THE EFFECTIVENESS OF *Vitis vinifera* (GRAPE) LEAF LITTER TO REMOVE U.S. EPA PRIORITY PHENOLS FROM SIMULATED AND INDUSTRIAL WASTEWATERS

By

WASIU OLALEKAN AFOLABI

Thesis submitted in fulfilment of the requirements for the degree

Master of Technology: Chemistry

in the

Faculty of Applied Sciences

at the

Cape Peninsula University of Technology

Supervisor: Prof Beatrice O. Opeolu
Co-supervisors: Prof Olalekan S. Fatoki
Prof Bhekumusa J. Ximba

Cape Town
September 2014

DECLARATION

I, Wasiu Olalekan Afolabi, declare that the contents of this thesis represent my own unaided work, and that the thesis 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 of Technology.

Signed **Date**

ABSTRACT

This study sought to prepare and characterise activated carbons from *Vitis vinifera* (grape) leaf litter, and assess the efficiency and potential application of the adsorbent for the removal of four phenolic compounds (phenol (P), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2-chlorophenol (2-CP)) from synthetic and industrial wastewaters.

Vitis vinifera (grape) leaf litter (GL) was obtained locally, and washed, dried and pulvirized. Chemically activated carbons were prepared using H_3PO_4 (GLA) and NaOH (GLB). The adsorbents were characterized with SEM, FTIR, EDX and proximate analysis was also carried out. Phenols were extracted from water samples with SPE and analysed with HPLC. The prepared adsorbents were used in sorption of phenols from simulated phenolic wastewaters for optimization of adsorption. Optimal adsorption conditions were then applied for removal of phenols from wastewater samples collected from influents of treatment plants. Column and desorption studies were also carried out.

The surface texture and morphology micrographs (using SEM) of the prepared materials/adsorbents showed that the prepared activated carbons possess improved pore structure, cavities and heterogeneous irregular surfaces capable of providing enhanced adsorption. EDX spectroscopy was used for elemental microanalysis and showed that the major constituent of the adsorbent is carbon. FTIR analysis revealed changes and absorption waveband drifts of surface functional groups after activation and adsorption. The proximate analysis of the prepared precursors demonstrated good quality of the active carbons. They had low moisture content (< 12%) and their inorganic matter content (ash) was less than 9% for the three sorbents. Iodine number value of the adsorbents was 342, 1065, and 571 mg/g for GL, GLA and GLB respectively.

Excellent recoveries (92.60 – 102.85%) were obtained for the phenolic compounds (P, 2-NP, 4-NP and 2-CP) using polymeric SPE cartridges.

Phosphoric acid activation yielded the most efficient activated carbon material relative to the non-treated biomass and those chemically activated with NaOH. Percentage removal was 92.70%, 99.92%, 99.98% and 99.90% for P, 2-NP, 4-NP and 2-CP respectively using GLA. Optimal pH for adsorption was 8, 4 and 7 for GLA, GLB and GL respectively at an equilibration time of 240 min.

The evaluation of adsorption kinetics showed the adsorption process of GLA and GLB followed a pseudo-second order kinetic model while adsorption using GL was best described by intraparticle diffusion model. Adsorption equilibrium data were well fitted with Freundlich isotherm model for all three adsorbents.

Adsorption capacity of GLA (for removal of phenols) was found to decrease with increase in temperature. In contrast, the sorption efficiency of GL and GLB increased when temperature was increased. Thermodynamic parameters of adsorption (ΔG^o, ΔH^o & ΔS^o) were evaluated. Results revealed favourability and exothermic nature of adsorption of the phenols using GLA. Adsorption processes using GLB and GL were spontaneous and endothermic.

Vitis vinifera leaf litter yielded good activated carbons and was effective in remediation of P, 2-NP, 4-NP and 2-CP from contaminated wastewaters.

ACKNOWLEDGEMENTS

I express thanks to:

- Almighty Allah, the Most Beneficent and Merciful, for His abundant grace, protection and guidance over the years and through the entirety of this study.

- My adept supervisor, Professor Beatrice O. Opeolu, for her devoted time, excellent guidance and patience throughout this research project.

- My proficient co-supervisors, Professor Olalekan Fatoki and Professor Bhekumusa J. Ximba for their guidance, contributed knowledge and support.

- Dr Olatunde S. Olatunji for his assistance in every step of this work, and for his moral encouragements during my stay in the Republic of South Africa.

- The technical staff of Analytical Chemistry Laboratory, Cape Peninsula University of Technology; Ms Mthembu Zandile for her co-operation in acquiring chemicals and guidance in the laboratory; Gillian Fanesy-Yon who mentored and trained me on HPLC; and Dr. Khanyisa Nohako for her willingness and readiness to assist at all times in the research laboratory.

- The head of oxidative stress research institute, CPUT, Professor Marnewick; and the laboratory staff, Mr R. Fanie and Mrs Olivia Parbunath for their support during sample assays.

- Mr Adrian Joseph at electron microscope unit, University of the Western Cape, and Ms Madelaine Franzenburg at imaging unit, Central Analytical Facilities, Stellenbosch University, for their help during sample analysis.

- The entire staff of Chemistry department, CPUT. Special thanks to Mrs Dawn Petersen and Mr Rafeeq Adams for their support during my programme. Also, thanks to Mr Solomon, Mrs Le Reoux, Dr Francois Wewers, and Mrs Shaheedah Adonis, for their kind gestures and academic enlightenments.

- The Cape Peninsula University of Technology, for granting University Research fund. Opinions expressed in this thesis and the conclusions arrived at, are those of the author, and not necessarily to be attributed to the Cape Peninsula University of Technology.

- My residence manager, Mrs Sharon Du Plesis and her family for their assistance, acceptance, and creating an enabling living environment.

- My parents, Mr Ishaq Afolabi and Mrs Ramat Afolabi, for their unwavering parental affection, financial support and serial advice ever before and throughout this study.

- My siblings, Abdul'Azeez, Aminat, Nusroh and Lateefah for their love and support.

- The families of Dr Hussein Okoro, Dr AMO AbdulRaheem, and my mentor, Professor F.A. Adekola, for their sustained support.

- My colleagues, Mr Zachariyah Jaji, Mr Adekola Olawale, Mr Omoniyi Oluseyi, Ms Elizabeth Omodanisi, Mr Erick Omollo, Mr Julius Oluwaseyi, Mr Imisi Akinyede, Mr Adeyi Oladayo, Ms Motulli Kweza and Ms Bukola Solanke, who were all more than friends for aiding me during my study, and in particular, for their support during my recovery (post - surgical) period. Thank you, wishing all of you the best in life.

- The staffs of Fundani student learning centre, CPUT for their cordial assistance and continual support at all times. Special thanks to Dr S Siyepu, Ms Jean Collins, Ms Omores Raissa and Ms Dorcas Zide, for their support.

- The members of Cape Town Dua group, for their frequent prayers and spiritual support. May Allah answer our prayers and ease our affairs, amen.

DEDICATION

To

Almighty Allah (S.W.T.)

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GLOSSARY

Terms	Definition/Explanation
ΔG^o:	Standard Gibbs free energy
ΔH^o:	Standard enthalpy change
ΔS^o:	Standard entropy change
2-CP:	2-Chlorophenol
2-NP:	2-Nitrophenol
4-NP:	4-Nitrophenol
AC:	Activated Carbon
BPA:	Bisphenol-A
DWAF:	Department of Water Affairs and Forestry
EDX:	Energy-dispersive X-ray spectroscopy
EU:	European Union
FTIR:	Fourier transform infrared spectroscopy
GC:	Gas Chromatography
GL:	Non-activated leaves of grape (*Vitis vinifera*) leaves
GLA:	Phosphoric acid – activated carbons from grape (*Vitis vinifera*) leaves
GLB:	Sodium hydroxide – activated carbons from grape (*Vitis vinifera*) leaves
LC:	Liquid chromatography
MS:	Mass spectroscopy
P:	Phenol
PCP:	Pentachlorophenol
PDA:	Photo diode array
RP HPLC::	Reversed Phase High Performance Liquid Chromatography
SEM:	Scanning electron microscopy
SPE:	Solid phase extraction
US DHHS	United States Department of Health and Human Services
US EPA::	United States Environmental Protection Agency
UV-Vis:	Ultra-violet Visible spectroscopy

CHAPTER ONE

INTRODUCTION

1.1 Background

The numerous important applications of phenols in chemical industries are as many as the hazardous and environmental persistence and/or bio-accumulative potentials of the compounds in discharged wastewaters. Phenols are essential compounds with a recorded yearly global production of six billion pounds, and an estimate exceeding three billion pounds for US alone (BCERC, 2007). Phenols are mainly utilized for synthesizing phenolic resins and for several industrial, pharmacological and agronomic applications. Phenols are being used in textile, electroplating, paints, disinfectants, intermediates for drugs, fertilizers, and also agro-chemicals production systems (Michalowicz & Duda, 2007). The widespread use of phenolic compounds has resulted in phenol-laden domestic discharges as well as runoffs from agricultural lands; hence elevated levels of toxic phenolic wastes in the environment (Nadavala *et al*., 2009). Furthermore, phenols are major constituents of wastes from petrochemical units, coal processing and oil refineries. Consequently, wastewaters emerging from these industries also contaminate the environment with phenols (Ahmed & Theydan, 2013). Water containing phenol even at trace (ppb) levels has characteristic unwanted odour, obnoxious taste, and is detrimental to organisms in aquatic ecosystems and to humans (Mishra & Bhattacharya, 2006). Phenols are genotoxic and teratogenic, induce carcinogenicity and immunotoxicity, and have accumulative potential in food chain (Gad & Saad, 2008; Paisio *et al*., 2009). Thus, it is essential to remediate phenols in discharges, most especially from industrial wastewaters, to acceptable limits before being released into natural water systems.

