 6 hours. The SWWTP was stabilized and optimized for seven days before the introduction of the AgNPs, after which the wastewater characteristics were tested at various stages of the treatment process before and after the exposure to AgNPs. The AgNPs were also characterized pre- and post-exposure.

The AgNP were characterized using different techniques including transmission electron microscopy (TEM), X-ray Diffraction (XRD) to establish NP morphology and chemical state, and an energy dispersive X-ray spectroscopy analysis (EDS) to determine the elemental composition. The specific surface area of

the AgNP nano-powder was analysed by BET. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the metal (Ag) concentration within the each sample.

The results obtained indicate that the physicochemical properties of the aqueous media are a critical governing factor that influences the transformation of AgNPs in the wastewater system. A comparison analysis into the result obtained from the two test units provides a distinct correlation between particle concentration and transformation process of AgNP in wastewater media, with the 10 mg/L AgNPs test unit having formed larger aggregates and a fast dissolution rate in the influent, sludge and effluent ICP-OES confirm that approximately 70% of Ag was collectively retained in sludge and effluent in both treatments, thus potentially posing a threat to both environmental and human health.

ACKNOWLEDGEMENTS

In every situation **(no matter the circumstances),** be thankful and continually give thanks to God. I give all the thanks and praise to God for his faithfulness upon my life and for giving me knowledge, understanding and the strength for the journey thus far.

I wish to thank all the people that helped me during the process of completing my Masters research. I wish to thank:

My supervisor, **Prof Chowdhury Mahabubur** (CPUT), for his excellent guidance, motivation, support and the opportunity to complete my masters under his supervision.

My co-supervisor, **Dr. Chavon Walters** (CSIR), for her patience, tireless support, input, scientific advice, research support and guidance during the process of completing my master’s degree.

Dr. Jessica Chamier's (UCT) for her scientific input and guidance, as well as the use of her facilities and ideas while analyzing my samples, are all gratefully acknowledged.

Prof T.V Ojumu for his support, guidance, advice, and mentoring throughout my academic year at the Cape Peninsula University of Technology.

I am grateful to **Mrs. H Small**, **Mr. Alwyn** and **Mrs. Elizma Alberts** the administrative and technical staff in the chemical engineering department for the tireless effort and round the clock assistance.

Dr. Babatunde Oladipo for his sincere advice, support and academic inputs.

And also, a special thanks to all members of my family for their support and love. I owe you all so much.

The financial assistance of **NRF Thuthuka Fund and CSIR** towards this research is acknowledged.

Opinions expressed in this thesis and the conclusions arrived at, are those of the author, and are not necessarily to be attributed to the National Research Foundation and CSIR.

DEDICATION

This thesis is dedicated to **My Mother Prof M.A Adefisoye**, **Mr. R.O Ajileye** and **Mrs. M.O Ajileye** for their unequivocal love and support throughout the years. Without their help, love, and patience, I would not have been able to further my studies.

“Without your help and guidance, my mother I would not have been able to do what I have been able to do today. I appreciate all you have done for me. You stand out from the crowd”.

LIST OF PUBLICATIONS AND PRESENTATIONS

Publications in preparation

BISI-JOHNSON, M., WALTERS, C., CHOWDHURY, MR. (2022) A review of nanomaterials in environment – evidence of behaviour, Impact, and potential for removal. Prepared for submission to Journal of Environmental Science & Health, Part A

BISI-JOHNSON, M., WALTERS, C., CHOWDHURY, MR., CHARMIER, J. (2022) Monitoring the behaviour of silver nanoparticles as emerging contaminants in urban wastewaters: a microcosm study based on OECD protocols. Submitted to Toxicological & Environmental Chemistry

Oral and Poster Presentations at Conferences

Walters, C., Chowdhury, M., Bisi-Johnson M., 2019. Behaviour of silver nanoparticles in a laboratory-derived wastewater treatment plant: a microcosm study based on OECD 303-A principals. SETAC Africa, Cape Town,

Walters, C., Chowdhury, M., Bisi-Johnson M., 2019. From waste to resource: silver nanoparticles as emerging contaminants in urban wastewaters. SETAC Africa, Cape Town,

Bisi-Johnson, M., Walters, C., Chowdhury, MR., 2020. Remediation of wastewater effluent impacted by silver nanoparticles. WISA 2020 conference held in Johannesburg, 7-11 December 2020.

Bisi-Johnson, M., Walters, C., Chowdhury, MR., 2021. Monitoring the behaviour of silver nanoparticles as emerging contaminants in urban wastewaters: a microcosm study based on OECD protocols. Centre for postgraduate studies 2021 conference held in Cape Peninsula University of Technology, 30 November 2021.

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ABBREVIATIONS AND ACRONYMS

AgNP	Silver Nanoparticles
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
ENMs	Engineered Nanomaterials
NM	Nanomaterials
NOM	Natural Organic Matter
NPs	Nanoparticles
OECD	Organizational for Economic Co-operation and Development
OM	Organic Matter
SWWTP	Simulated Wastewater Treatment Plant
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
WWTP	Wastewater Treatment Plant

GLOSSARY

Chemical Oxygen Demand	A biological method used to estimate the quantity of oxygen needed to oxide inorganic and organic nutrients found in water
Dissolved Oxygen	A measure of oxygen concentration dissolved or present in a water body
Organic Matter	The Amount of Carbon based compounds found in a natural or aquatic environment
Total Dissolved Solid	Method of measuring the combined ionized, molecular, or suspended form of organic and inorganic compounds in a solution

CHAPTER 1 INTRODUCTION, THESIS STRUCTURE AND OBJECTIVES

1.1 Introduction

Nanotechnology is a rapidly growing field in which nanometer-scale knowledge and control of matter are applied to the creation of novel structures, devices, and materials. This includes material manipulation on a near-atomic scale to manufacture new structures, materials, and devices. Nanotechnology has had a profound effect on the global market and is growing at an exponential rate. It has been estimated that nanoscience would be valued at $33.63 billion by 2030 (Tewari, 2021). Nanotechnology has been developed and applied in a wide variety of applications, and global investment in research and development has increased due to this science's potential.

Nanomaterials (NMs) can be categorized into three classes: natural, accidental, and engineered nanomaterials (ENMs) (Tiede et al., 2008, McGillicuddy et al., 2017). Natural NMs are formed from a variety of processes, including volcanic activity (Farré et al., 2009, Laborda et al., 2016), forest fires (Farré et al., 2009), and mineral weathering (Wigginton et al., 2007). Nanomaterials are created incidentally as a by-product of combustion activities (Nowack and Bucheli, 2007). Engineered NMs are categorized according to their chemical compositions, which are classified as carbon-based NMs, metal-based NMs, dendrimers, polymeric particles, and composites (Joner et al., 2008, Golbamaki et al., 2015).

Silver nanoparticles (AgNPs) are among the most widely used NMs found in a wide range of consumer goods, and represent the largest and fastest-growing class of all NMs (Li et al., 2013, Courtois et al., 2019). It is projected that AgNP production and use in commercial and domestic products will continue to rise in the coming years (Burkart et al., 2015). As a result, AgNPs will be found in wastewater effluent for the foreseeable future. Silver NPs, despite their apparent usefulness, have been shown to have detrimental effects on both human and environmental health (Walters et al., 2013, Rajput et al., 2018, Rajput et al., 2020). As such, AgNPs may be more hazardous than their bulk counterparts due to the enhanced dissolving rate of ions due to the larger surface area and smaller particle size of AgNPs (Fernando and Zhou, 2019). Accumulated ion concentrations in subcellular sites can be increased by the ability to adsorb biomolecules and interact with biological receptors of AgNPs.

1.2 Hypothesis and Research question

Advances in the use of nanotechnology and NMs may augment the release of NM from consumer products and industrial processes to municipal wastewater treatment plants (WWTPs). As such, the fate and behaviour assessment of NPs in WWTPs is a crucial step for their environmental risk assessment. Therefore, the aim of this study is to investigate the fate, behaviour, and transport of AgNPs in a simulated wastewater treatment plant (SWWTP) based on OECD protocols.

The following research questions will, therefore, be explored:

1. Do the physiochemical properties of the environmental media influence the properties of AgNPs in a simulated wastewater treatment plant?
2. Will NMs undergo physical and chemical changes in a simulated wastewater environment?

1.3 Aim and Objectives

The aim of this study is to investigate the fate, and behaviour of AgNPs in a simulated wastewater treatment plant (SWWTP) using OECD (OECD 303A) protocols. To accomplish this, the following specific objectives were accomplished:

1. Determine whether the AgNPs undergo any physical or chemical changes when exposed to simulated wastewater.

2. To assess the fate and behaviour of AgNPs in wastewater sludge from a SWWTP.

1.4 Thesis Outline

The focus of this thesis was to investigate the fate and behaviour of a commercially available metal-NP (AgNPs) used in several industrial applications and consumer products in a simulated wastewater treatment plant (SWWTP) in an attempt to mimic the treatment process in a traditional WWTP. To achieve this, the dissertation was divided into four chapters; two of the chapters have been prepared for submission to accredited journals (Chapters 2 and 3).

The thesis also contains an introduction (Chapter 1), and conclusions and recommendations for further work (Chapter 4). The details for each chapter are given below:

Chapter 1: Introduction, Thesis Structure and Objectives

This chapter provides a brief introduction to NMs. It also summarizes the study's aims and objectives and provides the structure of the thesis and what each chapter entails.

Chapter 2: A review of nanomaterials in wastewater – evidence of behaviour, impact, and potential for removal

This chapter explores the available studies on nanotechnology, the applications and implications of NMs, as well as the fate, behaviour, and transport of NPs. This chapter has been prepared for submission to Journal of Environmental Safety and Health: Part A.

Chapter 3: Monitoring the behaviour of silver nanoparticles as emerging contaminants in urban wastewaters: a microcosm study based on OECD protocols.

Chapter 3 investigates the fate and behaviour of AgNPs in a simulated wastewater treatment plant (SWWTP) based on the OECD protocols. This chapter has been submitted to Toxicological & Environmental Chemistry.

Chapter 4: Conclusions and Recommendations

Chapter 4 provides the highlights of the current research project and provides recommendations for future scientific research.

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CHAPTER 2 A REVIEW OF NANOMATERIALS IN WASTEWATER – EVIDENCE OF BEHAVIOUR AND IMPACT

This chapter has been drafted as a peer-reviewed manuscript to be submitted to Journal of Environmental Science & Health, Part A.

Abstract

As urbanization continues to expand to accommodate a growing global population, there remains a need to assess the impacts of resulting contaminants on urban waterscapes. Urban landscapes and waterscapes are hosts to an array of contaminants that impact water quality, with novel and emerging contaminants (ECs) posing new challenges to wastewater treatment systems and requirements for environmental monitoring. The increased manufacturing and use of a variety of engineered nanoparticles (NPs) have resulted in their entry into municipal wastewater treatment plants (WWTPs) and aquatic ecosystems as their final sinks. Decades of nanotoxicology research have shown that the interactions between nanomaterials (NMs) and the environment are remarkably complex. Studies are still trying to elucidate how the unique properties of NMs influence their behaviour, and fate in various media. This review seeks to provide an account of the occurrence, fate and behaviour of NMs as ECs, with specific focus on wastewater-derived NPs in urban waterscapes and the aquatic ecosystem.

Keywords: nanomaterials, nanoparticles, emerging contaminants

2.1 Introduction

The most important factors affecting the accessibility and quality of water in urban environments are population growth and the high level of industrial processes. The majority of the global inhabitants lived in urban regions in 2008 (Grimm et al., 2008), with the figure of urban inhabitants predicted to increase to 66% by 2050 (Atashgahi et al., 2015). According to Atashgahi et al. (2015), urban rivers are frequently impacted by untreated wastewater release comprising of excessive pollution loads that can severely affect water quality. The release of municipal wastewater into water resources is a prevalent feature of the urbanization process. Wastewater derived from industries, agriculture, and the general population contains chemical contaminants, including various NPs that can pose risks to human health and aquatic ecosystems. Furthermore, ageing infrastructure of existing water systems need to be adapted for the increased water demands and wastewater treatment resulting from a growing population. As such, wastewater treatment plants are regarded as a major entry point for many ECs, including pharmaceuticals, personal care products (PCPs), and nanoparticles (NPs) into the natural environment (Fono et al., 2006, Schoeman et al., 2015). Nanoparticles are considered among the most commonly occurring ECs in municipal wastewater networks (Brar et al., 2010, Musee et al., 2011, Musee et al., 2014). Generally, most conventional wastewater treatment plants have little or diminished capacity to adequately treat and remove all classes of contaminants resulting in their discharge to receiving waters. Furthermore, agricultural soils can also be exposed to NPs through the application of WWTP-derived sludge as fertilizers (Gottschalk et al., 2009). The likely pathways of NP release into the environment from WWTPs include soils, water systems, and air; through bio-solids, treated and untreated effluent (Figure 2.1) (McGillicuddy et al., 2017, Kühr et al., 2018). Gagnon et al. (2021) also identified WWTPs as a point source of NP distribution into the aquatic systems, with potential toxicity towards the aquatic ecosystem due to the chemical and physical transformation altering some specific properties of the NPs. Because of their distinctive antibacterial, antifungal, and comparatively antiviral properties, silver NPs (AgNPs) have been among the most promising engineered NPs for applications such as medicines, water treatment, clothing, and cosmetics (Panyala et al., 2008, Walters et al., 2014, Walters et al., 2016, Gwin et al., 2018). The intentional or accidental release of AgNPs (including uncoated Ag-NPs, ligand-coated Ag-NPs, and Ag2S-NPs) into the environment is therefore largely inevitable. The likely toxicity and bioaccumulation of AgNPs make it necessary to investigate their fate and transport in the environment.