1.2 Phenol

A phenol is structurally identified (Figure 1.1) as a compound with a hydroxyl group joined to six carbon aromatic ring(s). Phenols represent a universal name for compounds of organic nature that are having one or extra phenol groups. Phenolic compounds contain hydroxyl (-OH) group and may have methyl ($-CH_3$), chloro (-Cl) and/or nitro (NO_2) groups in their structures.

1.2.1 Properties of phenols

A phenol is a weakly acidic (pKa 9.89 at 25 ^{o}C) compound that appears as a white crystalline solid in physical form at room temperature, and soluble in water as indicated by Enclopaedia Britannica in *Phenol* (2014). When molten and pure, the liquid form is colourless which immediately changes to pink when exposed to the atmosphere. It has an irritating strong odour. The high boiling point (182 ^{o}C) and polarity of phenol is attributed to the presence of hydrogen bonding and a higher dipole moment (Phenol, 2014). Due to resonance, phenol is more of an acid than an alcohol because the oxygen atom on the phenol can become positively charged and similarly, resonance stabilizes the anion formed on loss of the hydrogen atom (Figure 1.2). Phenols exist in their molecular forms at acidic pH due to the availability of more protons, and as electron rich phenolates in a more basic medium.

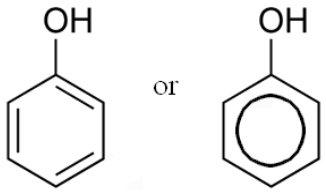

Figure 1.1: Structure of phenol
(Adapted from CliffsNotes, 2014)

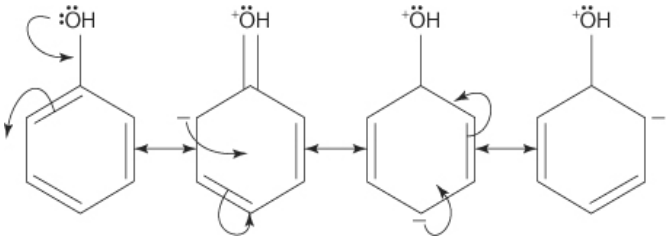

Figure 1.2: Resonance stabilization of phenol
(Adapted from CliffsNotes, 2014)

The hydroxyl and aromatic groups of phenols are reactive; they can resonate and initiate nucleophilic or electrophilic reactions including nitration, sulfonation and halogenation. The formation of phenolic resins is ascribed to electrophilic substitution reactions of an aromatic ring of a phenol and formaldehyde with an acid catalyst. Furthermore, the delocalization of the free electron pair available on hydroxyl group forms a phenoxide ion. The nucleophilic reactions of phenoxide ions (in base) with formaldehyde yields resole resins (Weber & Weber, 2010). These physical and chemical attributes of phenols provide the basis for their many uses.

Some specific physical properties of phenolic compounds are presented in Table 1.1.

Table 1.1: Selected properties of some phenolic compounds

Phenolic compounds	pKa	Boiling point (^{o}C)	Aqueous Solubility at 25 ^{o}C (g/L)
Phenol	9.89	182	93
2-Chlorophenol	8.97	214	26
2-Nitrophenol	7.17	215	2.0
4-Nitrophenol	7.15	279	1.69

(Source: Dabrowski *et al*., 2005)

1.2.2 Uses of phenols

Phenols are significant industrial products. They are utilized in the synthesis of phenolic resins, adipic acid, bisphenol-A (BPA) etc. which are fundamental intermediates for many construction, locomotive and appliance industries (Hernandez *et al*., 2003). BPA, which can be synthesized when a phenol is condensed with acetone, is widely used in the production of polycarbonate plastic materials and epoxy resins (Harris, 2013). Also, phenols have therapeutic, anaesthetic and disinfectant properties. These prompt the usage in many therapeutic and consumed products such as nasal and ear drops, sprays, antiseptic lotions, disinfectant, gargles, ointments and slimicides. Other applications of phenol include the manufacture of paint, paint removers, ink, dyes, perfumes, soaps and toys (BCERC, 2007). The reaction involving heat treatment of nitrochlorobenzenes with sodium hydroxide yields nitrophenols. Nitrophenols and chlorophenols are expansively used as fungicides, herbicides, insecticides, wood preservatives, glues, vegetable fibres, and tannery (Navarro *et al*., 2008). While the usage of some forms of phenols such as BPA and pentachlorophenol (PCP) is banned in many countries and by the European Union (Harris, 2013), these compounds are still found in pallets (woods), water bottles, containers, papers and cardboards.

1.3 Statement of research problem

Phenols are widely used in various domestic and industrial applications. Consequently, they are often released into aquatic systems through municipal and industrial wastewater discharges. Phenols are harmful to living organisms, especially in freshwater systems. In fact, there are reports (Brooks & Riviere, 1996; Bruce *et al*., 2001; McCall *et al*., 2009) on their adverse health effects on man and the environment. Hence the need to ensure their removal during wastewater treatment processes. Unfortunately, conventional methods of phenol removal other than adsorption are often expensive and inefficient. This study will therefore investigate bioremediation of phenols from industrial wastewaters. Levels of phenols in samples of some industrial wastewaters will be assessed. The available functional groups on adsorbent surfaces, effect of activation on surface morphology, biosorption capacity and effectiveness of phenol removal using *Vitis vinifera* (grape) leaf litter from simulated and industrial wastewaters will be investigated and elucidated. Adsorption parameters (pH, contact time, adsorbent dose, adsorbate concentration and temperature) will be optimized for improvement of adsorption efficiency.

1.4 Justification for research

A phenol is an essential chemical in the synthesis of several organic compounds used by humans. Therefore, groundwaters as well as wastewaters of different chemical, pharmaceutical and manufacturing industries contain phenols (Wallace *et al*., 1996). Even when the concentration is very low, phenols are toxic to living organisms (Senturk *et al*., 2009). Phenolic compounds (e.g., bisphenol A (BPA)) are reported to cause endocrine disruption and damage the neural network of organisms, thereby altering ovulation and initiating neurological disorders, respectively (Paisio *et al*., 2009).

Water is critical to the existence of all life forms. It is an important component of the hydro-geochemical cycle making up about 70 – 80% of the earth. The various benefits derived from water enhance socio-economic development. However, the worldwide water resources are under threat (Wyk, 1998). On a regional scale, South Africa had been classified as a dry country because the rainfall is about 450 mm (annual average). This value is much less than global annual average of 860 mm, and this implies water resource is limited in the country. Water pollution and other environmental conditions including climate change tend to limit the amount of available water for industrial and household uses (CSIR, 2010). Proper utilization of the available water is therefore important by attempting to improve its quality for re-use.

Effective treatment of wastewater directly from industrial and sewer point sources would reduce pollution to aquatic ecosystems. The methods of degradation by oxidation, micro-filtration, precipitation, microbial treatment and others are conventional techniques used in the abatement of phenols but these procedures are expensive and not easily available.
This necessitates continuous research into alternative methods such as bioremediation and biosorption procedures using cost effective, readily available and environmentally friendly materials. *Vitis vinifera* (grape) leaf litter biomass fits into this classification. To our knowledge, there is yet no report of its application as an adsorbent for contaminant removal from waters and wastewaters.

In 2011, the approximate land surface area used for grape cultivation globally is about 7.6 million hectares with production of 69.2 million tons of grape. South African vineyards cover a land area of 131,000 hectares producing about 58,000 tons of grapes. This positions the country as 14th in terms of land use as vineyard; among the top five producers of grape, and the 7th largest producer of wine in the world (Shifugu & Terry, 2011; International Organization of Vine and Wine, 2012). As a result, grape cultivation generates a huge amount of leaf litter. A large biomass is available during pruning which involves selective removal of plant parts for shaping (directional growth) and harvest purposes and increasing yield of fruits. There is also a seasonal shedding of the leaves, thus providing large biomass of leaf litter.

To date, there is no known economic use of grape leaf litter. This locally available material may be utilized as a biosorbent for abatement of phenols from waters. This study therefore is projected at investigating the potential and effectiveness of grape leaf litter as a novel adsorbent to remove phenolic compounds from contaminated waters and wastewaters.

1.5 Research questions

This study will seek to provide answers to these listed questions:

- Can grape leaf litter remove phenols from water?
- How could the leaf litter be chemically modified to enhance the adsorption efficiency?
- Is there variation in the sorption ability of non-treated, acid and alkaline activated forms of the prepared adsorbents?
- What are the optimal conditions required for effective removal of phenols from polluted water?

- What are the isothermal implications of the adsorption process and what isotherm model gives the best description of the adsorption?
- What deductions can be made from the mathematical kinetic models that best fit the adsorption?
- Are there prominent functional groups on the charred and uncharred grape leaf litter which may be responsible for phenol removal?
- Can the prepared adsorbent be used for the remediation of phenols from wastewater samples from the environment and what is the efficiency of the adsorption?

1.6 Research objectives

The central aim of this study is to investigate the effectiveness of grape leaf litter in the removal of some US EPA priority list of phenols.

Specific objective include:

- To investigate the capacity of grape leaf litter in the removal of phenols from wastewaters.
- To characterize the charred and uncharred grape leaf litter using FTIR, SEM, EDX.
- To optimize adsorption parameters such as pH, adsorbate concentration, contact time, adsorbent dosage and temperature in order to depict best conditions for adsorption.
- To evaluate isothermal parameters including standard entropy (ΔS^{o}), standard enthalpy (ΔH^{o}) and standard Gibbs free energy (ΔG^{o}) involved in the adsorption.
- To fit and analyse the data obtained after the adsorption process into kinetic and isothermal models for description of adsorption mechanism.

1.7 Significance of the study

Phenolic compounds are hazardous wastes which are released into the aquatic environment through effluents from industries. The presence of pollutants limits the use of water especially when the pollutants produce odour and are harmful to humans and other living organisms. The knowledge of abatement from point source will save the aquatic habitats from these adverse effects. Understanding the mechanism of uptake of phenols using grape leaf litter will provide information for bioremediation and environmental monitoring sectors. Its low cost relative to expensive synthetic resins provides an added advantage. This study may provide a beneficial way to positively utilize agricultural waste material to reduce a pollution problem in a more environmentally friendly way.

1.8 Delimitations

This research focuses on the efficiency of grape leaf litter in the sorption of some phenols listed in US EPA priority list of pollutants from synthetic contaminated water matrices and from some environmental discharges. Only grape leaf litter was modified and used for adsorption. Although wastewater matrices may contain several other contaminants, only four selected phenols in the US EPA priority list of pollutants were the target compounds due to their occurrence in the environment, availability of reference standards, and time to complete research, and as such, they were the main compounds in our laboratory synthetic contaminated water samples. Only these selected compounds were also analysed in environmental samples investigated for adsorption studies in this project.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sources of phenols and environmental fate

Phenols can be synthesized industrially through coal tar conversion process (Singh *et al*., 2008). The reaction of chlorobenzene with sodium hydroxide, and also, the oxidation of toluene are some synthetic routes for making phenol (Michalowicz & Duda, 2007).

There may be presence of phenols in air and in waters around areas where they are manufactured, utilized or discharged. Phenols are principally found in surface waters and in the immediate surroundings that are contaminated during industrial and commercial activities involving the production and use of phenols (Akintade *et al*., 2012). Phenols can also be formed naturally in the environment during decomposition of organic matter including plant materials (Fatoki & Opeolu, 2009). Also, phenolic compounds are produced in environmental matrices from interaction between chemical species. For instance, nitrophenols are formed in the reaction between phenols and nitrate ions contained in water in presence of sunlight.

The primary non-point source of polluting the environment with phenols comes from agricultural runoffs. This results from the application of phenolic-containing pesticides. Another non-point source is through chlorination of waters which contain phenols (Grynkiewicz *et al*., 2002). Nitrophenols are well known for their uses in the manufacture of parathion and methyl parathion. The biodegradation of these insecticides forms toxic 'byproducts' such as 4-Nitrophenol present in agricultural run-offs and wastewaters (Santhiago *et al*., 2014). 2-Nitrophenol can also be found in such matrices.

Industrial and domestic discharges significantly contribute to high concentration levels of phenols in the environment. Industrial discharges containing phenols are mostly released into surface waters thereby contributing to contamination of aquatic environments (Gad & Saad, 2008). Industrial wastewater discharges may contain phenols and their derivatives at a concentration of up to 1000 mg/L or more. The leaching of phenols in waste landfills is another point source, and phenolic leachates mainly pollute the soil and groundwater resources (El-Ashtoukhy *et al*., 2013).

Wastewaters from many industrial plants contain phenolic derivatives (Jain *et al*., 2004). For example, the manufacture of sebacic acid produces liquid wastes containing up to 2500 - 3000 mg/L of phenols (NEERI, 2007). Effluents originating from coal gasification and liquefaction processes and olive mill wastewaters contain phenols as the major organic components (Busca *et al*., 2008). Table 2.1 shows the approximate concentration of phenols in some wastewaters.

Table 2.1: Contamination level of phenols in some industrial wastewaters

Wastewater origin	**Approximate concentration of phenols (mg/L)***
Petroleum refineries	6 - 500
Coke conversion processes	28 - 3900
Coal conversion processes	9 - 6800
Manufacture of petrochemicals	2.8 - 1220
Pharmaceuticals, polymer industries, wood finishing, paint, paper & pulp	0.1 - 1600
*concentration of phenols are reported as 'total phenols'	

(Adapted from Busca *et al*., 2008)

The accumulation of phenols in the aquatic ecosystem is due to the increase in discharge of wastewaters containing these contaminants into natural water bodies. More frequently, the concentration of phenolic compounds in industrial wastewater is greater than the standard limits established for their release into environment. It often ranges between 200 – 2000 mg/L (Ahmaruzzaman & Sharma, 2005). This signifies that these pollutants are delivered into the aquatic environment on a scale that poses danger to both humans and the aquatic organisms. The concentration of phenol in water bodies is usually measured as total phenol content. However, some cases with high individual concentrations in waters had been documented. Michalowicz & Duda (2007) reported a concentration of 204 μg/L for 4-methylphenol in Hayashida River (Tatsuno, Japan) due to emissions from industrial sources.

The solubility of phenols in water enhances their ubiquitous presence in aquatic environments. Hydrophilic phenols (such as chlorinated phenols) are more readily found in the aquatic media. The medium-polar and non-polar phenols including the more chlorinated ones including pentachlorophenol are more persistent in the environment, specifically in soil and sediments (Boyd *et al*., 2001).

Although, aerobic and anaerobic degradation of phenols in soil may occur, mobility through soil is also possible. These compounds do not stick to soils but rather percolate, thus contaminating groundwater resources.

2.2 Toxicity of phenols

Exposure routes of phenols to humans include inhalation, ingestion and dermal contact. Phenol is said to possess corrosive action on tissues and it may also affect the respiratory and cardiovascular systems (Qadeer & Rehan, 2002). The health hazard of phenols on humans is usually compiled after examining exposed humans (US DHHS, 2008). Baker *et al*. (1978) reported that the unintended spill of 37,900 litres of phenol in a rural area of southern Wisconsin in July 1974 resulted in chemical contamination of groundwater. After humans drank the water, an estimated 10-240 mg exposure was recorded per individual on a daily basis and this resulted in diarrhoea, burns and sores in mouth, and dark urine. Documented cases of poisoning by phenol reveals that phenol in water can cause such illnesses (WHO, 1994). Water analysis and geographical estimations showed that groundwater pollution in the region may persist for decades (Baker *et al*., 1978, WHO, 1994).

Skin exposure may result in severe eczema, dermatitis and/or burns. The skin contains keratin and the disulphide bridges in this keratin can be disrupted by phenol. Phenol can also impair stratum conium leading to coagulation necrosis which can be lethal to organisms. This is because proteins in the skin are denatured and precipitated (Brooks & Riviere, 1996).

At lower concentrations, ingestion can be hazardous to central nervous system, liver, lungs and kidneys. In the intestines and liver, phenol is metabolized by straight conjugation with glucuronic acid and sulphates (Bruce *et al*., 2001). At higher concentrations, phenol is corrosive and irritating. Upon ingesting a lethal oral dose ranged 1 g to 65 g, phenol targets mucosal membranes in humans and animals (McCall *et al*., 2009). Post mortem examination of grossly exposed humans revealed mucosal lacerations in intestinal tract (US DHHS, 2008). Additionally, phenols are lipophilic. The transport of phenol into cells of organisms is attributed to lipophilicity; and this can be both rapid and passive (WHO, 1994). Phenol tends to denatures proteins after been ingested by cells.

In order to monitor the presence and levels of phenols in the environment and to know the distinctive toxic response of living organisms to phenols, different biomarkers (animals including rats, mice, fish, pigs, amphibian etc.) had been used in the past for monitoring and toxicity studies. Bruce *et al*. (2001) carried out studies on dermal lethality of phenol and surface area exposure on rats and guinea pigs. Disruption of neural system and damage to the liver, heart and lungs were reported harmful effects of short-term exposure to 100-200 mg/m^3.

Exposure of rabbits to 24 mg/cm^3/kg dose of phenol caused cardiac arrhythmia and convulsions in rats after being subjected to a phenol dose of 107 mg/kg of the animals (surface area not specified) (US DHHS, 2008).

El-Serafy *et al*. (2009) subjected *Oreochromis aureus* to different concentrations of phenols at sub-lethal levels of 20, 40 and 80% of median lethal concentrations (LC_{50}). The exposed fishes showed severe haemorrhage pynknosis, necrosis and cell proliferation (histopathological effects). Histochemically, phenol caused oxidative stress and caused reduction in the ability to store carbohydrates. Also, after exposure, some organs (liver, gills and spleen) were tested and the carcinogenic potential of phenol was confirmed. There was amplification of DNA in organs tested. Furthermore, mutagenicity screening tests showed that several phenols including 2,4,6 – trichlorophenol are potential animal carcinogens (Boyd *et al*., 1983).

Chlorination of water for purification purposes may lead to the formation of chlorophenol if the water intended to be purified contains phenols. Boyd, *et al*. (2001) assessed the toxicity of chlorophenol by comparing the bioluminescence activity of *lux*-marked bacteria at 50% active concentration (EC_{50}). The study revealed that an increase in chlorination tends to increase toxicity of chlorophenols. The toxicity response of biomarkers used in the study correlated with those of some other fresh water and marine organisms. This implies the hazardous potential of chlorophenols to organisms in aquatic biota.

According to Paisio *et al*. (2009), the embryos of *Bufo arenarum*, which is a representative amphibian, can be used to determine the toxicity of phenol by subjecting the embryos to different concentration of phenol at different life developmental stages. Neural disorder, edema and death were among the reported tetragenic and lethal effects of phenol on the amphibian.

Phenols are polar in nature but can also exhibit lipophilicity; consequently, they can form a network array within themselves and with a number of different other compounds (such as fats, lipids etc.) that are generally known to be hydrophobic or non-polar. The lipophilic characteristic of phenols therefore enables bio-accumulative potential in different media, cells, and tissues. Hence they occur in the food chain, posing danger to human health and the environment (El-Serafy *et al*., 2009).

2.3 U.S. EPA priority list of phenols

Phenolic compounds are contaminants of priority concerns due to their toxicity and harmful health effects (Archana *et al*., 2013). Phenols exhibit a high degree of toxicity and are tagged potential carcinogens. They can alter both taste and odour of potable water at levels as low as a few ng/L. Therefore, in order to create a solution and ensure a safe environment, both the U.S. Environmental Protection Agency (U.S. EPA) in Methods 604, 625, 8041 and the European Union (EU) has included some phenols in their lists of priority pollutants (Zhao & Lee, 2001). The chemical structure of the eleven (11) phenols listed as priority pollutants by the U.S. EPA are given in Figure 2.1.