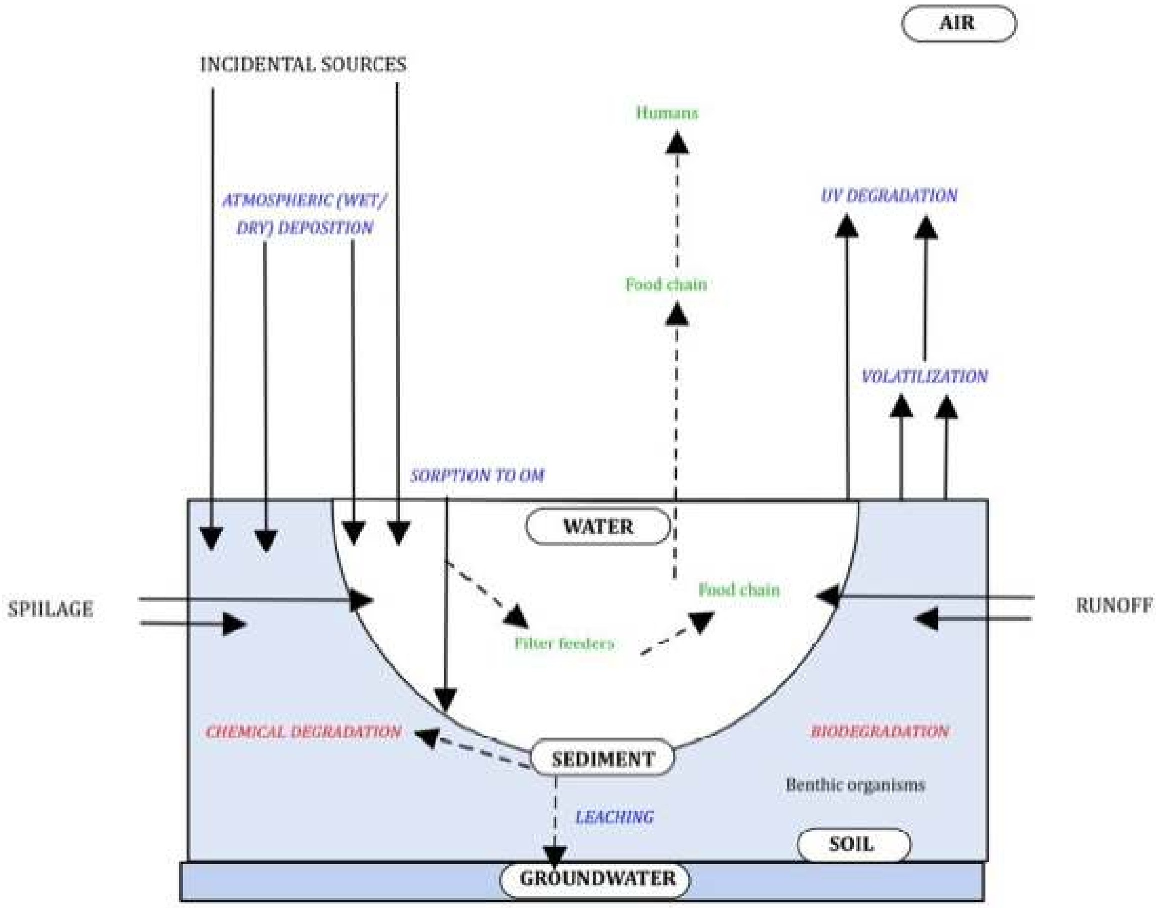

Figure 2.1: Potential engineered nanomaterials (ENMs) pathways in an aquatic ecosystem (Batley and McLaughlin, 2010)

Nanotechnology is one of the fastest-growing industries with vast potential to provide innovative solutions to a wide range of modern-day challenges in various fields such as environmental, food industry, construction, processing technology and addressing these challenges cost-effectively and sustainably (Zhu et al., 2004, Shariati et al., 2017, Pathakoti et al., 2018, Thiruvengadam et al., 2018). The potential market value for NPs in 2021 are valued to exceed US$2.5 billion per annum, while the production market value is estimated to increase by 6% in a compound annual growth rate between 2022 and 2028 (Preeti and Prasenjit, 2022).

Nanotechnology and nano-containing products have gained significant public awareness due to the needs and applications of nanomaterials (NMs) in many areas of industries, agriculture, medicine, and public health. Nanoparticles are a class of NMs with properties characteristically different from their bulk counterparts, with at least one dimension <100 nm (Walters et al., 2016). Although nanotechnology has great potential in various facets of human development, there are concerns that it may have led to the development of environmental hazards.

Recently, there has been an increase in the number of manufactured NPs incorporated into products and manufacturing processes due to the rapid innovation, commercialization, and extensive use of the field of nanotechnology (Najahi-Missaoui et al., 2021). From an inventory of nanotechnology consumer products by the Project on Emerging Nanotechnologies, it's reported that of the nanotechnology-based consumer products or product lines available on the market, nano-products containing silver (Ag) accounted for the largest and fastest-growing category (Li et al., 2013b, Chen et al., 2020). Furthermore, according to an inventory of nanotechnology consumer products by the project on Emerging Nanotechnology with over 1800 consumer products currently listed and Ag nano-products account for the most use with 443 products (Vance et al., 2015). Table 2.1 provides examples of some widely utilized NMs, and their applications. Water quality investigations have traditionally focused on nutrients, bacteria, heavy metals, and other priority pollutants. This chapter gives a review of literature pertaining to the occurrence, behaviour and impact mechanisms of the most common wastewater-derived NPs.

The exact concentrations of these novel contaminants have proved difficult to assess in contrast to their bulk counterparts. However, their toxicological significance has previously been reported (Walters et al., 2014, Walters et al., 2016). Environmental contamination and effects of NPs have been reported in several environmental matrices, including surface waters (Furtado et al., 2016), aquatic invertebrates (Walters et al., 2014), fish, terrestrial invertebrates (Chae et al., 2009, Bilberg et al., 2010, Yue et al., 2015, Yue et al., 2017), algae (Yue et al., 2017), drinking water (Tiede et al., 2016), wastewater (Brar et al., 2010), and sludge (Zhou et al., 2015, Gwin et al., 2018). Nanomaterial release into WWTPs is inevitable due to increased NM production and application over the past decades, as well as their predicted increased production and application in the future.

Table 2.1: A non-exhaustive list of the applications and sources of ENMs in domestic and industrial products (Gottschalk et al., 2009, Chaúque et al., 2014, Musee et al., 2014, Otero-González et al., 2014, Asadishad et al., 2018, Leareng et al., 2020)**.**

Source	**Nanomaterials**	**Examples of ENMs**	**Level of application in products**	**Applications**
Inorganic	Metals and alkaline earth metals	Ag	High	Food Packaging and Textiles
		Fe	High	Water treatment
		Al	High	Metal Coating
		Sn	-	Paints
		Cu	High	Microelectronics
		Au	Low	Electronic devices, materials science
	Metal oxides	TiO_2	High	Cosmetics products, Skin Care and Water Treatment
		ZnO	Low	Cosmetics products
		SiO_2	High	Coatings
Organic	Carbon Materials	Carbon nanotubes	High	Electronics, remove pollutants
		Fullerenes	High	Medical and cosmetics use

2.2 Nanotechnology Applications and Implications

Nanomaterials have a unique combination of chemical, physical, and mechanical properties, making them suitable for a wide variety of applications (Yang and Westerhoff, 2014). They are present in various consumer products, including cosmetics, electronics, food and beverages, and others (Farré et al., 2009, Yang and Westerhoff, 2014). Recent advancements, such as electrochemical and optical sensors, separation and extraction techniques, and chromatographic analysis, have increased their use in environmental analysis (Liang and Guo, 2009). Nanomaterials are constantly being developed in order to create new technologies and improve the efficiency of existing ones. This continuous development can result in tangible environmental benefits, such as the use of nano-porous membranes as filtration devices for the removal of ions or the separation of different fluids, such as those used in renal dialysis.

Today, over 1,000 consumer products contain NMs (Yang and Westerhoff, 2014). Nanomaterials have been studied for their potential applications in the development of lighter and stronger materials, the remediation of contaminated soil, the replacement of toxic chemicals in a variety of applications, the enhancement of the efficiency of solar cells, and targeted cancer treatment. Environmental remediation, pollution sensor detection, photovoltaics, medical imaging, and drug delivery all benefit from science. Nanotechnology is also used in the electronic, cosmetic, power, catalytic, and material sectors. NMs have been widely used to clean waste more efficiently and economically than current standard methods. While this application has benefited the human race significantly, the disadvantage is that the disposal or production of this waste has resulted in serious environmental issues.

As has been the case with other emerging technologies, such as pesticides and genetically modified foods, there has been widespread concern and uncertainty about the environmental and human health risks associated with ENMs. As a result, researchers face numerous obstacles in obtaining reliable and relevant data on which to base risk assessments for environmental and human health. While efforts have been made to advance nanotechnology development, South Africa has yet to develop a national research strategy to examine the environmental and human health risks associated with such technologies (Musee et al., 2010).

Engineered NMs are found in many commercial and household products. Their potential for entry into the environment and subsequent effects on the ecosystem and human health are becoming a growing concern. Anthropogenic emissions of inorganic NPs have more than doubled the flux of NPs released into the atmosphere, with production facilities, manufacturing processes, and wastewater treatment plants accounting for most anthropogenic NP sources (Farré et al., 2011, Sharma et al., 2015, Silva et al., 2020). Subsequently, determining their environmental fate, behaviour, transport, and bioavailability is critical. When NPs are released into the environment, several factors alter their shape, chemical composition, and structure. Nanomaterials enter the aquatic environment from both direct and indirect pollution. They can be discharged unintentionally when used as tools for remediating contaminated soils or inadvertently through atmospheric wet and dry deposition, surface run-off (from industries and wastewater treatment plants) and spillage during their use and disposal.

Once released into the environment, several processes and factors can affect the functional properties of NMs, thereby affecting their likelihood of being absorbed by aquatic organisms and their toxicity (Liu et al., 2018, De Marchi et al., 2019, Kansara et al., 2022). Figures 2.1 and 2.2 depict the critical physiochemical pathways and modifications that regulate the fate and transport of NMs. The primary processes governing NP behaviour in aquatic ecosystems are based on transformation and bioaccumulation processes such as aggregation and dissolution (Stegemeier et al., 2017, Shevlin et al., 2018, Lekamge et al., 2020). Nanoparticles tend to aggregate in aquatic environments, making them less mobile. These aggregates can be dissolved by sedimentation or absorbed by benthic (sediment-dwelling) organisms, resulting in biomagnification (Farré et al., 2009). Water solubility also plays a significant role in the fate, transport, and bioavailability of NP. Certain NMs are coated to increase or decrease their solubility, depending on their application. Additionally, these coatings may affect their interactions with and in various environments (Bundschuh et al., 2018, Demangeat et al., 2018, Buchman et al., 2019). In addition, NPs will deposit on other surfaces, such as natural colloids (Arvidsson et al., 2011, Peng et al., 2017, Lai et al., 2018), increasing their available surface area for deposition and sedimentation (Quik et al., 2014, Besseling et al., 2017).

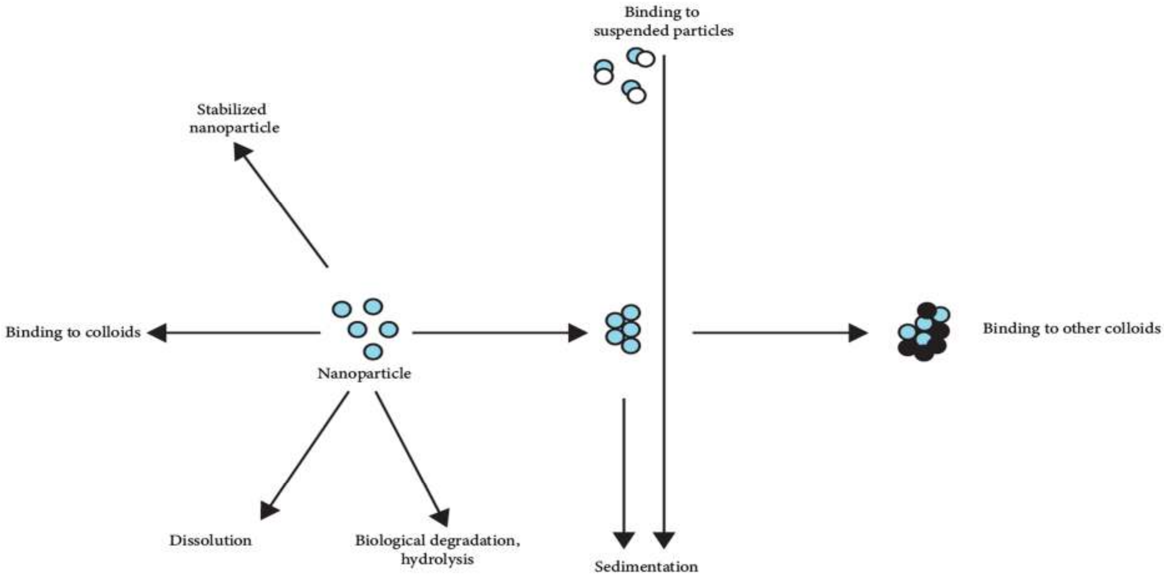

Figure 2.2: Nanomaterial modifications in an aquatic ecosystem (Batley and McLaughlin, 2010)

The aggregation potential of NPs in sediments is enhanced by the higher ionic strength of pore waters compared to surface waters (Batley and McLaughlin, 2010), culminating in particle entrapment and decreased mobility. Sediments are a critical ecological component of aquatic ecosystems and are widely considered as the primary repository for NPs in the aquatic environment (Klaine et al., 2008, Koelmans et al., 2009). As such, they are a significant source of contaminants for organisms that live in the sediment. Organic matter (OM) content is another environmental factor known to affect the chemical and biological properties of NMs. Recent research has revealed strong correlations between the size of NPs and the presence of OM, confirming the role of OM in the physicochemical properties of NMs (Qiu et al., 2020).

2.3 Description of the database

For this review, we selected 115 publications related to the behaviour, impact and mechanism of action of some of the most common NPs. About one-third (35%) of the selected papers originated from the journals classified by us as "ecotoxicology and environmental chemistry journals," 22% from "toxicological," 18% from "nanotechnological," 10% from "chemical" and 8% from "medical" journals. The 115 publications originated from 24 journals and others: Environmental Science and Technology (14 papers), Nanotoxicology (3), Toxicology reports (1), Toxicology (1), Environmental Science Europe (2), Environmental Science Nano (5), Environmental Science and Pollution Research (4), Chemical Engineering Journal (2), Environmental Science and Health (3), Chemosphere (6), Environmental Pollution (3), Langmuir (2), Journal of Nanoparticle Research (2), Chemical Reviews (2), Science of the Total Environment (12), Aquatic Toxicology (2) , Journal of Hazardous Material (3), Scientific Reports (2), Water Research (3), Particle and Fibre Toxicology (2), Environmental Science and Engineering (1), Energy and Environmental Sciences (1), Toxicological and Environmental Chemistry (1) and others (38) (Appendix A).