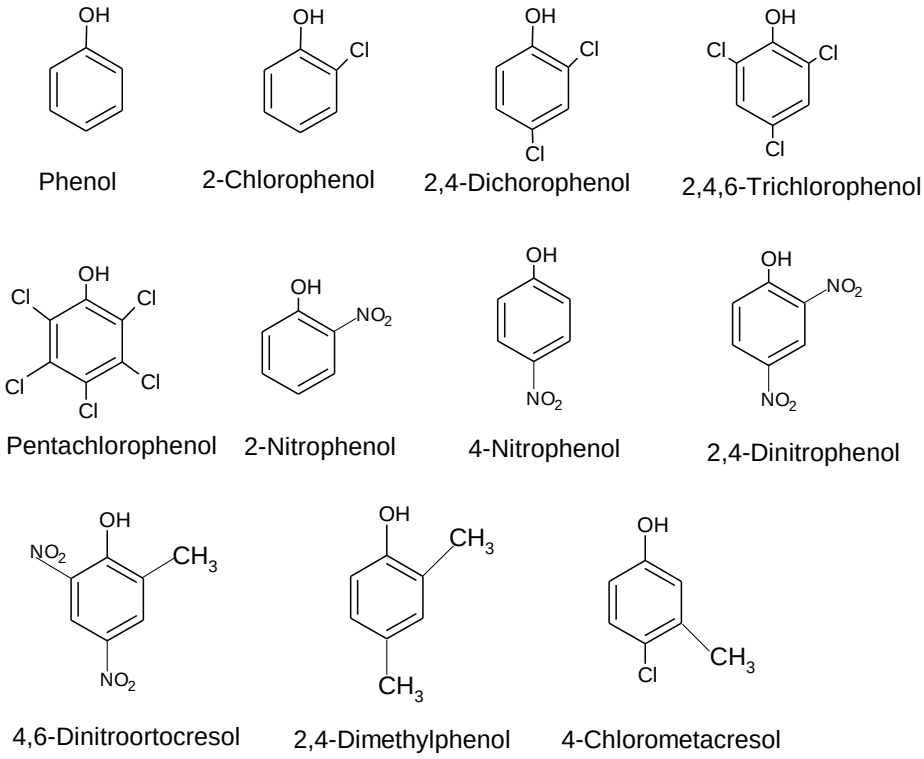

Figure 2.1: Chemical structures of US EPA priority list of phenols

2.4 Legislation on phenols' concentration in waters and wastewaters

In order to minimize the concentration of contaminants in water systems to levels of insignificant hazards to humans and aquatic life, there are water quality standards and regulations (Pieterse, 1989). These water standards are sets of requirements designed to ensure quality of water bodies (Pieterse, 1989). The majority of these standard limits and regulations are based on monitoring contamination levels in drinking water; there is however scarce information on regulated limit for wastewater discharge into open water bodies of seas, rivers and streams.

Toxicity of phenols and potential of altering the quality of water had led to the establishment of acceptable guideline values in water bodies across the globe. The EU directive (2455/2001/EC) regulated maximum level of phenols to 0.5 μg/L in drinking water and their individual concentration should not exceed 0.1 μg/L (Rodriguez *et al*., 2000). The U.S. EPA also recommended the concentration to be 0.001 mg/L in waters meant for drinking purposes. The Nigerian standard and the World Health Organization (WHO) also set a maximum permitted level of 0.001 mg/L for phenols in drinking water (Akintade *et al*., 2012).

Furthermore, for levels of phenols in effluents, the US EPA set a maximum concentration level of 0.3 mg/L for total phenols to be discharged into surface waters like streams and lakes. After treatment, a maximum concentration of 0.1 mg/L of phenol in final effluents for discharge onto lands and water bodies is the permissible limit in South Africa according to the South African National Water Act (DWAF, 2004). Effluent wastes and sewer discharges are regulated to contain a maximum of 1 mg/L and 5 mg/L total phenols respectively in India before release into the environment (Rao *et al*. 2009). In order to avoid risks to health of humans and aquatic life, there is the need for effective treatment of industrial wastewaters and sewer effluents to these acceptable levels before discharge into the environment.

2.5 Adsorption

Adsorption is a procedure which is fundamentally based upon the binding of atoms, ions, or molecules of gas, liquid or solids (dissolved) to the surfaces of an adsorbent. The transfer of adsorbate onto the surfaces of an adsorbent continues until equilibrium is reached (Abdullah *et al*., 2009). The interaction is predominantly attributed to weak van der waals attractions.

This weak chemical bond in the adsorbate - adsorbent molecules improves adsorption; modifications can however be made to the surface of the adsorbent to facilitate such chemical interaction (Shukla *et al*., 2009).

In adsorption studies, equilibrium adsorption depends on factors such as the surface morphology of the adsorbent, pH, temperature, time, adsorbent dosage and concentration of the adsorbate. For instance, if the temperature of an adsorption reaction system is fixed, adsorption isotherms are evaluated from the data obtained from the amount adsorbed at different concentrations (Sharma & Sharma, 1980). Thus, an adsorption isotherm reveals how the amount adsorbed depends on the equilibrium concentration of the solution at constant temperature.

There are several forms of equilibrium relationships for various adsorbate-adsorbent interactions observable in adsorption. The more popular adsorption isotherms are Langmuir and Freundlich isotherm models. A detailed theory of adsorption isotherms and other available models is given in Chapter 3 of this work.

2.6 Carbonisation and chemical activation

Carbonisation refers to the transformation of an organic material into a carbon char; this is usually achieved by destructive distillation or most commonly by a pyrolysis process. Pyrolysis of solid materials can be categorised as heterogeneous chemical reaction. These reactions involve rupture and rearrangement of chemical bonds (White *et al*., 2011) in materials to form charred products. Activated carbons have high porosity, and are synthesized by subjecting a charred (carbonised) material to oxidising gases or by impregnation of a carbon-containing material with dehydrating agents and a further thermal treatment.

The porous structure of activated carbon is determined by the type of raw material precursor used in the preparation and also depends on the mode and extent of activation. The precursors can be physically activated by pyrolysis in an inert atmosphere and a further partial gasification of the charred product with steam or CO_2 (Roman *et al*., 2013).

Chemical activation processes are done in a single step, and involve lower activation temperatures and result in higher yield than physical activation.

Chemical activation involves the impregnation of raw materials by compounds such as H_3PO_4 or $ZnCl_2$ followed by pyrolysis and finally washing to remove the activating agent.

Several activating agents have been used for activation of various biomass, for example H_2SO_4 for cherry stones (Marin *et al*., 2013), KOH for activated carbons from corn (Bagheri & Abedi, 2009), and others.

After the activation step, activated carbons have been shown to possess greater pore network and high surface areas (Martin & Wj, 1997). The sorptive characteristic of activated carbons is attributed to their rough irregular surfaces, and available surface functional groups (Ali et. al., 2012).

Based on possibility of producing materials with high surface areas, porosity and overall effectiveness, the remediation of wastewaters with active carbons is a considerable competent method for the abatement of phenols from effluents (Qadeer & Rehan, 2002).

2.7 Techniques for treatment of phenolic contaminated wastewaters

There are several methods designed for the removal of phenolic compounds from aqueous matrices and wastewaters in order to attain regulated standards. The revised methods include ion exchange chromatography (Carmona *et al*., 2006), electro-coagulation (El-Ashtoukhy *et al*., 2013), and reverse phased osmosis (Goncharuk *et al*., 2002). Oxidation methods such as ozone treatment and supercritical water oxidation (Guan *et al*., 2011) have also been reported for removal of phenols. In addition, degradation techniques including degrading by TiO_2 photocatalysis (Laoufi *et al*., 2008), degradation by zero valent iron (Gunawardana *et al*., 2011), aerobic biodegradation (Vazquez *et al*., 2006) and various biological degradation treatments (Rigo & Alegre, 2004; Adav *et al*., 2007; Yotova *et al*., 2009) have been widely utilized. Other methods such as sedimentation, ultra-centrifugation and micro-filtration have also been used (Navaro *et al*., 2008; Jablonska, 2012). However, these conventional methods are expensive and involve complex processes. These methods are also selective for specific type of pollutants and in most cases; they are inefficient in the treatment of contaminants at low concentrations (Busca *et al*., 2008).

Removal of phenols from wastewaters using separation techniques involving pervaporation and membrane-based solvent extraction had been studied by Kujawski *et al*. (2004). The method is efficient, however, membranes utilized in filtrations are vulnerable to fouling

(resultant of slime formation); this depicts a setback to continuous use of this technique (Sumbu *et al*., 2012).

Oxidation of phenols by ozone is an environmentally friendly remediation technique. The pathway for the breakdown of phenol can be summarized as follows:

Phenol → hydroquinone → benzoquinone → maleic acid + fumaric acid

In most cases, the reaction continues to complete mineralization of the phenols, and generating H_2O and CO_2 as final products (Bielicka-Daszkiewicz *et al*., 2012). Heterogeneous photocatalysis is an advanced oxidation method that can also be used for the degradation of several phenols (Yasmina *et al*., 2014).

The catalytic oxidation and attempted complete mineralization of phenols using aqueous catalyst of titanium dioxide was reported by Laoufi *et al*. (2008). The study incorporated the use of UV irradiation for phenol degradation. The efficiency of the method depended upon concentration of catalyst used, intensity of light, time of UV irradiation and pH. Results showed that after a UV irradiation treatment of 6 h, 99% of phenol was degraded.

A similar oxidation technique was employed by Adam *et al*. (2010) where heterogeneous iron-silica was used as catalyst for the oxidation of phenols. A 95.2% conversion of phenol was achieved with selective formation of 63.1% catechol and 38.7% hydroquinone.

Despite the efficiency of oxidation processes, the high energy requirement for photo-oxidation is a major demerit that offsets the benefit of this technique (Dixit *et al*., 2010). Also, chemical treatment processes have the tendency to transform the pollutants into other forms of toxic materials.

Bioremediation employs the utilization of microorganisms, plants or their enzymes in the treatment of polluted media and locations (Megharaj *et al*., 2011). The application of microorganisms for phenol degradation is among the latest reported studies on bioremediation. Rigo and Alegre (2004) isolated twenty two microorganisms from phenolic wastewater to determine strains that can degrade phenols.

It was reported that *Candida parapsilopsis* was capable of growth on a medium with as high as 1 g/L phenol, thus, such microbes can be employed for degradation purposes.

Studies on enrichment and isolation of cultures for species capable of degrading phenol have also been investigated by Murialdo *et al*. (2003) and Oboirien (2011). The major drawback in the usage of biological processes for treatment of phenolic wastewaters is the selectivity and sensitivity of the microorganisms to pH and temperature (Kumar *et al*., 2007).

Apart from high cost, complexity and selectivity, the methods based on chemical oxidation, biological degradation, reverse osmosis, ion exchange, and solvent extraction require the use of large-scale facilities and have shown low efficiency for the removal of trace levels of contaminants (Payne & Abdel-Fattah, 2005).

The application of adsorption techniques in removal of phenols remains adequate for phenolic removal in simple operations (Nagda *et al*., 2007). Adsorbents such as activated carbon are usually used in adsorption of organic compounds including phenols and many other pollutants (Dabrowski *et al*., 2005). Activated carbons possess tremendous adsorption capability as their mode of manufacture can be manipulated to yield materials of similar rough surface with enhanced pore structures (Dabrowski *et al*. 2005).

The benefits of using activated carbon in adsorption are sometimes offset by the rising cost and as such contribute to limitations of the usage (Shukla *et al*., 2009). Adsorption is still more frequently used due to the simplicity and lesser cost of the method; low cost materials, often from plant and animal origins are constantly investigated. Thus, there is need for continued research into developing alternative low cost adsorbents that are readily available.

2.8 Adsorption of phenols

There are several methods and techniques for the removal of phenols in wastewaters but adsorption is considered the most efficient due to economic feasibility and the potential to remove all types of phenols (Singh *et al*., 2008). The technique is suitable for treatment of wastewaters due to its simplicity in set-up, easy operations and possibility of removing several organic and inorganic pollutants with the process. Pollutant-selective methods are not convenient for the treatment of wastewaters that is a mixture of several contaminants (Jain *et al*., 2004).

Activated carbons possess the best adsorption characteristics among other adsorbents and are most widely used for removal of pollutants from wastewaters (Qadeer & Rehan, 2002). Activated carbon (AC) is a frequently used adsorbent for effective removal of organic compounds like phenols.

Literatures abound on several other adsorbents which have been utilized in adsorption. These include synthetic resins, Fe_3O_4, silica filled epoxidized natural rubber, fly-ash, activated carbon, carbon nanotubes (Lin & Juang, 2009; Abdullah *et al*., 2009; Ayanda *et al*., 2013; Gupta & Saleh, 2013). ACs have shown a removal efficiency of up to 200-400 mg of phenol per gram of the adsorbent (Busca *et al*., 2008).

In a broader view, taking into account several pollutants which may be available in wastewater matrices, several low cost materials that have been used in biosorption include bark of woods and other carbonaceous and tannin-rich materials (Palma *et al*., 2003). Material from plant origin such as peat moss (Aroguz, 2006), chitosan (Li *et al*., 2009), coconut shell (Mohd Din *et al*., 2009), fruit wastes (Hossain *et al*., 2012), seaweed and algae (Rathinam *et al*., 2011) have been found to remove various organic pollutants with efficiencies of 80 - 99.9% (Ahmaruzzaman & Sharma, 2005; Megharaj *et al*., 2011).

Studies on the utilization of maize cob as an adsorbent for removal of lead (II) from aqueous solutions and industrial effluents were reported by Opeolu *et al*. (2009). The adsorbent showed a removal efficiency of 99.99% in the removal of Pb^{2+} ions from battery effluents. Chemical activation of date stones using $ZnCl_2$ for the adsorption of methylene blue (Ahmed & Dhedan, 2012) and the use of pistachio hull waste for biosorption of chromium (Moussavi & Barikbin, 2010) are included in biosorption studies involving the use of low cost biomaterials for effective removal of contaminants.

Al Bahri *et al*. (2012) prepared activated carbons from grape seed for the removal of diuron from water. Activated carbons were prepared from grape seeds via chemical activation using phosphoric acid and thermal treatment at 350-550 ^oC. The surface of the carbon was chemically modified to obtain a surface area of 1139 m^2/g to achieve optimum adsorption capacity.

A removal efficiency of >97% of Ni (II) and Cu (II) from aqueous matrices was achieved using grape tree (Escudero *et al*., 2008). According to Chand *et al*. (2009) grape waste showed efficient adsorption in removal of Cr (VI), Cr (III), Fe (III), Zn (II), Cd (II) and Pb (II) from solutions. The adsorption of these ions onto the grape waste biomaterial was shown to be dependent on the solution pH; Cr(VI) was selectively adsorbed over other metals with a maximum adsorption of 1.91 mol of Cr(VI) per kg of adsorbent at pH 4 (Chand *et al*., 2009).

A high maximum loading capacity of 1.9 kg gold per kg dry weight of adsorbent was reported by Parajuli *et al*. (2008) after investigating the removal of Au (III) from a solution using grape waste.

All these studies reflect the potential effectiveness of grape plant biomass as biosorbents for the removal of contaminants. There is however no known studies on the utilization of grape leaf litter in biosorption.

Biosorption is a widely used technology for the removal of toxic pollutants from wastewater. Adsorbents manufactured from agricultural waste materials serve as cost-effective preferences for wastewater treatment by adsorption in developing countries (Gupta & Saleh, 2013). These adsorbents are effective in removal of contaminants from effluents because their surfaces can be modified to achieve higher surface areas; this in turn increases their adsorption capacity.

Agricultural materials contain proteins, polysaccharides and lignin which are related surface functional groups influencing adsorption (Chand *et al*., 2009). Agricultural and cellulosic wastes are inexpensive, available and do not need to be regenerated when used as biosorbent in remediation of water pollutants. Biosorbents of plant origin have been broadly studied and have been effective in adsorption of toxic pollutants in wastewater. There are existing scopes for manufacturing adsorbents from low-cost materials such as wood, rice husk, and others (Ahmaruzzaman & Sharma, 2005).

A study on biosorption of phenol using charred sawdust was reported by Dutta *et al*., (2001). The fractional removal of phenol after 25 min was 0.77 at an initial concentration of 61.27 mg/L. In another study, *Acacia leucocephalia* bark powder exhibited adsorption capacities of 94.33, 147.05 and 181.81 mg/g for phenol, 2-cholorophenol and 4-chlorophenol (Kumar & Min, 2011).

Activated carbons produced from hazelnut biomass have also been used for adsorption of phenols. The carbon was chemically activated using $ZnCl_2$ to improve the quality and sorption capacity of the material; the equilibrium removal capacity was 99.27 mg of phenol per gram of adsorbent at 45 ^{o}C (Karabacakoglu *et al*., 2008). Also, when coal material was activated with phosphoric acid, an equilibrium adsorption of 142.8, 256.4, and 243.9 mg/g for phenol, *p*-nitrophenol, and *p*-chlorophenol, respectively was reported by Ahmaruzzaman and Sharma (2005).

The utilization of *Shorea robusta* leaf litter had also been reported for adsorption of phenol (Mishra & Bhattacharya, 2006). The leaf litter was reported to effectively adsorb 76% of phenol at a high initial phenol concentration of 1000 mg/L and a pH of 6.

Jain *et al*. (2004) developed low cost adsorbents from industrial wastes (slag, dust, sludge and slurry) of fertilizer and steel plants. The wastes were treated with hydrogen peroxide and further thermal treatment (500 ^{o}C for 1 h). Thereafter, the potential of applying these industrial wastes for remediation of chlorophenols was investigated. It was reported that 17.2, 50.3, 57.4, and 132.5 mg of phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol, respectively per gram of adsorbent was removed from aqueous solutions. Ahmaruzzaman and Gayatri (2011) also used activated neem leaf in a fixed bed column for the adsorption of phenol, 4-chlorophenol and 4-nitrophenol from 1000 mg/L simulated wastewater with a removal efficiency of 2.50%, 13.22% and 88.71% respectively.

Abdullah *et al*. (2009) stated that contact time of adsorbate – adsorbent in solution, surface area of adsorbent and pH are major factors that strongly influence the sorption capacity of different sorbents. The authors reported that ionization of phenol in water is a function of pH of the medium; thus pH may influence sorption efficiency of biomaterials. In Lazo-Cannata *et al*. (2011) using carbon nanospheres showed that adsorption of phenols were favoured in acidic medium (pH 3) and that the presence of ionic salts such as NaCl favoured the uptake of phenols in neutral solution (pH 7) due to ‘salting-out’ with consequent reduction in the solubility of the non-electrolyte.

Equilibrium and kinetic studies on biosorption of 2,4-dichlorophenol (2,4-DCP) onto seagrass by Demirak *et al*. (2011) also reported optimal pH of 5 for the adsorption process. A further increase in solution pH resulted in decreased adsorption. The observation was attributed to increase in amount of negative phenoxide ions on the adsorbent surfaces and the negative functional groups at pH > pKa.

2.9 Analysis of phenols

In recent past, several techniques have been established for determining phenols in water systems. Some of these methods include kinetic, electrochemical, capillary electrophoresis, gas chromatography (GC) and high performance liquid chromatography (HPLC).