2.4 Occurrence of nanomaterials in the environment

Wastewater effluent contains an array of chemical contaminants that can pose risks to human and environmental health (Edokpayi et al., 2017). Wastewater effluent is usually diluted by water from other sources (for example, freshwater from a nearby river), and, as such, the concentrations of wastewater-derived contaminants are reduced often to levels below detection or concern to downstream water users. Nevertheless, during conditions of low-flow, effluent can account for a significant fraction of contaminants of emerging concern (Fairbairn et al., 2016). Wastewater-derived contaminants, such as NPs, are likely be exposed to all environmental compartments due to activities such as cleaning, abrasion, burning, or degradation of materials or products containing NPs (Giese et al., 2018).

Nanomaterials are introduced into the wastewater stream via discharge from industrial processes, discharge of consumer domestic products, application of NMs in WWTPs, and unintentional release from degrading consumer products disposed of in waste management sites (Figure 2.2) (Wang et al., 2012, Park et al., 2017, Malakar et al., 2021). According to a study by Kunhikrishnan et al. (2015), the application of NMs in medical sciences such as drug delivery, tissue imaging, cancer therapy, and neuroprotection can be a point source of NMs released into wastewater. The review further noted that the release of NMs in the biological and medical sciences could be at different stages, ranging from discharge from pharmaceutical companies during manufacturing to the administration of drugs and disposal in hospitals wastewater discharge. Further studies also discussed the potential of NMs application in the textile industry as another point source of NPs contaminant in wastewater sinks (Kunhikrishnan et al., 2015, Pourzahedi and Eckelman, 2015).

The use of AgNPs in the textile industry has also resulted in their discharge in the wastewater due to the daily wash of textile products. As reported in some studies, high volume commercial production of NMs is directly linked to a notable concentration of NMs deposited in industrial effluents, which will ultimately end up in the wastewater streams and sludge (Yang et al., 2014, Abbas et al., 2020, Gagnon et al., 2021). The increase in the production and application of NMs, therefore, allows for the increase in NPs released into wastewater (Zhao et al., 2021).

Figure 2.3. Introduction of NPs from wastewater to the environment

Several studies have reported the occurrence of various NPs in discharged wastewater and receiving watersheds. For example, Li et al. (2016) reported the effects of wastewater-derived AgNPs in surface water and concluded that, although more than 96.4% of AgNPs from wastewater influent were removed, effluent AgNP concentrations still ranged between 0.7−11.1 ng/ L. Other studies investigating laboratory-based studies reported that 96.6% nano-CeO_2 was removed during activated sludge treatment and about 0.11 mg/L Ce was found in the effluent (Gómez-Rivera et al., 2012). Gartiser et al. (2014) reported that more than 95% of TiO_2 NPs was removed during the municipal activated sludge wastewater treatment and 3-4% of the NPs were found in the effluent. During the removal of NPs in the biological wastewater treatment process, an elevated concentration of the AgNPs was reported to accumulate in the biosolid biomass in the activated sludge and transformed into a silver sulphide (Ag_2S). Similar observations were reported for other metallic NPs (Wang et al., 2012, Brunetti et al., 2015).

According to Bundschuh et al. (2018), an increase in the use and variety of NP products is expected to contribute to a wider range of pollution in the environment, both in quantity and product variety. With the most common emission cases identified to be prominent during the use of NP products, manufacturing phase and waste handling process (such as WWTP, landfills). Subsequently, there are three common potential modes of NP release into the environment (Figure 2.4). These modes of release are governed by the NP's fate, behaviour and life cycle as identified by Abbas et al. (2020).

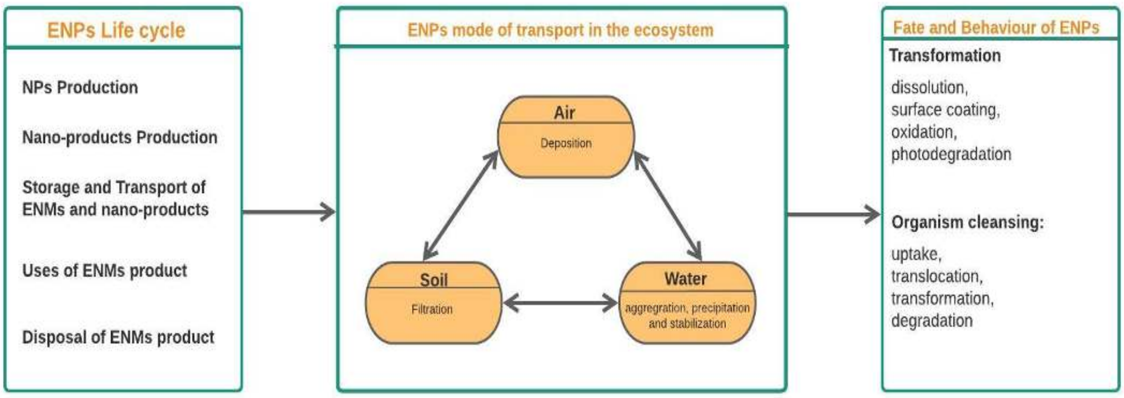

Figure 2.4 Nanomaterial fate, transport and behaviour in the environment (Abbas et al., 2020).

The distribution of NMs at various stages of the lifecycle in waste streams largely depends on the concentration and size of NPs. The concentration is dependent on the environmental conditions, properties of the NMs, the quantity of the NMs produced or used, type of NMs product application (domestic or commercial), and the degree of transformation of NMs such as dissolution, aggregation, agglomeration, and interaction with natural occurring moieties. Jahan et al. (2017) reported that the concentration of dissolved NM ions has a greater impact on the distribution and transportation of NMs into the environment but emphasized that the aggregation of NMs is important in the long-term distribution of NMs. Other studies reported that NMs could be detected and characterized solely in attribution to their physicochemical properties. However, there can be a drawback when using this attribute alone in quantifying the concentration of ENMs in the environment, as the application of NPs varies depending on which application it is intended to be used in, which results in the diversity of the physicochemical characteristics of NMs detectable.

Nanoparticles have an adverse effect on the bacterial population in wastewater treatment (Hegde et al., 2016). For example, Miao et al. (2016) reported that, due to the nature of NP chemical complexity, it is unlikely the NP original form or structure is retained once released into the wastewater system. In previous studies, it was indicated once NPs are released into the environment, they have an adverse effect on the organisms in such an ecosystem. The system most affected is the aquatic systems, which are affected most by the behaviour, fate, and transformation processes of the NPs (Hegde et al., 2016, Miao et al., 2016, Peng et al., 2017b, Shevlin et al., 2018).

2.5 Behaviour and physicochemical properties of nanomaterials in the environment and wastewater

Reports have shown that the environmental fate and behaviour of NMs are dependent on biological, chemical, and physical transformation. The biological transformation involves the disintegration of capping agents and phase alteration (Peijnenburg et al., 2015); physical factors include aggregation, agglomeration, disaggregation, deagglomeration, deposition, and formation (Peijnenburg et al., 2015); while chemical factors include the rate of sorption of the NMs, dissolution, redox reaction, and phase alteration (Peijnenburg et al., 2015). Furthermore, the stability of NPs controls their aggregation/agglomeration, dissolution, sedimentation, fate, and behaviour in the aquatic ecosystem and consequently, legitimately affects their conveyance and take-up by organisms in this system.

Nanomaterials have unique substantial adsorption capacities due to their particle size (relatively nanoscale structures), making them more likely to associate with other molecules forming a complexation (Peijnenburg et al. (2015)). Hence, sorption forms a crucial process, which affects the fate, behaviour, and transport of NMs (Kulikova et al., 2020). For example, studies explained the interactions between the NPs and natural organic matters and concluded that the physicochemical properties indeed alter and result in a new nanoscale surface coating formation and the sorption characteristics changed (Tang et al., 2014, Wu et al., 2016).

Under specific environmental conditions (such as pH, temperature, organic matter), NPs can dissolve, aggregate, or remain suspended as single particles. Aggregation and disaggregation processes regulate NM speciation, transport, fate and bioavailability, particle concentration, and toxicity. For instance, large aggregates will precipitate out and their transport and bioavailability (and consequently toxicity) will be significantly restricted. This was observed by Walters et al. (2016) who reported that higher temperatures resulted in increased toxicity owing to the formation of smaller aggregates at elevated temperatures. Similarly, the release of metal ions from metal NPs in wastewater is more prominent under acidic conditions and low ionic strength (Wang et al., 2017). Under alkaline conditions, Musee et al. (2014) observed that most of the metal NPs show a strong affinity for the sewage sludge rather than dissolved or dispersed in the filtrate.

Wastewater-derived NPs transform through a variety of mechanisms including biotransformation and photolysis. And subsequently undergoes significant changes in speciation during the anaerobic phase of the wastewater sludge treatment process. Fono et al. (2006) reported on the significance of biotransformation over photolysis for most wastewater-derived pharmaceuticals.

2.5.1 Aggregation and Agglomeration

Aggregation and agglomeration are terms used to describe one of the transformational processes that influence the fate and behaviour of NMs in the environment, and are sometimes used interchangeably (Murugadoss et al., 2020). Only few reports differentiate between the two processes. Both aggregation and agglomeration are clusters of NPs. Agglomeration is described as a mass conserving process where particles of similar properties interact and form a cluster bonded together by van der Waal forces and where particles are combined loosely, while aggregation is referred to as strong and dense particle collectives (Zare, 2016, Ashraf et al., 2018, Shevlin et al., 2018).

In recent studies, exposing different NPs to various aqueous environmental condition (such as rainwater, wastewater, tap water, and lake water) was conducted to understand how the environmental behaviour (aggregation) varies with different source point of exposure (Mui et al., 2016, Liu et al., 2018). Liu et al. (2018) reported that aggregation of NPs in aqueous media can be impacted by wide range of various water chemistry and results from this study shows that aggregation of NPs in different aqueous media varies; in the study it can be understood that increase in hydrodynamic diameter of NPs is proportion with an increase in time. From the Liu et al. (2018b) study, the results indicated that NPs aggregation was more prominent in tap water and with lake water having less aggregate formed. Based on the morphology and larger aggregates of NPs formed in the aqueous media, the water source were ranked from tap water to lake water (tap water > wastewater > lake water) (Liu et al., 2018). Aggregation of NPs in activated sludge during the wastewater treatment process was observed, and it was reported that wastewater characteristics such as natural organic matter, pH, metal ions and ionic strength, are known to alter the NPs surface properties which in turn affects aggregation (Wang et al., 2016, Ouyang et al., 2017, Ren et al., 2017).

According to Murugadoss et al. (2020), NP agglomeration is sensitive to environmental changes such as temperature, pH, and medium of transport, and can affect NP size, mobility and bioavailability. These environmental conditions may also be conducive to de-agglomeration. This was supported by Walters et al. (2013) (Figure 2.5) which reported a formation of loosely packed aggregrate and when AgNP suspension was exposed to an ambient temperature condtion of 14.6ºC showed a more pronounce image of aggregration and increase particle size after day 4 and after exposing the sample to different temprature conditions at 28ºC reported a larger aggregration particle size of AgNPs, and thus concluded that large aggregates represent reduced levels of bioavailability and toxicity. The application of a surface coating, however, may be useful although drawbacks include the formation of homo-aggregation (Surette et al., 2019, Herchenova et al., 2020, Wang et al., 2021).

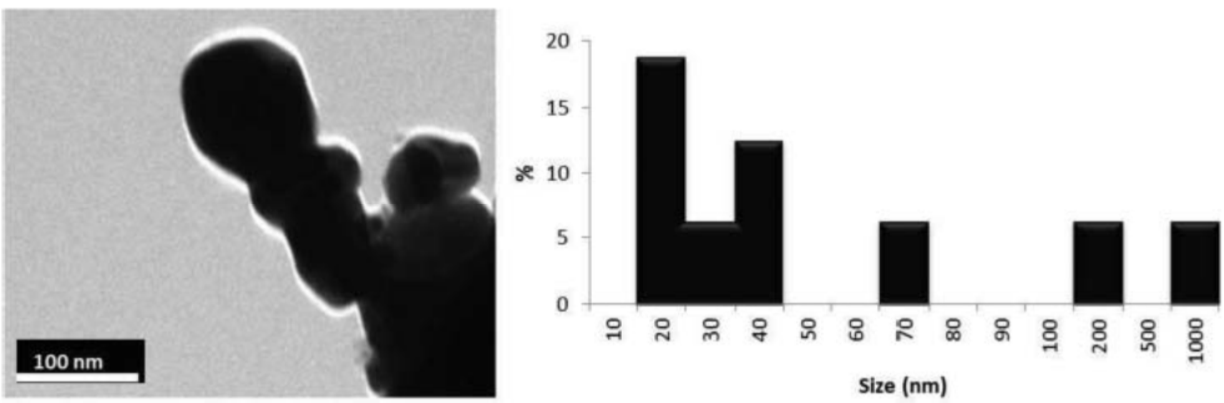

Figure 2.5. TEM image of AgNP in aqueous phase with corresponding particle size distribution (Walters et al., 2013).

2.5.2 Sedimentation

Sedimentation is a transformation factor that causes the flux of NPs to settle in an aqueous medium as a result of NP accumulation (Ganguly and Chakraborty, 2011, Markus et al., 2015) . Despite significant progress in recent years, there is still a gap in our understanding of the sedimentation behaviour of NPs (Quik et al., 2014), due to the complexity of the underlying interparticle interaction mechanisms, as most studies use a theoretical model or analytical equipment to fully detail the mechanism process of NPs sedimentation (Ganguly and Chakraborty, 2011, Stebounova et al., 2011, Babakhani et al., 2018a, Babakhani et al., 2018b, Gupta et al., 2019). For example, Ganguly and Chakraborty (2011) considered the use of the Langevin formalism of particle transport a model to better understand and investigate the sedimentation properties of NPs. In another study, the rate of sedimentation of AgNPs was quantified using UV-Vis spectroscopy by monitoring the changes of the surface plasmons resonance peak intensity as a function of time (Stebounova et al., 2011).