Chromatographic methods are widely used and efficient in the analysis of phenols (Fiamegos *et al*., 2003). GC techniques may be used for the analysis of phenols at trace concentrations. The detection of phenols is often achieved by coupling a GC system with flame ionization detector (FID) (Bagheri *et al*., 2005), electron capture detector (ECD) (Bagheri & Saraji, 2001) or mass spectrometric detector (MS) (Selvaraj *et al*., 2014). Gas chromatographic methods involve derivatization of the phenols to compounds of lesser polarity to improve selectivity. Derivatization of phenols can be achieved with compounds such as *bis*(trimethyl) - trifluoroacetamide (Zhang *et al*., 2014). Similarly, in another study, methylated phenols were iodinated and were subsequently analysed on a GC-ECD (Gruzdev *et al*., 2013).

Olujimi *et al*. (2012) derivatized priority phenols into their respective t-butyldimethylsilyl compounds. Derivatization was achieved with N-(t-butyldimethylsilyl)-N-methyl-trifluoroacetamide (MTBSTFA). Analysis of recovered derivatives was carried out on a GC-MS.

The major demerit attributed to GC techniques is that a derivatization protocol is needed; this step increases the time required for sample preparations; errors may also be introduced into the analytical procedure when derivatizing the analytes of interest (Zhao & Lee, 2001). Hence, other forms of analysis such as HPLC will be considered.

2.9.1 Qualitative and quantitative analysis of phenols with HPLC

Liquid Chromatographic (LC) methods are more frequently applied for the separation, identification and quantification of phenols due to absence of volatile compounds in the pre-concentrated samples which are perhaps, some form of ‘poison’ in columns of GC (Xuan & Li., 2002). LC is a desired analytical approach for determination of phenols due to its high selectivity. High performance liquid chromatography (HPLC) is very suitable for analysing water samples as the process can be automated and the compounds of interest can be determined directly in an easy and time saving operation (Yang *et al*., 2006).

Reversed-phase high performance liquid chromatography (RP-HPLC) is used more recently for the analysis of phenols. Reversed-phase techniques involve the use of non-polar organic stationary phase column-packed materials and polar aqueous mobile phase systems. In a brief description of RP mechanism, hydrophobic compounds are more easily attracted to and often bonded to the non-polar hydrophobic stationery phase.

However, there is interaction between the polar mobile phase and hydrophilic compounds such as phenols present in the sample, thus non-polar compounds spend more time on the column while polar compounds have a lower retention time. Organic stationery phase materials employed in RP-HPLC include octadecyl- C18, octyl- C8 and dimethyl- polymeric materials. The choice of mobile phase composition depends strongly on the polarity of the compounds of interest. It is also essential to consider miscibility of solvents and solvent-compound interaction when optimizing methods on HPLC. Commonly used polar solvents in RP analysis include methanol, acetonitrile, isopropylalcohol, acetone, ethanol etc. and more often, ionization of compounds of interest are prevented by adding suppressants (such as acetic acid, trifluoroacetic acid, tetrahydrofuran) to the mobile phase mixture.

There are several detectors that can be coupled with HPLC for the quantification of phenols in different matrices. For different environmental samples, some HPLC hyphenated (coupled) methods of detection available for quantifying phenols includes ultra violet-visible (UV-Vis) detection (Almasi *et al*., 2011), diode array detection (DAD), mass spectrometry (MS) (De la Torre-Carbot *et al*., 2005) and fluorescence detection (Gomez-Alonso *et al*., 2007).

A detailed method development procedure for the extraction of eleven phenols in U.S. EPA priority list of pollutants using solid-phase extraction and a post extraction analysis using HPLC and UV detection was reported by Opeolu *et al*. (2010). The study utilized a Waters C8 3.9 mm × 150 mm and 5 µm particle sized column for the separation of phenolic compounds. Further, for the quantitation of phenols, optimal conditions were achieved using a mobile phase composition of methanol and water, both containing 1% volume of acetic acid at a flow rate of 1 mL/min, a column temperature of 45 ^{o}C and UV detection at 280 nm. There was efficient resolution of the phenolic compounds confirming the effectiveness of HPLC method in analysis of phenols.

2.9.2 Extraction of phenols

Proper extraction is essential to have reliable results when analysing environmental samples. The techniques of stir bar sorptive extraction (SBSE), solid phase micro-extraction (SPME), liquid-liquid extraction (LLE) and solid phase extraction (SPE) can be applied in extraction of phenols.

Stir bar sorptive extraction (SBSE) is a stirring extraction procedure that involves stirring of samples containing compounds to be extracted and bars (functionalized monolith materials). Huang *et al* (2008) studied the extraction of 2-chlorophenol and 4-nitrophenol in lake and sea water with SBSE by using a poly (vinylpyridine-ethylene dimethacrylate) monolith material; excellent recovery was achieved with 15% per weight vinylpyridine in the monomer mix, pH 6 and extraction time of 6 h. SBSE may be effective, but the technique is selective, depends on polarity of compounds, does not have lower detection limits, requires longer time for coating of monolith material and stirring is involved for a period of time. Also, the technique may be expensive since complex monolith materials and solvents are needed for extraction.

For efficient and suitable sample extraction and pre-concentration, solid phase extraction (SPE) and solid phase micro-extraction (SPME) protocols are more often employed. Liquid-liquid extraction (LLE) has also been used in some cases. However, SPE and SPME are substituting LLE techniques for the reasons that LLE procedures have tendency of foam formation, longer time for sample preparation, more effort is required for automation and a high volume of organic solvent is often involved in extraction processes (Rodrieguez *et al*., 2000).

SPME procedure is often an employed pre-concentration step for analytical methods such as GC-MS, GC-FID and LC-MS. Simoes *et al*. (2007) utilized SPME-GC/MS for the qualitative extraction and analysis of phenols in different water matrices using polyacrylate fibres micro-extracting materials. The studies reported that optimal recovery was achieved with 10% NaCl, at pH 4.0, extraction time of 40 min, temperature of 35 ^{o}C and stirring speed of 1000 rpm. However, the demerits of SPME methods are similar to SBSE as stirring and longer time is required. In addition, the technique involves derivatization of the compounds of interest.

SPE is a well-known and concrete separation method which involves the use of solid phase sorbent materials. This mode of extraction is faster and requires lesser volume of solvents. The sorbents may be polymeric materials and recovery of compounds of interest depends on properties of these solid phase materials.

For solid phase extraction of phenols, silica based and carbon based sorbents such as C18, C8 and cyclohexyl have been used in the past for pre-concentration procedures. Polystyrene divinylbenzene (PS-DVB) copolymers are also often used as SPE sorbents because they have

higher interaction with polar analytes and have higher surface areas of up to 1000 m^2/g (Bielicka-Daszkiewicz *et al*., 2012).

The sorbents used in SPE are packed in holders or devices of desired sizes. Such devices used in SPE include cartridges, columns and syringes. The choice of solvent used in the elution of retained analyte in SPE process depends on the kind of solid phase sorbent, the polarity of the analyte, the type of sorbent - analyte interaction, and the chosen instrumental method of analysis. Based on the chosen method of instrumentation and the phase of analysis (reverse phased or normal phased), elution is done with organic solvents such as ethyl acetate, acetonitrile, ethanol, methanol etc. or mixtures of the solvents.

The extraction of 26 phenols from wastewaters with the technique of SPE was done by Morales and Cela (2000). Functionalized styrene-divinylbenzene packed cartridge was used as the solid phase sorbent material and non-aqueous capillary electrophoresis was used for quantification of extracted phenols. Since it is essential that the choice of elution solvent mixture must agree with the type of instrumental analysis employed, after loading the wastewater samples onto extraction cartridges, the phenolic compounds were eluted with a solution of ammonium acetate dissolved in N-methylformamide and acetonitrile (75:25 v/v). Recovery values ranged 65.3 – 113.4% was reported for the phenols.

In another study which incorporates SPE into reversed-phase (RP) HPLC, Alsingery (2013) used hydrophobic sorbent materials for extracting pentachlorophenol (PCP) from water samples; PCP was eluted from the sorbent using 8 mL volume of methanol containing 0.1% (v/v) of acetic acid (Alsingery, 2013).

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Chemical reagents

Standards of phenol (P), 2-chlorophenol (2-CP), 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) were purchased from Sigma Aldrich, USA. Acetonitrile and methanol (LC-grade) were also purchased from Sigma Aldrich, USA. Phosphoric acid (H_3PO_4), Sodium hydroxide (NaOH), hydrochloric acid (fuming), potassium bromide (KBr), methylene blue dye, sodium thiosulfate and iodine were supplied by Merck, South Africa. Milli-Q water (Synergy Ultrapure Water System, Millipore, France) was used for all solution preparations.

3.2 Preparation of adsorbents

Vitis vinifera (grape) leaf litter was collected from vineyards in Paarl, South Africa. The biomass (leaf litter) was washed several times to remove debris and other unwanted adhering particles, and subsequently oven dried at 110 ^{0}C for 24 h. The dried leaf samples were pulverized. A portion was taken from the ground samples, stored in airtight vials in a desiccator and designated GL. Other parts (50 g each) of the sample were separately impregnated with solutions of H_3PO_4 and NaOH (activator to precursor ratio of 2:1 w/w).

The method of Benadjemia *et al*. (2011) was employed for chemical activation. In their study, it was revealed that the amount of H_3PO_4 used for activation yielded different results, and best activated carbons were prepared by using a ratio of 2:1 (weight of H_3PO_4 to weight of raw materials to be activated). A ratio of 2:1 H_3PO_4 to *V. vinifera*, and 2:1 NaOH to *V.vinifera* leaf litter was therefore used for this study.