Stebounova et al. (2011) also reported that the rate of sedimentation of AgNPs was affected by factors including NP size, surface area, and solvent dielectric current. In another study, variable sedimentation rates were observed for different NPs were (Quik et al., 2014, Peng et al., 2017, Li et al., 2019, Surette et al., 2021), which was explained by the different in chemical composition and NP characteristics (including NP coating, concentration and size) (Smitha et al. (2008) and Stebounova et al. (2011). Xu (2018), discussed the role of particle properties and aquatic environment factors (figure 2.5) on a few physicochemical factors and sedimentation of titanium oxide nanopaticles (TiO_2 NPs) and it was reported that due to brownian motion, gravity and interparticle attraction, aggregation is a driving factor for nanoparticle sedimentation. According to Liu et al. (2018), by altering aggregation through the use of NOM or stabilizing agents, electrolytes and ionic strength of the aquatic environment (figure 2.6), suspension viscosity, and other environmental characteristics that might affect NPs stability, this environmental properties influence sedimentation rates. According to the results of a study, the rate at which NPs partially deposit as sediments increases as the agregates grow larger and the gravitational settling force acting on the agregates increases (Liu et al., 2018).

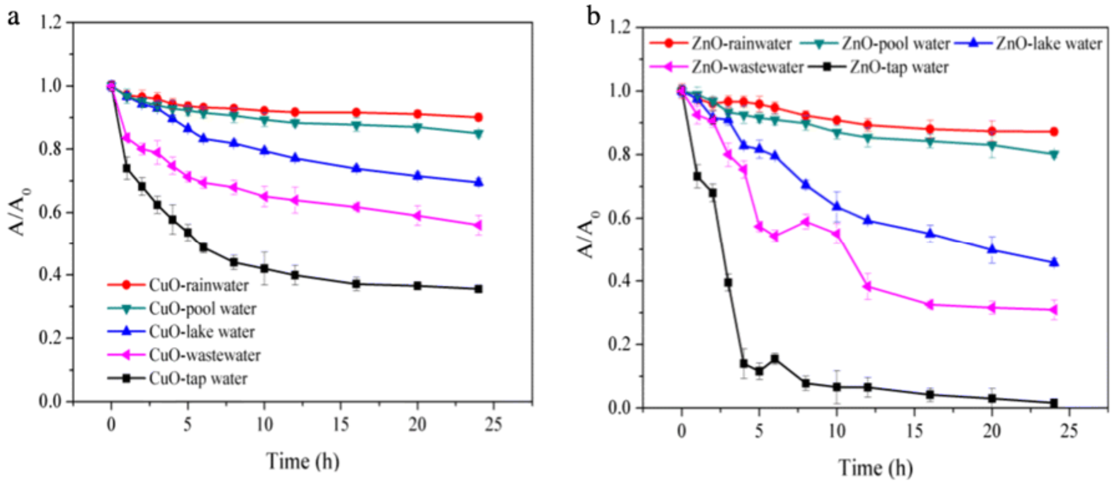

Figure 2.6. CuO (a) and ZnO (b) NPs Sedimentation kinetics of exposed NPs to various aqueous source points (Liu et al., 2018)

2.5.3 Dissolution

Dissolution is an important characteristic that influences the mode of action, fate, and interaction of NPs in the environment (Misra et al., 2012, Duncan and Pillai, 2015). Misra et al. (2012), further described that the dissolution of particles has a dynamic process in which components of a dissolving solid molecule are transported via a diffusion layer from the surface of a particle to the bulk solution. A look into previous studies, indicated that size distribution, surface coating, surface structure, particle size, environmental media and concentration are factors considered to play a major role in the dissolution of NMs in aqueous media (Loza et al., 2014, Conway et al., 2015, Molleman and Hiemstra, 2015, Utembe et al., 2015). These factors are contributors to the distinct feature characteristic phenomenon which aid the dissolution of NMs. This characteristic includes the solubility and the concentration gradient between the bulk solution and particle surface. It is considered that the concept of solubility is a vital physicochemical characteristic of NPs which is an important factor in their risk assessment, and can primarily aid in the understanding of the stability and toxicology effect of NPs in the environment; most especially in the aquatic ecosystem and wastewater system (Bian et al., 2011, Lisjak et al., 2015, Zhang et al., 2015).

Loza et al. (2014) in their study, conducted a comparative analysis on the factors that affect dissolution, by using different functionalized AgNP, size, concentration and a variety of environmental media. The study indicated that all these factor contributes to the rate of dissolution, with different dissolution rate observed; for example, a 70 nm AgNP, Polyvinylpyrrolidone (PVP) capped particles showed a 2% dissolution at 25ºC in an oxygen free water and compared to 8%

dissolution rate for a PVP capped, 70 nm AgNP particles immersed in 0.9% sodium chloride (NaCl) at 25ºC. For example, another study on dissolution rate of 30 nm copper (CuO NPs) and copper oxide nanoparticles (CuO particles) in an osterhout's medium showed a 2% dissolution rate for CuO NPs and 0.12% for bulk CuO particles (Mortimer et al., 2010). Additional in a review by Misra et al. (2012), the reseracher elaborated on numerous factors that affects dissolution such has particle size, surface area, surface morphology, crystallinity, pH of media, ionic strength, temperature, environmental media chemistry, organic components and shape modification; in recent studies other researcher indicated and attest that these factors play a significant role on dissolution rate of nanoparticples, for example surface morphology and coating (Elhaj Baddar et al., 2019), pH of media (Fernando and Zhou, 2019), environmental media chemistry (fig 2.7) (Liu et al., 2018b, Fernando and Zhou, 2019), organic components (Gunsolus et al., 2015, Jiang et al., 2015), size (Axson et al., 2015), surface area and surface morphology (Raza et al., 2016).

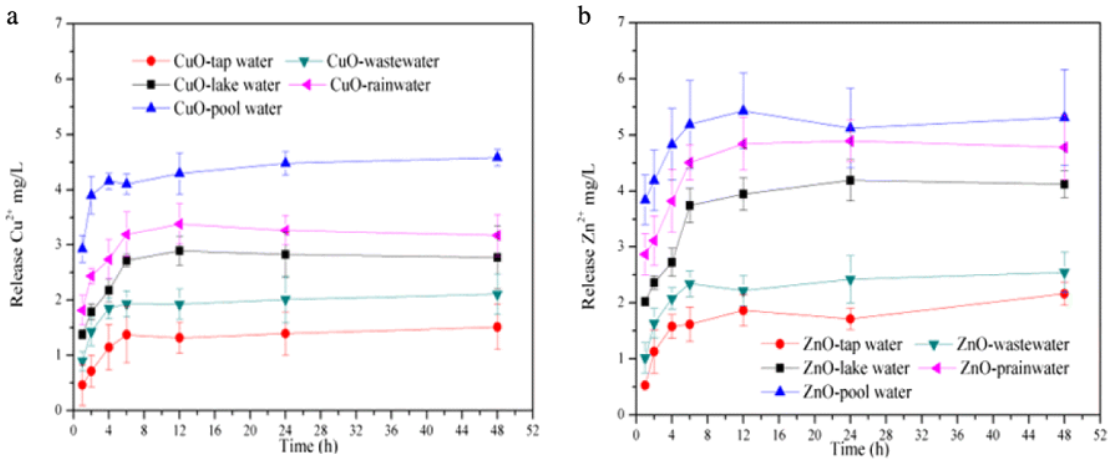

Figure 2.7. Dissolution Kinetics of ZnO and CuO NPs exposed different water source (Liu et al., 2018)

2.6 Impacts of nanomaterials on the ecosystem

The impact or toxic effects of NPs on the environment and aquatic ecosystem are mainly dependent on the NP behaviour and transformation (such as aggregation, sedimentation and dissolution) in the environment (Fernando and Zhou, 2019). Nanoparticles present in wastewater sludge is widely applied as an agricultural fertilizer. As such, this application represents a significant source of NPs to soil and microorganisms. Several studies have investigated and reported on the impact of various NPs in microorganisms. For example, Michels et al. (2017) reported a 60-71% reduction in specific nitrite production rate in ammonia oxidizing bacteria when exposed to various concentration of AgNPs. Similarly, Zhang et al. (2018a) reported a reduction in nitrogen removal and bioactivities of ammonia oxidizing bacteria exposed to CuO-, ZnO- and TiO_2-NPs. Shen et al. (2015) reported inhibition of enzyme activity DH and FDAH in ammonia oxidizing bacteria following exposure to ZnO-NPs. The authors also reported on the effects of soil pH on NP toxicity, with more acidic soils representing higher toxicity levels.

Studies indicate that 90% of Ag ENPs are trapped in sewage sludge and biosolids and increased dinitrogen monoxide (N_2O) flux and altered microbial activities, biomass, and extracellular enzyme activity. From few research studies, it shows that the ammonia-oxidizing bacteria activities when exposed to AgNPs exhibit a great effect on the nitrification and the decline in the population of this nitrifying organism is distinctive after exposure to AgNPs when compared to dissolved Ag+ which in turn shows a distinct effect on denitrifying bacteria (Throbäck et al., 2007, He et al., 2016). Further studies observed that the nitrifying bacteria shows enzymatic growth inhibition at low concentrations of AgNPs (Hu, 2010, Barker et al., 2018), and high concentration leads to cell death (Barker et al., 2018).

Only a limited number of studies have investigated the ecotoxicological impacts of NMs to aquatic plants. Jiang et al. (2014), observed bioaccumulation of AgNPs and dose-dependent increases in reactive oxygen species (ROS) in the aquatic plant *Spirodela polyrhiza*, while Movafeghi et al. (2018), observed significant reduction in growth parameters, photosynthetic pigment and the activity of certain oxidative stress controlling enzymes after *S. polyrrhiza* exposure to TiO_2NPs. Oukarroum et al. (2014) observed pH-dependent toxicity of AgNPs on green alga *Chlamydomonas acidophila*.

Several studies have examined the impacts and ecotoxicity of various NPs on aquatic and terrestrial organisms. Scown et al. (2010) observed dose-dependent mortality in zebrafish exposed to AgNPs. Negative effects have also been reported for other NPs. For instance, a decrease in hatching rate of zebrafish was observed when exposed to ZnONPs versus dissolved Zn. Other studies reported negative effects to zebrafish embryo, including ROS generation, loss of dopamine, defective digestive guts and impaired transport activity for TiO_2 NPs, CuNPs, and CdNPs (Hu et al., 2017, Kteeba et al., 2017, Verma et al., 2018, Zhang et al., 2018b, Tian et al., 2019).

Nanoparticles are known to generate reactive oxygen species (ROS), causing oxidative stress disturbing the functioning of biomolecules such as proteins, enzymes, and DNA (Ahn et al., 2014, Walters et al., 2016). For example, Bar-Ilan et al. (2013) reported dose-dependent ROS in zebrafish exposed to TiO_2-NPs. In other studies, exposure of AgNPs to Japanese medaka shows cellular and DNA damage (Chae et al., 2009, Kim et al., 2013, Lee et al., 2014). Other ecotoxicological impacts of NPs have been reported. For instance, Gomes et al. (2013) report time response-induced DNA damage due to oxidative stress in the mussel *Mytilus Galloprovincialis* when exposed to AgNPs, while Qiang et al. (2020) reported peroxisomal disorder in the mRNA expression in zebrafish exposed to AgNPs.

Effects of NP characteristics such as size and surface coating have also been reported. In a study investigating the effects of AgNPs on Crustean *Daphnia magna*, citrate-coated AgNPs was more toxic compared to PVP-coated AgNPs, while smaller particle size (<60 nm) AgNPs proved more toxic compared to larger particle sizes (>100 nm) (Hou et al., 2017). In a previous comparative study, on the effect of two different coated AgNPs (PVP-coated and protein-coated) on the harmful effect of AgNPs on two aquatic animals, *D. magna* and *Thamnocephalus platyurus.* The result showed that the two different coated AgNPs were highly toxic to the two aquatic animals resulting in the mortality of adult *D. magna* and *T. platyurus.* Possible effects on the decrease in reproduction of offspring were not determined as 50% of the population has decreased before the reproduction endpoint were tested (Blinova et al., 2013).

2.7 Studies investigating the removal of nanomaterials

Wastewater treatment involves sequential processes for the removal or conversion of the harmful constituents present in wastewater. In conventional WWTPs, ECs undergo two main elimination pathways: (1) sorption to sludge and (2) biodegradation during biological treatment (Kiser et al., 2010). However, several factors affect their removal including sludge age, activated sludge tank temperature, and hydraulic retention time (Schoeman et al., 2015, Naseem and Durrani, 2021). Additional treatment options such as photolysis, hydrolysis, biodegradation, volatilization, sorption, flotation, flocculation, coagulation, membrane filtration, nano-filtration, ultrafiltration and simple dilution, may assist to minimize the concentrations of various ECs in aquatic environment (Naseem and Durrani, 2021).

In the past years, the need to address numerous scientific and technological challenges associated with various contaminants has led to the increased proposition for the adoption of membrane separation technology (Oun et al., 2017). The two most extensively utilized technologies for wastewater treatment are adsorbents and membrane-based separation techniques. Although the short adsorption-regeneration cycle of conventional adsorbents reduces their cost-effectiveness, those based on nanomaterials (such as nano-sized metal or metal oxides, graphene and nanocomposites) often have large specific areas, high reactivity and fast kinetics, as well as specific affinity to various contaminants. This makes them more cost-effective than conventional adsorbents. When it comes to specific pollutants, their adsorptive performance may be many orders of magnitude better than that of conventional adsorbents (Ali, 2012, Khajeh et al., 2013). A significant component of the polishing step is membrane separation, which removes impurities primarily through size exclusion, allowing water recovery from unusual water sources such as municipal wastewater.

However, there are still many obstacles to further forward membrane separation technology, i.e., the inherent trade-off between membrane selectivity and permeability, high energy consumption, fouling, and operational complexity. To address these issues, advanced nanocomposite membranes were developed by introducing functional nanoparticles into the membrane. This new class of membrane showed enhanced physiochemical properties such as improved mechanical or thermal stability, porosity, and hydrophilicity. Some exhibited unique properties like enhanced permeability, or anti-fouling, antimicrobial, adsorptive, or photo-catalysis capabilities (Pendergast and Hoek, 2011, Yin and Deng, 2015).