The resultant slurry obtained by separate impregnation of leaf litter with H_3PO_4 and NaOH was evenly mixed, and dried at 110 ^{0}C to form a tar. This was followed by thermal treatment (chemical activation) at 500 ^{0}C for 90 minutes to produce activated carbons. The activated carbons were then washed several times with hot and cold Milli-Q water, dried at 105 ^{0}C to constant weight and stored in air tight vials till further use in adsorption. The prepared activated carbons were designated GLA and GLB for H_3PO4 and NaOH activated samples respectively. Same coding will be used subsequently in this study.

3.3 Characterisation of adsorbents

3.3.1 pH determination

The pH of each of the materials was determined by dispersing 0.1 g of sample in 50 mL of Milli-Q water and boiled gently for about 5 min (Fatoki *et al*., 2012). The solutions were allowed to cool to room temperature and the pH readings were recorded using a pH meter (Crison GLP 21+, Lasec, South Africa).

3.3.2 Point of Zero Charge determination (pHpzc)

The point of zero charge indicates the surface charge of carbon materials in solution. In this study, pHpzc determination was done using pH drift method (Benadjemia *et al*., 2011). 0.1 g of the sample was added to 50 mL solution of 0.1 mol/L NaCl. The pH of the solutions was then adjusted from pH 2 to 12 using 0.1 M HCl and NaOH.

Final pH of the resulting solution was taken after 48 h. The pHpzc is the point where initial pH equals final pH.

3.3.3 Moisture content

The moisture content of each of the activated carbons was determined by accurately weighing 0.5 g of the sample in ceramic crucibles and oven drying at 110 ^{0}C to constant weight. The sample was cooled to room temperature in a desiccator and weighed. The percentage moisture content was calculated using Eq. 3.1.

$$\% \text{ moisture} = \frac{(M_1 - M_2)}{M_1} \times 100 \qquad (3.1)$$

Where:
M_1: mass of original sample (g)
M_2: mass of the oven dried sample (g)

3.3.4 Ash content

For ash content determination, 0.1 g of the activated carbons was subjected to heat in a Carbolite Sheffield muffle furnace at 600 ^{0}C for 4 h. The resultant ash was allowed to cool to room temperature in a desiccator. The percentage ash content was calculated by difference using the Eq. 3.2. All experiments were performed in triplicates.

$$\% \text{ ash content} = \frac{W_2}{W_1} \times 100 \qquad (3.2)$$

Where:
W_2: mass of residue after ashing (g)
W_1: mass of original sample (g)

3.3.5 Scanning Electron Microscopy (SEM) analysis

Analysis of surface morphology of the adsorbents was carried out by viewing the electron micrographs of these materials. Analysis was done with a Zeiss LEO® 1450 Scanning Electron Microscope at Electron Microscope Unit, University of the Western Cape, South Africa. In the sample preparation for SEM analysis, a thin layer of adhesives serving as carbon glue was attached onto a stub, and very small amount of the materials to be viewed were spread on the stub materials and subsequently viewed in the instrument to obtain micrographs.

3.3.6 Energy-Dispersive/Wavelength-Dispersive X-ray (EDX/WDS) Microanalysis

The elemental analysis and/or phase compositions of the adsorbents were accomplished using a Zeiss EVO® MA15 Scanning Electron Microscope at the Stellenbosch University. Quantitative analysis and also secondary imaging require gold coating to improve conductivity and achieve a flat surface. Identification of samples was done with secondary electron (SE) and/or secondary electron images, and compositions were quantified by Energy Dispersive X-ray (EDX) spectroscopy using an Oxford Instruments® X-Max 20mm^2 detector and Oxford INCA software. Beam experimental conditions for the quantitative analysis were 20 KV, a working distance of 8.5 mm and a beam current of approximately 20 nA. The counting time was 10 seconds live-time. Pure Co were used periodically for corrections in detector drift.

3.3.7 Fourier Transform Infrared Spectroscopy

A qualitative analysis for identification of prominent functional groups on the surfaces of the activated carbons was done with a Perkin-Elmer Spectrum one FT-IR Spectrometer. The adsorbents were prepared for FTIR analysis using potassium bromide (KBr) pellet method. The method entails adding dried powdered sample to dried KBr (±1: ±250 mg w/w) in an agate mortar, mixing homogeneously and grinding to fine powder. The mixed sample was placed between the two metal pellets in a die. A plunge was positioned on the metal pellets and compressed using a hydraulic press by exerting pressure of about 14 tons for 10 min.

The resultant pellet disc of the sample was then removed, and placed in FTIR disc holder. Absorption spectra scan was obtained in the range of 4 000 – 400 cm^{-1}

3.3.8 Iodine Number

The Iodine number of the activated carbons was determined by standard method (Ahmed & Dhedan, 2012). For blank titration, 10 mL of 0.1 N iodine solution was titrated with 0.1 N sodium thiosulfate until colour changes to colourless using starch solution (1 wt %) as indicator. Thereafter, activated carbon (0.05 g) was added to 15 mL of 0.1 N iodine solution in a flask. The mixture was shaken for 4 min and filtered. The filtrate (10 mL) was then titrated with standard sodium thiosulfate solution using 2 drops of starch solution as indicator. The corresponding values of iodine number were evaluated using Eq. 3.3.

$$\text{Iodine number} = \frac{(Vb - Vs).N.(126.9).(15/10)}{m} \qquad (3.3)$$

Where:
V_b: volume of sodium thiosulfate solution used for blank titrations (mL)
V_s: volume of sodium thiosulfate solution used for sample titrations (mL)
N: normality of thiosulfate solution (mol/L)
m: mass of activated carbon used (g)
126.9: atomic weight of iodine.

3.3.9 Methylene Blue Adsorption capacity

Methylene blue (MB) cationic dye, 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride ($C_{16}H_{18}N_3SCl$) was used as probe molecule in this study to investigate mesoporous volume of the activated carbons and the capability of treatment of coloured solutions. MB molecule has a size of 1.43 x 0.61 x 0.40 nm^3 and a molecular weight of 319.87 g/mol. A stock 1000 $mg.L^{-1}$ solution of MB was prepared in Milli Q water. Working solutions of different concentrations were prepared by dilution from stock. A standard calibration curve was constructed from absorbance readings of the standard solutions.

The adsorption of MB on the adsorbents was carried out using a batch technique. For the adsorption study, activated carbons of varying masses (0.025 – 0.4 g) were added to 25 mL of MB solutions (1000 mg/L) in 100 mL size Erlenmeyer flasks. The solutions were placed on a shaker at 200 rpm and kept for 4 h to attain equilibrium.

After equilibrium was attained, the solutions were filtered and residual MB concentrations in filtrate samples were analysed with a UV-Spectrophotometer (Shimadzu UV-1800) at a maximum absorption wavelength of 663 nm. The amount of MB adsorbed at equilibrium and percent adsorption was calculated with the following equations:

$$q_e = \frac{(Co - Ce)V}{W} \quad (3.4)$$

$$\text{Percent adsorption (A \%)} = \frac{(Co - C)}{Co} \times 100 \quad (3.5)$$

Where:
q_e: amount of MB per unit mass of adsorbent at equilibrium (mg/g)
Co: initial concentrations of MB solutions (mg/L)
Ce: equilibrium concentrations of MB solutions (mg/L)
C: concentration of MB after adsorption at any time (mg/L)
V: volume of MB solution used in adsorption (L)
W: weight of activated carbon used (g).

All experiments were performed in triplicates

3.4 Wastewater sample collection and pre-treatments

Influents into two different wastewater treatment plants, W1 and W2, were collected in 1 L sized amber coloured glass bottles, and filled to the brim. The first collection, W1, was from wastewater pool that primarily contains domestic discharges. The sample W2 was influent of wastewater treatment plant, hence higher in particulate load. The pH and other physico-chemical characteristics of the water samples were measured on-site. The water samples were filtered through 0.45 µm nylon filters into amber glass bottles. The wastewater samples were then acidified with 10% H_3PO_4 to pH 3-4 (USEPA method 8047). Acidification reduces pH of the solution. This is necessary because phenolic compounds may exist as negative phenolate ions at pH values above pKa. It is equally necessary to acidify because acidification improves the quantitative recovery of phenolic compounds; eliminate inferences such as phenol degrading bacteria and also, to prevent biological and chemical oxidation. The collected water samples were placed in boxes containing ice and transported to the laboratory where they were stored at 4 ^{0}C. This sampling and storage procedure would preserve the samples for 28 days (USEPA method 8047); however, analysis was done within 3 days of sampling.

3.5 Preparation of stock phenol solutions

Calibration curve was prepared in the range (1 – 1000 µg/mL) by serial dilution from a standard stock of 1 mg/mL containing P, 2-NP, 4-NP and 2-CP in methanol.

A synthetic stock phenol solution for use in adsorption was prepared in Milli-Q water. The stock solution contains 1000 mg/L of P, 2-NP, 4-NP and 2-CP. Lower concentrations were prepared by dilution as required. Where necessary, the pH of solutions was adjusted with 2 M HCl and 2 M NaOH. All solutions were stored in amber bottles and refrigerated at 4 ^{0}C.

3.6 Sample preparation for HPLC analysis

Milli-Q water was spiked with known (1 – 300 µg/mL) standard concentrations of P, 2-NP, 4-NP and 2-CP to evaluate recovery. For the SPE protocol, Strata™ -X SPE 500 mg/6mL polymeric sorbent cartridges were used (Phenomenex, South Africa). The tubes were conditioned with 5 mL of methanol and 5 mL Milli-Q water. Spiked water sample (250 mL) was then loaded onto the SPE tubes at a flow rate of 5 mL/min. Subsequently, the cartridges were allowed to dry under gentle vacuum and elution was done with 2 × 2.5 mL volume of methanol containing 0.1% acetic acid.

The processing of the wastewater samples through SPE was also done as stated above. The extract samples were filtered through Phenex™ Nylon 0.45 µm syringe filters (Phenomenex, South Africa). A 10 µL volume of the sample was injected into the RP-HPLC system for analysis.