Innate surface and external functionalization are the two most important properties of nano-adsorbents. Surface structure and apparent size are other factors that influence their qualities in terms of chemical, material, and physical properties, which has enabled recent research into NMs as potential adsorbent. The smaller size of the NPs enhances the surface area which increases the chemical activity and adsorption capacity of nanoparticles for the adsorption of materials on their surface (Gubin et al., 2005, Kalfa et al., 2009). The adsorption capacity depends on adsorption coefficient ($\mathbf{k_d}$) and recitation partitioning of contaminants i.e., organic or heavy metal contaminants under equilibrium conditions (Gharbani et al., 2011, Xu et al., 2012). Moreover, for persistent inorganic pollutants, a redox reaction is favoured to start the ionic structure transformation (Saha et al., 2015). However, some scholars strongly agree that changes in redox conditions influence the toxicity of these contaminants (Chen and Mao, 2007, Lim et al., 2014). The commonly used NPs for heavy metal adsorption are activated carbon, graphene, carbon nanotubes, zinc oxide, manganese oxide, magnesium oxide, titanium oxide and ferric oxides (Gupta and Saleh, 2013). As such, it is important to utilize non-toxic, high adsorption capacity, able to adsorb pollutants at lower concentrations, readily removed, and re-usable nanoparticles as an adsorbent for EC removal, as well as adsorbent materials that are easy to recycle

2.8 Conclusions

In this review, a non-exhaustive summary is given on NPs behaviour and transport, and toxicity at various trophic levels. Although useful, these particles should be regarded as a double-edge sword since the toxicity effects observed globally may outweigh their benefits. Currently, there are little to no regulations about the use of NPs in consumer and industrial products or the disposal. Therefore, it is critical to understand the effect or impact of NPs, because there are still some gaps in understanding their ecotoxicity. This review brings to light the importance of care during the manipulation and disposal of nanomaterials in order to prevent unintended environmental impacts, as well as the need for studies on mechanisms and factors that increase the toxicity to enhance risk management.

2.9 Acknowledgements

This work was supported by the NRF Thuthuka Grant no. TTK170418227366. The authors wish to thank the anonymous reviewers for the comments and unbiased review.

2.10 Conflict of interest

The authors report no conflict of interest and are responsible for the content and writing of the article.

2.11 Ethical considerations

The authors report no conflict of interest and any ethical considerations

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CHAPTER 3 MONITORING THE BEHAVIOUR OF SILVER NANOPARTICLES AS EMERGING CONTAMINANTS IN URBAN WASTEWATERS: A MICROCOSM STUDY BASED ON OECD PROTOCOLS

This chapter has been submitted to Toxicological & Environmental Chemistry.

Abstract

The release of nanomaterials (NMs) into wastewater treatment plants (WWTPs) is inevitable due to their increased production and applications. In this study, the effects of the disposal of the commonly used silver nanoparticles (AgNPs) were investigated on a laboratory-scale simulated WWTP (SWWTP) constructed in accordance with the Organization for Economic Co-operation and Development (OECD 303A) criteria. Nanoparticles physicochemical and morphology characteristics were assessed from various sampling points and stages of the SWWTP (namely raw wastewater influent, aeration chamber, sludge and effluent) to analyze the effects of a sewage treatment plant on NP properties. Using inductively coupled plasma optical emission spectrometry (ICP-OES), silver concentrations were determined at different phases of the wastewater treatment process. The results reported indicated that a large amount of AgNPs introduced into the wastewater system are retained in the sludge during the treatment process and only a small fraction of the AgNPs escape into the treated effluent. Based on our findings, we concluded that the physicochemical properties of the aqueous media influence the fate, behaviour and pathways of AgNPs, and the transformation of NPs plays a critical role on the impact of NPs on the environment.

Keywords: activated sludge, aggregation, dissolution, OECD 303A, silver nanoparticles, wastewater

3.1 Introduction

The impact of urban pollution on aquatic ecosystems has been well described in the literature (Rodriguez-Narvaez et al., 2017, Gogoi et al., 2018, Taheran et al., 2018, Rathi et al., 2021). Significant loadings of point and non-point pollution, as well as inputs from wastewater treatment plants (WWTPs), have emerged as threats to the ecological values of the water ecosystems (Abdulsada et al., 2021). The most significant impacts reported refer primarily to the handling of many substances in daily life, which has resulted in the generation of a diverse variety of contaminants in urban wastewater systems. Peña-Guzmán et al. (2019), detailed categories of contaminants as compounds that are introduced into the environment, such as industrial waste compounds. The other category contains substances that have been introduced to the environment over a lengthy period and only recognized recently as contaminants. The last category has been studied and measured for some time and are recognized as having the potential negative impacts on ecosystems or humans. These contaminants were categorized into food preservatives and additives, personal care products, pharmaceuticals, etc. which all consist of nanomaterials (Adam et al., 2018, Peña-Guzmán et al., 2019, Abdulsada et al., 2021).

The impacts on urban water quality have been a major concern nanotechnology, with nanoparticles (NPs) being incorporated into various consumer products (Sharma et al., 2019, Srikanth et al., 2019, Li et al., 2020). Silver nanoparticles (AgNPs) are extensively used in several consumer products, including personal care products, home appliances, laundry additives, paints and textiles (Maynard et al., 2006, Temizel-Sekeryan and Hicks, 2020). Given the diverse application of AgNPs, there is some debate about the total amount manufactured each year, despite numerous estimations being predicted. An online inventory of nanotechnology-based consumer items cites silver NPs (AgNPs) as the largest group, making up over 50 % of all NPs produced worldwide (Temizel-Sekeryan and Hicks, 2020). As such, AgNPs will likely be released into the aquatic environment as NPs, NP aggregates or agglomerates, or soluble ions which will serve as a source of Ag exerting toxic effects on aquatic life (Zhang et al., 2018, Zhang et al., 2019). However, little is known about the impacts of AgNPs derived from wastewater effluent, although recently, few studies have been published on how to examine the release of Ag from consumer products that contain AgNPs and quantifying (Pourzahedi and Eckelman, 2015, Pourzahedi et al., 2017). The studies better enhance the knowledge of the behaviour of AgNPs in real-world situations and aid in risk evaluations. In urban waterscapes, wastewater treatment plants' effluent is regarded as a major entry or emission point for emerging contaminants into the natural environment (Furtado et al., 2016, Riva et al., 2019). As a result of this, studies have demonstrated that AgNPs, ultimately end up in the natural environment, and the silver ion (Ag^+)

produced from the AgNP negatively impact aquatic organisms (Zhang and Wang, 2019, Kusi and Maier, 2022).

Silver NPs were selected for examination in this study due to their wide use in a variety of products, and their reported occurrence and effects in environmental media. The objective of this research was to interpret the fate and behaviour of AgNPs in a simulated WWTP (SWWTP), developed in accordance of the Organization for Economic Co-operation and Development (OECD) guideline 303A (OECD, 2001). The changes in AgNPs and wastewater quality parameters when exposed to two different concentrations of AgNPs were monitored. .

Results obtained from this research could improve our understanding of the fate, transport and effects of AgNPs in wastewater, and also their potential environmental impact and risks to the aquatic environment (their final receiving point).

3.2 Materials and methods

3.2.1 Synthetic wastewater

Synthetic wastewater was prepared according to the OECD 303A guideline (Table 1). Chemicals were purchased from Merck (South Africa), Sigma-Aldrich (South Africa) and Kimix (South Africa). The synthetic wastewater served as the exposure medium in both control and test units.

Table 3.1: Composition of the synthetic wastewater

Constituent	Supplier	Concentration (mg/L)
Peptone	Merck	80
Meat extract	Kimix	55
Urea	Merck	15
Anhydrous dipotassium hydrogen phosphate	Merck	14
Sodium chloride	Merck	3.5
Calcium chloride dehydrate	Merck	2
Magnesium sulphate heptahydrate	Merck	1

3.2.2 Preparation of the AgNP suspension

Commercially available AgNP was purchased from a local supplier (Sigma Aldrich, South Africa; catalogue number 7440-22-4). It was supplied as a black powder with a purity of 99% and a specific surface area of 5.0 m^2/g, as described by the manufacturer. Two suspensions of AgNPs at concentrations of 5 and 10 mg/L were prepared by adding 0.1250 and 0.2500 g respectively of Ag nanopowder to 1 L of deionized water. Using a sonicator, the suspensions were agitated at 20 kHz for 30 min (250 W for 1 hour) to disperse the aggregates before each suspension was added to the simulated wastewater in the influent holding tanks. Each treatment (i.e. 5 and 10 mg/L) was achieved by adjusting the volume to 5 L using synthetic wastewater. The stock suspensions were stored at 4ºC and used for no more than one week.

3.2.3 Nanoparticle characterization

Nanoparticles were characterized in the virgin (pre-exposure) state and suspension. The AgNPs were characterized using different techniques, including transmission electron microscopy (TEM) and X-ray Diffraction (XRD) to establish NP morphology and chemical state, respectively. Energy dispersive X-ray spectroscopy analysis (EDS) was used to determine the elemental composition. The specific surface area of the AgNP powder was analysed by BET. For TEM imaging, samples were prepared by placing a drop of each dispersion medium on a punctured carbon-coated Cu TEM grid and drying them for several hours at room temperature prior to observation. Micrographs were carried out on a JEOL 2010 analytical TEM, which has a resolution of 0.19 nm, an electron probe size down to 0.5 nm, and a maximum specimen tilt of 108º along both axes. The instrument is equipped with an Oxford instruments LZ5 windowless energy dispersive X-ray spectrometer controlled by INCA. Similar characterization techniques were undertaken for exposed AgNPs.

3.2.4 Simulated Wastewater Treatment Plant (SWWP)

The fate and behaviour of the commercially available AgNP were assessed in a simulated wastewater treatment plant (SWWTP) using synthetic wastewater as per OECD Guideline 303A (OCED, 2001; Figure 3.1). The SWWTP consisted of three units (a control containing no NPs, and two test units (containing 5 mg/L and 10 mg/L, respectively)) which were run in parallel under identical conditions. Each unit consisted of a 5 L influent holding tank containing the synthetic wastewater, an aeration chamber with a 3 L working volume, and a settling with a 1.5 L working volume (used to separate the treated effluent (contained in a 5 L tank) from the sludge). The wastewater influent in the holding tanks was constantly stirred at 1 800 r/min using a benchtop overhead stirrer to keep the influent and its contents in suspension. Influent was fed continuously into the aeration chamber using a benchtop peristaltic pump at 0.5 L/h. The aeration chamber was aerated at a flow rate of 0.29 L/min to maintain the dissolved oxygen above 2 mg/L by using compressed air through a glass frit and continuously stirred using an overhead stirrer to ensure thorough mixing of the substrate. The influent was introduced at a constant feed flow rate of 0.5 L/h using peristaltic pumps to obtain a hydraulic retention time (HRT) of 6 h in the aeration chamber. The sludge was pumped intermittently from the settling vessel to the aeration vessel to recycle about 1-1.5 L per hour. The SWWTP was stabilized and optimized for 7 days before introducing the AgNPs. For the test unit, the influent wastewater was spiked with the test substance (AgNP) to obtain the relevant concentrations, i.e., 5 mg/L (T1) and 10 mg/L (T2). No AgNP was added to the influent of the control unit. The SWWTP was monitored daily for pH, temperature, electrical conductivity (EC) and dissolved oxygen (DO) in the influent, aeration chambers, settling vessel and final effluent and consequently sampled weekly for four weeks.

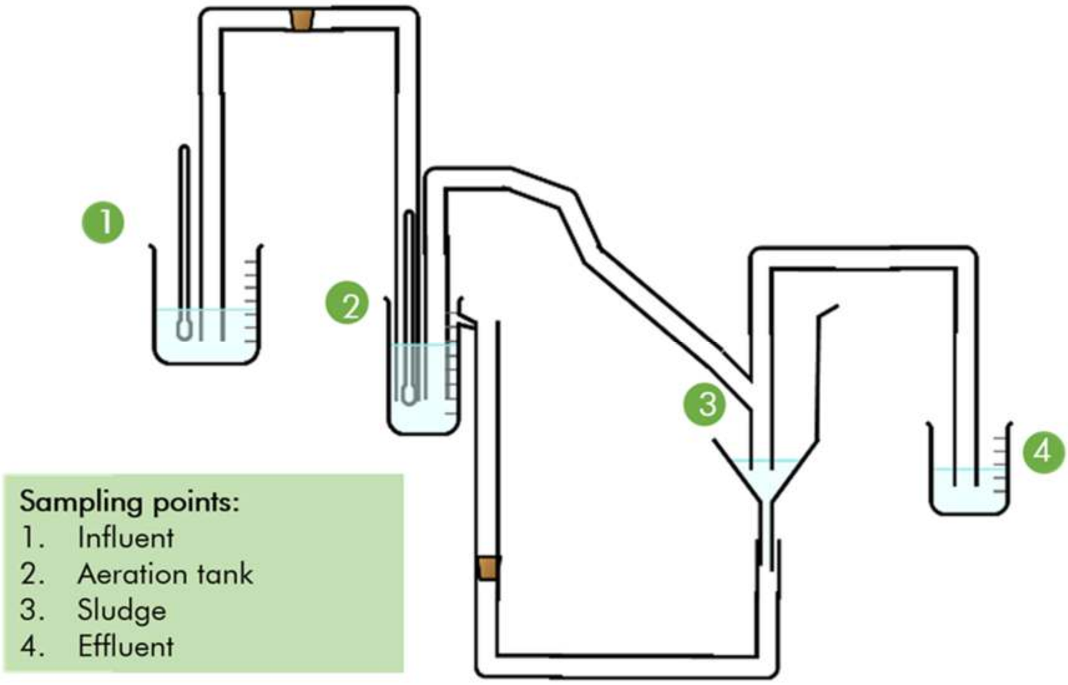

Figure 3.1: Schematic Diagram of the OECD 303A SWWTPs and the respective sampling points

3.2.5 Determination of AgNP dissolution

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, with concentrated HNO_3 under pH >2) was done to determine the dissolution of AgNPs in the wastewater. The influent and effluent were sampled weekly.

3.3 Results and Discussion

3.3.1 Initial particle characterization of the commercially manufactured pre-exposed AgNP

Characterization of the pre-exposed AgNPs indicated the formation of small loosely packed aggregates with a diameter less than 100 nm (as indicated by the SEM and TEM images in Figure 3.3). The spherical nature of the AgNP powder was also confirmed in the TEM image, while the size distribution of the particles revealed that most of the particles have a diameter of <10 nm, with only a small quantity of the larger particles in the 40-100 nm range. The EDX analysis confirmed the presence of elemental Ag, and the PXRD pattern of the AgNP was recorded between angles of 2ϴ from 3 to 90 degrees and revealed the crystalline properties of AgNP.

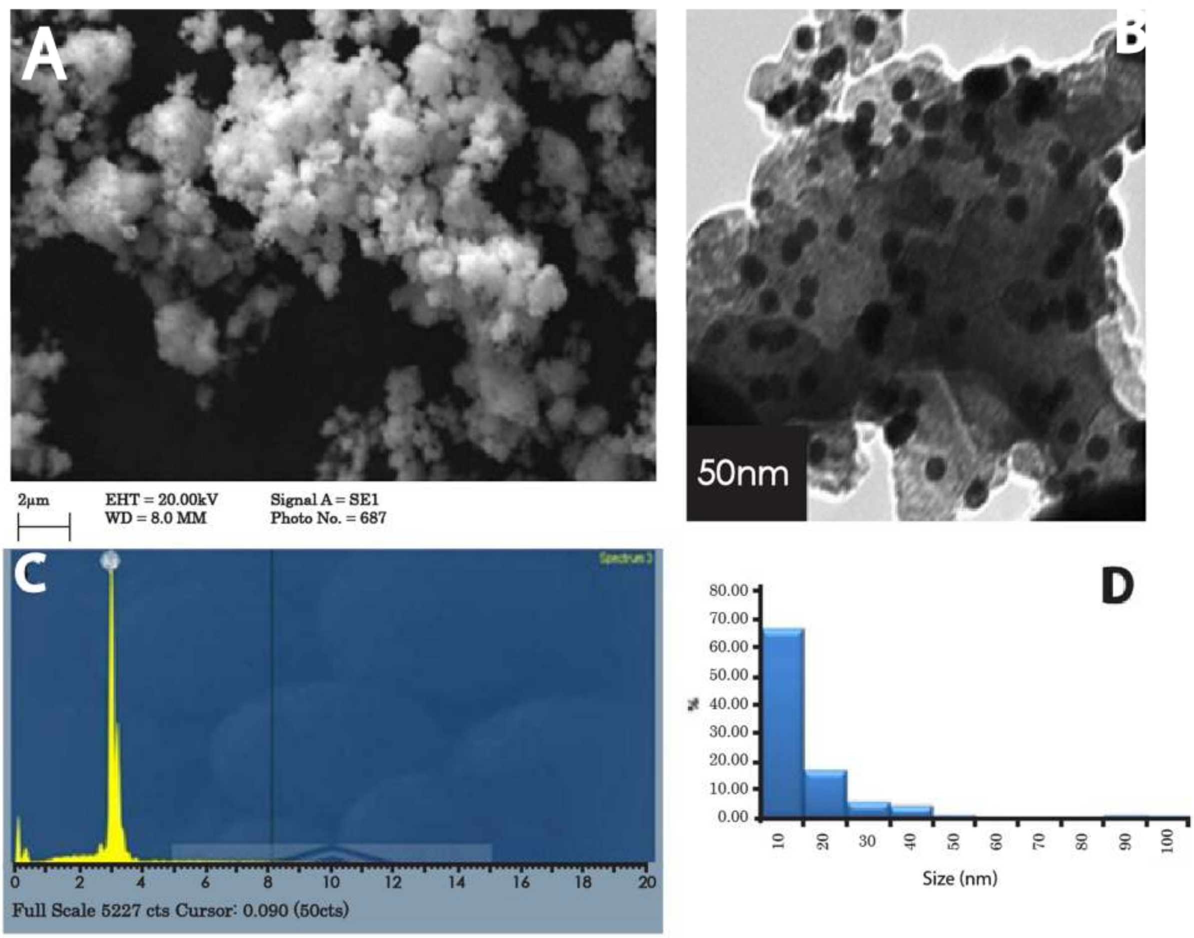

Figure 3.2: SEM image of AgNPs showing spherical particles in the order of 100 nm (A), TEM image of AgNPs (B), corresponding EDX spectrum showing elemental Ag composition (C), and the corresponding particle size distribution (n = 200) (D).

3.3.2 The fate and behaviour of AgNPs in a simulated wastewater treatment plant

The aggregation of NPs varies widely depending on the chemical environment of the media. The shape and structure of AgNPs also play an essential role in determining their environmental fate. The TEM and SEM analyses are generally used to determine the structure, size distribution and presence of AgNPs. In this study, minimal aggregation was observed in the influent of the 5 mg/L treatment (Figures 3.4 and 3.5), while larger aggregates were observed in the effluent and sedimentation tanks (i.e. in sludge). The physico-chemical nature of the synthetic wastewater is summarized in Table 3.2. Nanoparticle behavior is known to vary between neutral, acidic and alkaline conditions (Fernando and Zhou, 2019), with larger aggregates formed with lower pH. For the 5 mg/L treatment, the pH values ranged between 5 – 7 in the influent, neutral in the aeration chamber and activated sludge, and >8 in the effluent. TEM images obtained for the influent (at pH 5-7, acidic to neutral) depict more stabilized individual particles compared to the images obtained at alkaline conditions. TEM imaging at higher pH indicates that the AgNPs aggregated in clusters. As such, a positive correlation between pH and NP aggregate size was observed. This is in contrast to what is generally reported, and suggests that other factors could influence NP morphology. It can be concluded that the decreased aggregation / increased aggregation to the quantity of AgNP concentration present in the solution. It is critical to understand how AgNPs dissolve in order to understand their environmental behaviour and fate. Once released into the wastewater system, AgNPs undergo oxidative dissolution, which typically results in the formation of Ag^+. According to Badawy et al. (2010), the stability of AgNPs in wastewater correspond with their dissolution. The corresponding ICP-OES results (Figure 3.5) indicates that the Ag concentration was largely contained in the effluent and sludge. Gartiser et al. (2014) reported that the metal content in the effluent is largely influenced by the content of suspended solids in the effluent (sludge overflow). This was confirmed in the current study as TSS was positively correlated to Ag (R^2 = 0.86; Figure 3.6). This observation potentially poses environmental implications considering that effluents are mostly released into freshwater resources and sludge is often applied in agricultural soils (similar results have been reported by Mahlalela et al. (2017), and Simelane and Dlamini (2019)). While Musee et al. (2014) reports an inverse relationship between metal concentration and pH, the current study reports weak positive correlations (R^2 = 0.5), which suggests that an increase in metallic concentration is proportional to an increase in pH which can be observed between the 10 mg/l and 5 mg/l concentration of AgNP; where the pH value for the 10 mg/l is slightly higher than the 5 mg/l.

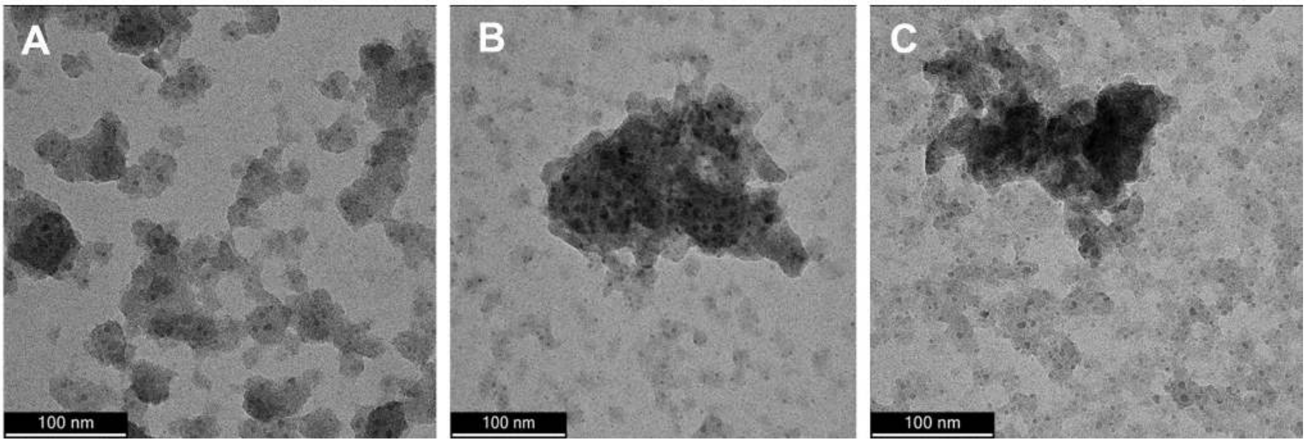

Figure 3.3: TEM image of the AgNPs 5 mg/L treatment at A) influent, B) Settlement vessel, and C) effluent

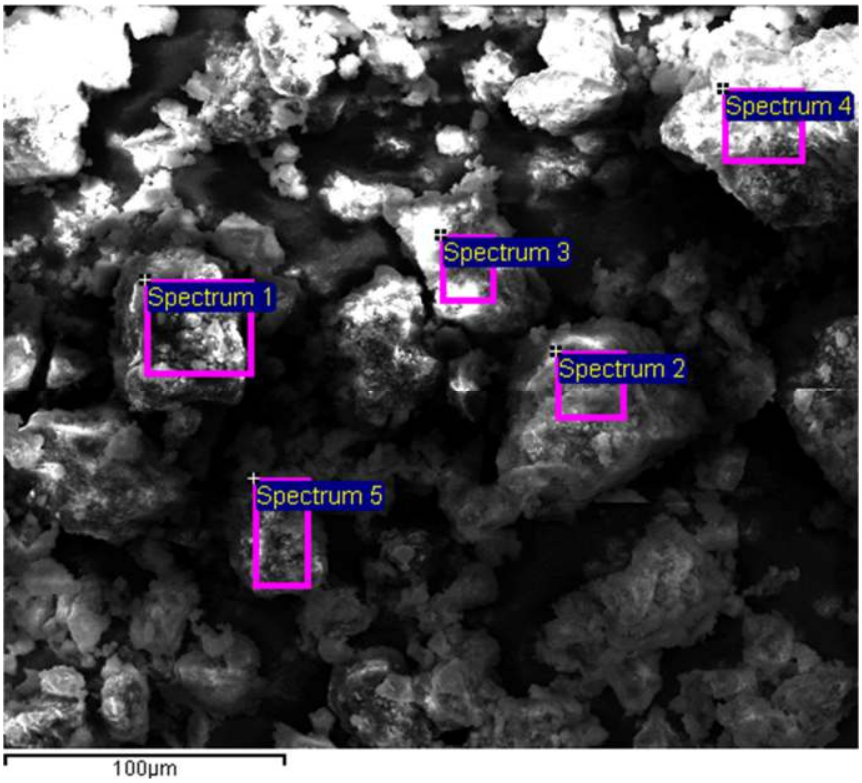

Figure 3.4: SEM image of AgNPs powder exposed to the activated sludge in the wastewater system (5mg/l dosage)

Table 3.2 Summary of wastewater characteristics in the 5 mg/L treatment

	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Influent							
pH	5.89	5.92	6.4	6.6	6.85	7.14	5.84
Salinity	2.27	2.33	2.74	2.8	2.98	3.4	3.28
Conductivity	3.7	4.24	5.4	5.65	5.84	6.62	6.44
TSS	3.21	3.27	3.84	4	4.16	4.71	4.57
DO	1.9	1.6	1.3	2	1.5	1.8	0.6
COD	3557	3584	3558	3650	3420	3670	4869
T(°C)	19.8	20	18.6	19.36	18.9	15.6	21
Aeration chamber							
pH	6.09	6.17	7.6	7.9	8.08	8.27	7.08
Salinity	2.33	2.3	4.4	4.36	4.35	4.53	2.26
Conductivity	4.63	4.64	8.41	8.35	8.35	8.66	4.6
TSS	3.28	3.07	5.97	5.93	5.92	6.15	3.25
DO	2.3	3.23	4.6	2.24	2.4	2.8	1.9
COD	2520	2514	2498	2580	2486	2540	-
T(°C)	18.6	18.5	18.6	18.7	18.5	18.5	21.9
Settling vessel							
pH	7.02	6.98	7.01	7.08	6.95	7.12	7.9
Salinity	3.23	3.15	3	3.36	3.58	3.6	4.56
Conductivity	5.8	6	6.23	6	6.38	6.58	6.54
TSS	4.56	4.23	4.15	4.43	3.98	4.25	5.45
DO	2.1	1.9	2.3	2	2.4	2.6	2.1
COD	-	-	-	-	-	-	-
T(°C)	21	21.1	21.3	21.8	22	21.5	19.8
Effluent							
pH			8.04	8.23	8.34	8.35	7.68
Salinity			4.38	4.42	4.64	4.77	4.58
Conductivity			8.41	8.46	8.92	9.14	8.78
TDS			5.98	6	6.31	6.47	6.23

DO			5.6	4.5	3.2	3.9	3.5
COD			2266	2242	2243	2240	2295
T(°C)			20.1	21.1	20.8	19.8	20.2

The pH in the influent ranged between 5-7, while the pH value in the activated sludge and effluent ranged 7-8, which can be considered as another attribute that contributed to the formation of larger AgNP aggregates; this phenomena was reported elsewhere by Fernando and Zhou (2019), which was discussed in their findings that at acidic and neutral pH values there was larger and higher rate of aggregate formed.

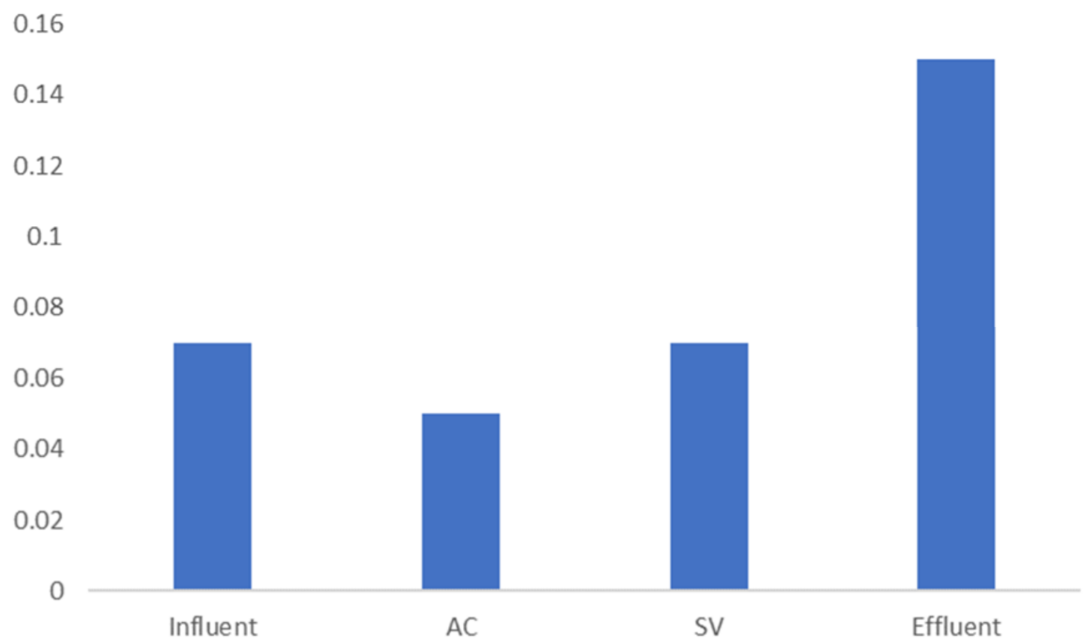

Figure 3.5: ICP-OES results of silver measured in the influent, aeration chamber (AC), settlement vessel (SV) and effluent in the 5 mg/L treatment

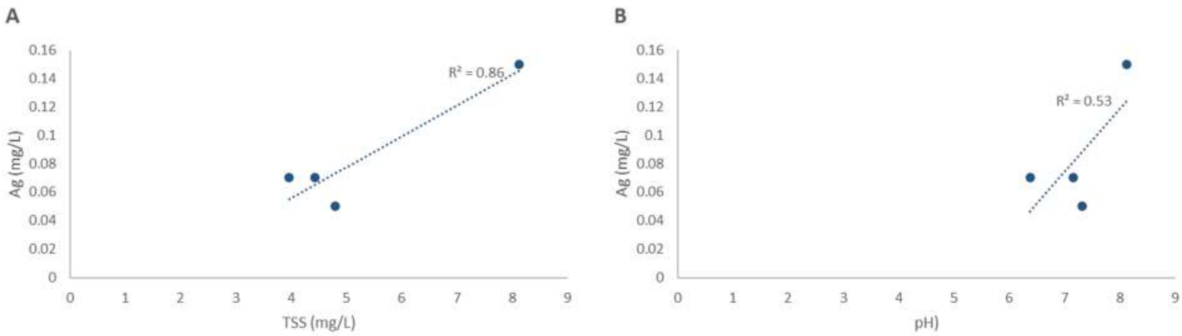

Figure 3.6 Correlation of Ag and TSS (A), and Ag and pH (B)

The physico-chemical nature of the synthetic wastewater for the 10 mg/L treatment is summarized in Table 3.3. Slightly lower pH values in the 10 mg/L treatment were recorded compared to the 5 mg/L, which could explain the larger aggregates observed in the TEM images (Figure 3.7). In addition, the larger aggregates formed in the 10 mg/L could be due to the concentration-dependent affects. This observation was reported in other published studies which investigated the effect of NP concentration on dissolution and aggregate size. For example, Baalousha (2009) reported smaller aggregates at lower iron oxide NP concentrations, while Baek (2011) reported a decrease in the solubility of copper oxide, zinc oxide and nickel oxide NPs increased NP concentrations. The corresponding ICP-OES results (Figure 3.9) indicate that Ag was largely contained in the effluent and sludge, similar to what was observed in the 5 mg/L. However, in contrast to the 5 mg/L treatment, the 10 mg/L treatment showed an inverse relationship between metal concentration and pH (Figure 3.10); as observed by others (Musee et al., 2014).

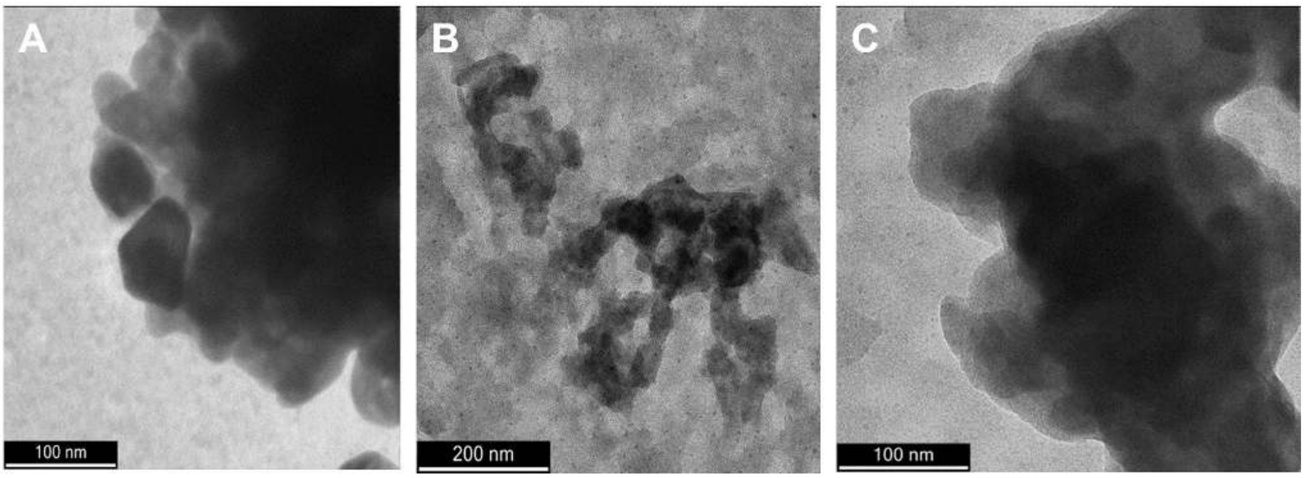

Figure 3.7: TEM image of AgNP in the 10 mg/L treatment at (A) influent, (B) settlement vessel, and

(C) effluent

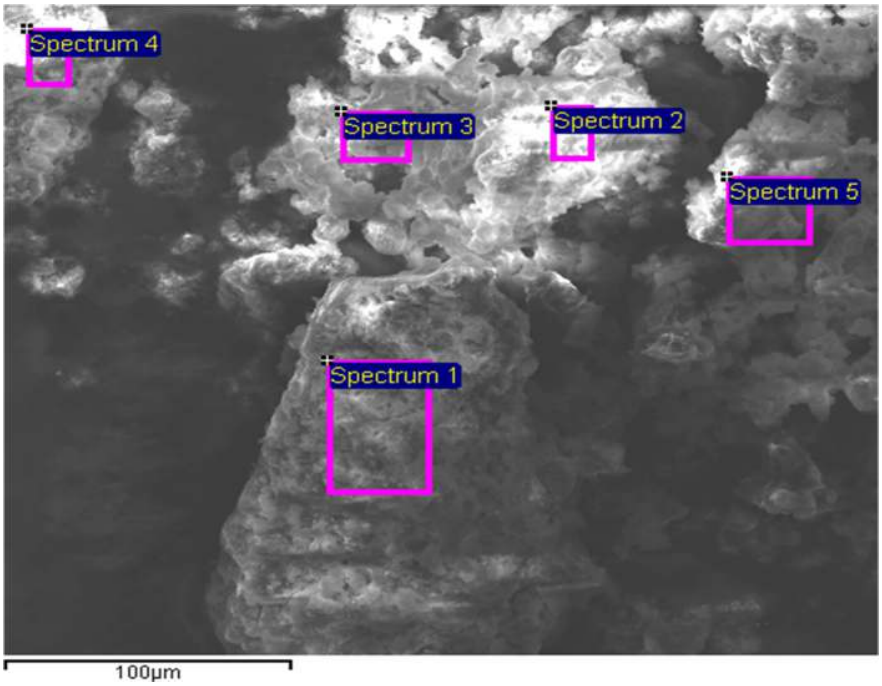

Figure 3.8: SEM Image of AgNP exposed to the activated sludge in the wastewater system (10 mg/l dosage)

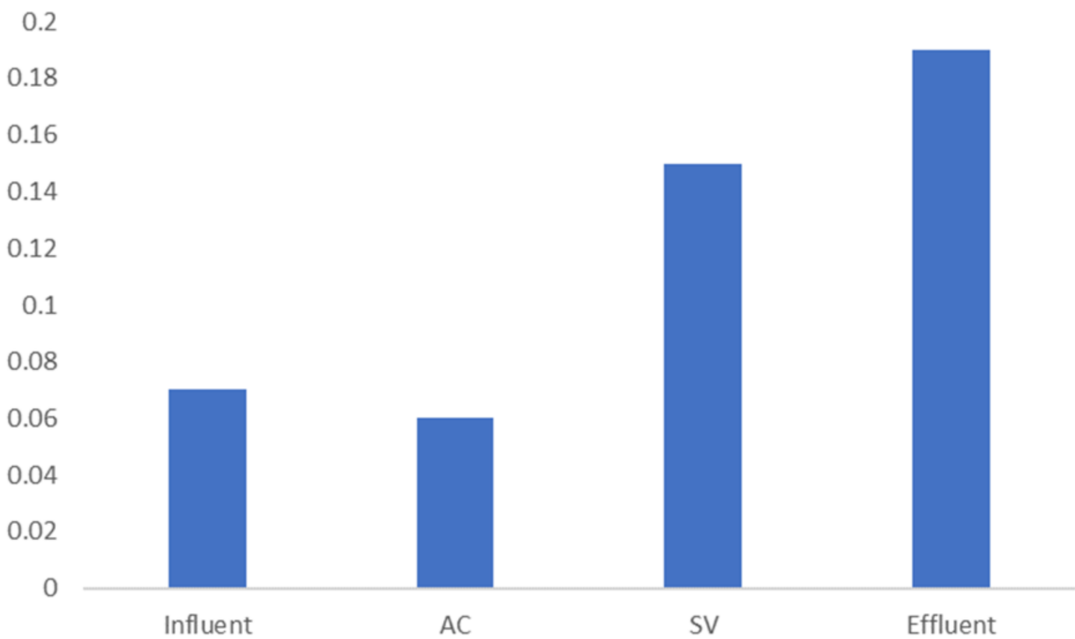

Figure 3.9: ICP-OES results of total Ag (TotAg) measured in the influent, aeration chamber (AC), settlement vessel (SV) and effluent in the 10 mg/L treatment

Table 3.3 Summary of wastewater characteristics in the 10 mg/L treatment

	Day 1	**Day 2**	**Day 3**	**Day 4**	**Day 5**	**Day 6**	**Day 7**
Influent							
pH	5.88	5.9	6.32	6.5	6.7	6.84	5.83
Salinity	2.87	2.78	3.15	3.26	3.33	3.53	3.23
Conductivity	5.65	5.49	6.21	6.35	6.54	6.9	6.3
TSS	4.02	3.9	4.4	4.52	4.62	4.88	4.47
DO	1.2	1.4	1.9	1.5	1.3	1.6	1.3
COD	3444	3417	3428	3426	3510	3436	3980
T(°C)	19.2	19.5	19.5	19.7	19.6	19.4	19.1
Aeration chamber							
pH	6.1	6.21	7.26	7.48	7.73	7.82	5.87
Salinity	2.92	2.87	4.48	4.45	4.56	4.67	3.84
Conductivity	5.7	5.64	8.55	8.56	8.67	8.86	7.45
TSS	4.06	3.99	6.06	6.07	6.17	6.32	5.28
DO	7.35	5.36	3.25	4.36	2.3	3.6	2
COD	-	-	-	-	-	-	-
T(°C)	19.6	18.9	19.4	19.6	19.5	19.6	18.9
Settling vessel							
pH	7.28	7.33	7.34	7.4	7.52	7.51	6.23
Salinity	3.48	3.68	3.56	3.54	3.58	3.6	3.78
Conductivity	6.23	6.05	6.15	6.25	6.18	6.19	7.42
TSS	4.59	4.58	5	5.02	5.15	4.6	4.56
DO	2.1	2	1.9	2.1	2.3	2.2	2.1
COD	-	-	-	-	-	-	-
T(°C)	19.8	19.5	19.6	19.9	20.1	21	19.5
Effluent							
pH	-	-	7.68	7.88	7.9	8.06	6.48

Salinity	-	-	4.58	4.61	4.78	4.97	3.86
Conductivity	-	-	8.78	8.91	9.21	9.54	7.48
TDS	-	-	6.23	6.32	6.48	6.77	5.37
DO	-	-	3.5	2.9	3	4.5	2.3
COD	-	-	2295	2322	2360	2345	2410
T(°C)	-	-	20.2	19.8	21	19.6	19.8

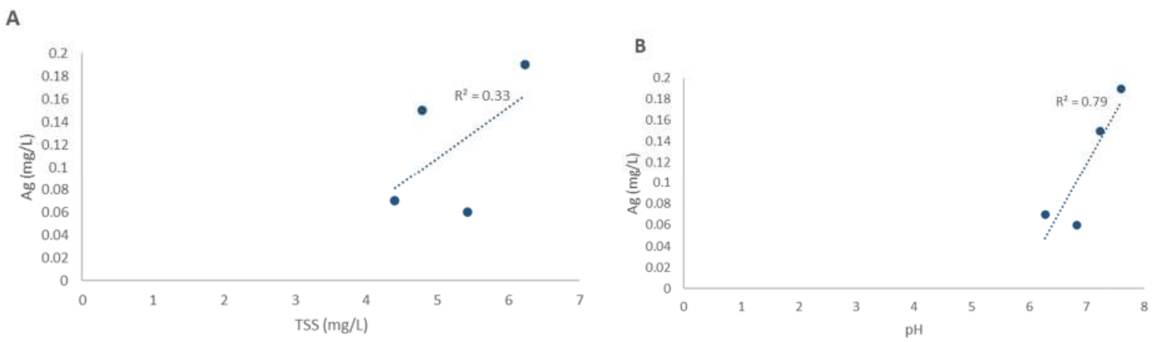

Figure 3.10 Correlation of Ag and TSS (A), and Ag and pH (B)

3.4 Conclusions

The results obtained in our study suggest that the OECD 303-A testing guideline is applicable for assessing the fate, transport and transformation of NPs. The monitored physico-chemical properties of the synthetic wastewater proved to influence the NP characteristics. Larger aggregates were observed in the 10 mg/L treatment when compared to the 5 mg/L, and suggests that more particles in the solution providing a higher total AgNP surface area for the particles to interact. Aggregation of ENPs is a key factor that influences the behaviour, fate and toxicity of NPs in the aquatic environment. Furthermore, the release of Ag from AgNPs in wastewater was more significant under acidic conditions in the 10 mg/L treatment when compared to the 5 mg/L treatment. The OECD-based SWWTP resulted in significant Ag in the effluent and retained in the sludge, in both treatments. Nanoparticles received by wastewater treatment plants will therefore reach the environment through wastewater release and sludge application.

3.5 Acknowledgements

This research was supported by the National Research Foundation (NRF) Thuthuka Grant No.

TTK170418227366. The authors wish to thank the valuable comments from the anonymous reviewers.

3.6 Conflict of interest

The authors report no conflicts of interest and are responsible for the content and writing of the article.

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CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1 General Conclusion

The ever-increasing production of consumer products containing NMs are raising concerns about the potential negative effects of human exposure to NMs. The dangers of NMs fate and behaviour in the environment are often unpredictable and challenging to quantify. The wastewater and aquatic ecosystem are susceptible to the effects of NPs because it is the main end-point receiver of ECs.

The aims of this study was to (1) determine whether the AgNPs undergo any physical or chemical changes when exposed to simulated wastewater, and (2) to assess the fate and behaviour of AgNPs in wastewater sludge from a SWWTP. The fate and behaviour of AgNPs in wastewater were found to be impacted upon by synthetic wastewater characteristics as well as NP concentrations.

The study utilized an OECD-based SWWP to investigate the fate and behaviour of AgNPs. Two AgNPs concentrations (i.e. 5 mg/L and 10 mg/L) were prepared and changes in their physicochemical properties as well as effects on the synthetic wastewater chemistry were assessed and was observed that larger aggregates were formed and a rapid dissolution rate was observed in the 10 mg/L treatment when compared to the 5 mg/L treatment. Although these observations can be explained by the nature of the experimental medium (i.e. synthetic wastewater characteristics), previous research has also highlighted the significance of NP concentration-dependent effects on aggregation and dissolution.

This study also reports on significant Ag concentrations measured in the effluent and sludge which have environmental implications. In conventional wastewater treatment systems (WWTW), NM are likely to be introduced into the environment through the release of ill-treated effluent to aquatic resources, as well as during the use of sludge for agricultural purposes.

4.2 Recommendations

The objectives of this research were achieved based on the results obtained. However, gaps have been identified for future work, as follows:

1. This study assessed the fate, and behaviour of AgNPs commonly used in commercially available products. Future studies should investigate the pathways and toxicity mechanisms of commercially available nano-enabled products to assess whether a risk to environmental and human health exists.
2. The significant Ag concentrations present in the sludge and effluent suggests that further treatment process would require additional steps to remove the metals, especially considering that in excess of 90% of sludge from conventional WWTPs is utilized for agriculture.
3. Further work is required to assess the possible long-term effects of accumulation of NMs in landfills.
4. Further work to focus the development of appropriate methodologies for the removal of NPs before the disposal.

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APPENDICES

APPENDIX A: Description of Database

Table A.0.1: Description of Database

Nanoparticles (NP)	Mechanism Process	Environmental Condition	References
ENPs	Behaviour, fate and transformation	Aggregation, dissolution and sedimentation	(Abbas et al., 2020)
Ag	Toxicity	Nematode DNA damage	(Ahn et al., 2014)
Ag, ZnO, CuO, TiO2	Toxicity	Growth Inhibition	(Asadishad et al., 2018)
NPs	Behaviour	Aggregation and agglomeration	(Ashraf et al., 2018)
Vinyl Chloride	Toxicity	Growth Inhibition and cell damage	(Atashgahi et al., 2015)
Ag	Behaviour	Aggregation and dissolution	(Axson et al., 2015)
graphene oxide	Behaviour	Sedimentation and aggregation	(Babakhani et al., 2018a, Babakhani et al., 2018b)
TiO2	Toxicity	Zebrafish DNA damage	(Bar-Ilan et al., 2013)
Ag	Toxicity	enzymatic and growth inhibition	(Barker et al., 2018)
NPs	Fate and behaviour	Aggregation, Dissolution and Sedimentation	(Batley and McLaughlin, 2010)
ZnO	Behaviour	Dissolution and aggregation	(Bian et al., 2011)
AgNP	Toxicity	Respiratory Organ Stress (ROS) and Cell Damage	(Bilberg et al., 2010)
Ag	Toxicity	Acute toxicity to Daphnia magna	(Blinova et al., 2013)
Metal NPs	Fate, behavior and impact	Release of NPs into the Aquatic environment Inhibition of organism growth	(Brar et al., 2010)
Ag, ZnO	Fate and Behaviour	Transport of NPs into aquatic ecosystem Transformation of Ag and ZnO into sulphides (AgS, ZnS)	(Brunetti et al., 2015)
NPs	Fate, behaviour and Impact	Transformation of NPs when discharged into the ecosystem	(Bundschuh et al., 2018)
AgNP	Toxicity	Cell and DNA damage in Japanese medaka	(Chae et al., 2009)
ZnO	Behaviour	Increase in particle sizes Stability is influenced by NOM, pH and Ionic Strength	(Chaúque et al., 2014)
TiO2	Application	-	(Chen and Mao, 2007)
AgNP	Behaviour and Toxicity	Acute toxicity to zebrafish embryo	(Chen et al., 2020)
Cu	Transformation	Aggregation and dissolution	(Conway et al., 2015)
Cu	Transformation	Dissolution and desorption	(Duncan and Pillai, 2015)
ZnO	Transformation	Sorption and Dissolution	(Elhaj Baddar et al., 2019)

NP	Fate	Transport	(Fairbairn et al., 2016)
Ag	Behaviour	Aggregation, Dissolution	(Fernando and Zhou, 2019)
Ag	Fate and Transformation	Agglomeration and dissolution of NPs upon exposure to surface water	(Furtado et al., 2016)
Ag	Fate, Behaviour and Removal	95% AgNP was removed and less than 8% present in the effluent system	(Gagnon et al., 2021)
NP	Transformation	Sedimentation	(Ganguly and Chakraborty, 2011)
TiO2	Behaviour and Removal	95% removal of TiO2 NPs in the wastewater treatment system	(Gartiser et al., 2014)
TiO2	Application	-	(Gharbani et al., 2011)
Ag, SiO_2, CeO_2	Fate and Impact	Release of NPs into the freshwater and low risk of harmful effect on organism	(Giese et al., 2018)
CuO, Ag	Genotoxicity	DNA damage	(Gomes et al., 2013)
CeO_2	Fate and Removal	96.6% removal of CeO_2 NPs	(Gómez-Rivera et al., 2012)
TiO2, ZnO, Ag, CNT, Fullerenes	Fate	Potential release into surface water	(Gottschalk et al., 2009)
Magnetic	Application	-	(Gubin et al., 2005)
Ag	Behaviour and Toxicity	Aggregation and dissolution	(Gunsolus et al., 2015)
TiO_2	Transformation and Toxicity	Aggregation and sedimentation Reduction in toxicity towards aquatic animal	(Gupta et al., 2019)
Carbon, Fullerene	Behaviour	Sorption	(Gupta and Saleh, 2013)
Ag	Behaviour and Toxicity	Release of Ag^+, a key factor in influencing AgNP toxicity	(Gwin et al., 2018)
FeO, Ag	Toxicity	Inhibition of microbial metabolic activities	(He et al., 2016)
NP	Impact	Potential adverse effect on microbial activity	(Hegde et al., 2016)
TiO_2	Transformation	Aggregation of TiO_2NPs	(Herchenova et al., 2020)
Ag	Toxicity	RNA polymerase damage	(Hou et al., 2017)
TiO2	Impact	Gene alteration and induced neurotoxicity	(Hu et al., 2017)
Ag	Application	-	(Hu, 2010)
Ag, ZnO, TiO_2, graphene oxide, Carbon nanotubes	Fate, behaviour, and transformation	Acute toxicity to aquatic organisms	(Jahan et al., 2017)
ZnO	Transformation	Dissolution of NPs	(Jiang et al., 2015)
Ag	Toxicity	Respiratory organ stress	(Jiang et al., 2014)
Ag	Toxicity	Acute toxicity towards Japanese medaka	(Kim et al., 2013)
ZnO	Toxicity	Mitigates hatching rates of embryos	(Kteeba et al., 2017)
Ag	Toxicity and Behaviour	Low level of toxicity towards freshwater amphipod	(Kühr et al., 2018)
Ag	Impact and fate	Stability of AgNP is enhanced by humic substance in soil matter	(Kulikova et al., 2020)
TiO_2, Fullerenes	Fate and Behaviour	Discharge of NPs into the surface water and potential source of contaminant	(Kunhikrishnan et al., 2015)

ZnO, FeO	Behaviour and Toxicity	Ecotoxicity is influenced by aqueous media physicochemical properties	(Leareng et al., 2020)
Ag	Impact	Acute toxicity towards Japanese medaka	(Lee et al., 2014)
Ag	Fate and transport	Potential source of NP discharge into surface water	(Li et al., 2013a)
Ag	Fate and Transport	Potential source point of NP discharge into surface water	(Li et al., 2016)
Graphene oxide	Transformation	Aggregation and sedimentation	(Li et al., 2019)
TiO_2	Application	-	(Lim et al., 2014)
Fluoride	Transformation	Dissolution of NPs	(Lisjak et al., 2015)
CuO, ZnO	Transformation	Aggregation, dissolution, and sedimentation of NPs	(Liu et al., 2018b)
ZnO	Fate	Transformation of NPs	(Lombi et al., 2012)
Ag	Transformation and Impact	Dissolution of NPs	(Loza et al., 2014)
NP	Fate, transport and Impact	Discharge of NPs into the environment and potential for acute toxicity	(Malakar et al., 2021)
NPs	Transformation	Aggregation and sedimentation of NPs	(Markus et al., 2015)
Ag	Fate and Impact	Potential source point of contaminant	(McGillicuddy et al., 2017)
CuO	Removal and Transformation	Aggregation of CuONPs exposed to wastewater systems	(Miao et al., 2016)
Ag, magnetite	Impact	Inhibition of ammonia oxidizing bacteria	(Michels et al., 2017)
NP	Transformation and Impact	Dissolution of NPs	(Misra et al., 2012)
Ag	Behaviour and Transformation	Dissolution of AgNPs	(Molleman and Hiemstra, 2015)
CuO, ZnO	Impact	Acute toxicity of CuO and ZnO NPs towards aquatic organisms	(Mortimer et al., 2010)
TiO_2	Impact	Reduction of peroxidase activity in plants	(Movafeghi et al., 2018)
TiO_2	Transformation, behaviour and Impact	Agglomeration of TiO_2NPs	(Murugadoss et al., 2020)
Ag, ZnO	Fate and Behaviour	Aggregation and dissolution of NPs when exposed to sewage water	(Musee et al., 2014)
NMs	Behaviour and Impact	Aggregation of NPs in surface water	(Navarro et al., 2008)
ZnO	Fate and Impact	Methanogenic inhibition over extensive exposure period	(Otero-González et al., 2014)
Ag	Impact and Behaviour	Ecotoxicity	(Oukarroum et al., 2014)
ZnO	Behaviour	-	(Ouyang et al., 2017)
Ag	Fate	-	(Panyala et al., 2008)
NP	Removal	-	(Park et al., 2017)
NMs	Fate	-	(Peijnenburg et al., 2015)
NMs	Removal	-	(Pendergast and Hoek, 2011)
ZnO	Behaviour	The stability of NPs is influenced by pH	(Peng et al., 2017b)
Ag	Transport	Source point of NP as ecological contaminants	(Pourzahedi and Eckelman, 2015)
NM	Transformation	Aggregation and sedimentation of NPs in natural water	(Quik et al., 2014)
Ag	Fate and Behaviour	-	(Raza et al., 2016)

TiO_2	Transformation and Behaviour	Aggregation of TiO_2 NPs in sewage effluent	(Ren et al., 2017)
Ag	Impact	Acute toxicity of AgNPs	(Scown et al., 2010)
ZnO	Impact	Acute toxicity of ZnO NPs towards soil organisms	(Shen et al., 2015)
Ag	Fate and Behaviour	-	(Shevlin et al., 2018)
Ag	Transformation	Aggregation, dissolution and sedimentation of AgNPs	(Stebounova et al., 2011)
Au	Fate	-	(Surette et al., 2021)
NP	Behaviour	-	(Surette et al., 2019)
NM	Removal	-	(Tang et al., 2014)
Ag	Impact	-	(Throbäck et al., 2007)
Cd	Impact	Gene alteration and ROS in Zebrafish embryos	(Tian et al., 2019)
NP	Impact	-	(Tiede et al., 2016)
NM	Transformation and Impact	Dissolution	(Utembe et al., 2015)
TiO2	Impact	ROS and protein ligand alteration	(Verma et al., 2018)
Ag	Transformation	Aggregation and dissolution of NPs exposed to surface water under different environmental conditions	(Walters et al., 2013)
Ag	Impact	Acute toxicity of NPs	(Walters et al., 2014)
TiO_2	Impact	Aggregation of NPs	(Wang et al., 2021)
Ag, TiO_2, Fullerene	Fate and Impact		(Wang et al., 2012)
Ag	Impact	-	(Wijnhoven et al., 2009)
Silicon Oxide	Behaviour	-	(Wu et al., 2016)
FeO	Removal	-	(Xu et al., 2012)
Metal	Fate	-	(Yang et al., 2014)
Ag	Impact	Acute toxicity of AgNPs to fish gills	(Yue et al., 2015)
Ag	Impact	Acute toxicity of AgNPs to fish gills	(Yue et al., 2017)
NP	Transformation	Aggregation	(Zare, 2016)
NM	Fate and Transformation	Dissolution	(Zhang et al., 2015)
CuO, ZnO, and TiO_2	Impact, Behaviour and Fate	Inhibition of ammonia oxidizing bacteria activity	(Zhang et al., 2018b)
CuO	Impact	Acute toxicity towards zebrafish embryos	(Zhang et al., 2018c)
ZnO, TiO_2	Behaviour and Transformation	Dissolved organic matter contributes to stability of NPs	(Zhou et al., 2015)