3.7 RP-HPLC analysis of phenols

The HPLC system is an Agilent 1200 series, (Agilent Technologies, USA) controlled by a ChemStation software. The Liquid chromatographic system (G1316A) is equipped with an online degasser (G1322A), quaternary pump (G1311A), auto-sampler (G1329A), diode array detector (G1315D) and thermostatic column compartment. Separation of P, 2-NP, 4-NP and 2-CP was achieved using an octadecyl C18 150 mm × 4.6 mm internal diameter, 5 µm particle sized column (YMC Co., South Africa). The employed isocratic protocol entails a mobile phase composition of methanol/0.1% acetic acid in water (35:65 v/v), a flow rate of 1 mL/min, and operating temperature of 23 ^{o}C. Detection with photo diode array detector (PDA) was at maximum wavelength of 270, 275, 320 and 275 nm for P, 2-NP, 4-NP and 2-CP respectively.

Qualitative analysis for identification and matching of each peak to corresponding compound was done with by injecting 10 µL pure individual standard of P, 2-NP, 4-NP and 2-CP. For quantitative measurements, standards of different concentrations were injected in order to prepare a calibration curve. External calibration was used for extrapolation of concentrations.

3.8 Adsorption experiments

Batch adsorption experiments were conducted by weighing required masses of GL, GLA and GLB into 100 mL sized Erlenmeyer flasks containing 25 mL of 100 mg/L (of P, 2-NP, 4-NP and 2-CP) solution. The flasks were stoppered with a cork and the mixtures were allowed to equilibrate on a mechanical shaker (Labotec OrbiShake) at 200 rpm for a required period of time. After equilibration, the resulting aqueous solutions were filtered, processed through SPE cartridges and concentrated into methanol. Analysis of residual concentration of P, 2-NP, 4-NP and 2-CP in the filtrates was done using HPLC. The adsorbent after adsorption were analysed with FTIR and SEM. Adsorption experiments were conducted in triplicates.

The amount of phenol adsorbed at equilibrium and percent adsorption was calculated using Eq. 3.6 and Eq. 3.7 respectively.

$$q_e = \frac{(Co - Ce)V}{W} \quad (3.6)$$

$$\text{Percent adsorption (A \%)} = \frac{(Co - C)}{Co} \text{ X } 100 \quad (3.7)$$

Where:
q_e: amount of P, 2-NP, 4-NP and 2-CP per unit mass of adsorbent at equilibrium (mg/g)
Co: initial concentrations of P, 2-NP, 4-NP and 2-CP in solutions (mg/L)
Ce: equilibrium concentrations of P, 2-NP, 4-NP and 2-CP in solutions (mg/L)
C: concentration of P, 2-NP, 4-NP and 2-CP after adsorption at any time (mg/L)
V: volume of MB solution used in adsorption (L)
W: mass of activated carbon used (g).

3.8.1 Effect of adsorbent dosage

A varying mass of adsorbent (0.05, 0.1, 0.2, 0.4 and 0.7 g each of GL, GLA and GLB) was weighed into 25 mL solutions containing 100 mg/L phenols (P, 2-NP, 4-NP and 2-CP). The experiment was to determine the influence of increasing dose of adsorbent dose on adsorption. Initial concentrations of the solutions were 100 mg/L and the experiment was conducted at 23 ^{o}C for 240 minutes.

3.8.2 Effect of contact time of adsorption

The effect of varying contact time (kinetic study) was done by repeating the adsorption experiments at different time intervals of 15, 30, 60, 120 and 240 min to obtain optimal time required for adsorption. The kinetic data obtained were fitted into kinetic models of pseudo-first order, pseudo-second order, Elovich, Intraparticle diffusion and Fractional power.

3.8.3 Effect of pH

The efficiency of adsorption of P, 2-NP, 4-NP and 2-CP at pH range of 4 – 9 was carried out by adjusting the initial pH of the solutions with 2 M HCl and 2 M NaOH. The optimal mass of the adsorbents (0.3 g) and optimal contact time (240 min) was used and all other adsorption conditions were constant.

3.8.4 Effect of concentration

The effect of varying initial concentration was investigated by varying the initial concentration of solutions containing P, 2-NP, 4-NP and 2-CP and carrying out adsorption studies with 0.3 g of the adsorbents (GL, GLA and GLB). The equilibrium data obtained from effect of initial concentration were fitted into Freundlich, Langmuir, Temkin and D-R adsorption isotherm models.

3.8.5 Effect of temperature

A mass of 0.3 g of GL, GLA and GLB respectively was dispersed in Erlenmeyer flasks containing 25.0 mL solutions of P, 2-NP, 4-NP and 2-CP with initial concentrations of 100 mg/L. Adsorption experiments were conducted at different temperatures of 30, 40, 60 and 70 ^{o}C and a stirring speed of 200 rpm for 240 min. The resultant solutions were filtered and the residual concentrations of P, 2-NP, 4-NP and 2-CP in the filtrate samples were analysed.

3.9 Mathematical adsorption models

3.9.1 Adsorption kinetics

The adsorption of P, 2-NP, 4-NP and 2-CP onto the prepared adsorbents was evaluated using pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion and fractional power kinetic rate equations.

3.9.1.1 Pseudo-first order model

The linearized form of the pseudo first-order model (Abdullah *et al*., 2009) is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3.8)$$

Where:
q_e: amount of P, 2-NP, 4-NP and 2-CP adsorbed per unit weight of the adsorbents at equilibrium (mg/g)
q_t: amount of P, 2-NP, 4-NP and 2-CP adsorbed at any time (mg/g)
t: time (min)
k_1: pseudo-first order rate constant of adsorption (1/min).

The values of $\boldsymbol{q_e}$ and $\boldsymbol{k_1}$ were determined from the linear plot of $\mathbf{log}\ (q_e - q_t)$ against $\boldsymbol{t}$. Pseudo-first order kinetic models give a best fit for adsorption processes where the rate of adsorption of an adsorbent depends on concentration of adsorbate in the bulk solution (Abdullah *et al*., 2009).

3.9.1.2 Pseudo-second order model

The linearized form of the pseudo second-order model is represented in Eq. 3.9.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3.9)$$

Where
q_e: equilibrium concentration of P, 2-NP, 4-NP and 2-CP (mg/g)
q_t: amount of P, 2-NP, 4-NP and 2-CP adsorbed at a given time (mg/g)
t: time (min)
k_2: pseudo-second order rate constant (g/mg.min).

The values of $\boldsymbol{qe}$ and $\boldsymbol{k_2}$ are extrapolated from the slopes and intercepts of the linear plot of $\boldsymbol{t/q_t}$ against $\boldsymbol{t}$ (Abdullah *et al*., 2009).

When an adsorbent depends on the available sites rather than concentration of adsorbate in solution for optimal adsorption, the rate of adsorption is well correlated with pseudo-second order, and the overall adsorption may be controlled by chemical process such as covalent sharing of electron between adsorbate and adsorbents (Li *et al*., 2010; Dural *et al*., 2011).

3.9.1.3 Intraparticle diffusion model

The slowest step in an adsorption process is usually taken as the rate determining step. This step is often attributed to pore and intraparticle diffusion. Since pseudo first and pseudo second order models cannot provide information on effect of intraparticle diffusion in adsorption, intraparticle diffusion model can be used (Ahmed & Dhedan, 2012).

The intraparticle diffusion model based on the theory proposed by Weber and Morris is expressed as:

$$q_t = k_3 t^{1/2} + C \qquad (3.10)$$

Where:
q_t: amount of P, 2-NP, 4-NP and 2-CP adsorbed at a given time (mg/g)
t: time (min)
k_3: intraparticle diffusion rate constant (mg/g.min$^{1/2}$)
C: constant which gives an understanding of the thickness of the boundary layer.

The linear plot of $\boldsymbol{q_t}$ versus $\boldsymbol{t^{1/2}}$ gives a straight line when particle diffusion has effects on rate of adsorption. If intraparticle diffusion is the rate determining step in an adsorption process, the linear plot passes through the origin. A value of $\boldsymbol{C}$ closer to zero implies that the rate limiting step of the adsorption is the diffusion step.

3.9.1.4 Elovich model

The Elovich rate equations represented in Eq. 3.11 (Ayanda *et al*., 2013) was also used in modelling the kinetics of adsorption of P, 2-NP, 4-NP and 2-CP onto the adsorbents. The Elovich rate equation is given as:

$$q_t = (1/\beta).\ln(\alpha_\varepsilon/\beta) + 1/\beta.\ln(t) \qquad (3.11)$$

Where:
q_t: amount of P, 2-NP, 4-NP and 2-CP adsorbed at a given time (mg/g)
α_ε and β: Elovich constants
t: time (min).

A linear plot of q_t against *ln (t)* can be used in evaluating the values of α_ε and β.

3.9.1.5 Fractional power

The Fractional power model can be expressed in the linearized form as:

$$\log q_t = \log k + v \log t \qquad (3.12)$$

Where:
q_t: amount of P, 2-NP, 4-NP and 2-CP adsorbed at a given time (mg/g)
k and v: fractional power constants
t: time (min).

The values of ***v*** and ***k*** can be extrapolated from the linear plot of ***log qt*** against ***log t***.

3.9.2 Adsorption Isotherm

There are several available theories that can be used to explain the underlying mechanism of any particular adsorption phenomenon. These theories are referred to as 'adsorption isotherms' and are used in modelling adsorption process. The isotherm models are for investigating maximum adsorption capacity of any particular adsorbent and for establishing the relation between the amounts of adsorbate adsorbed onto the surfaces of an adsorbent and concentration (Abdullah *et al*., 2009). The isotherm models used in this study include Langmuir isotherm, Freundlich isotherm, Temkin and Dubunin-Radushkevich isotherms.

3.9.2.1 Langmuir Adsorption Isotherm

The Langmuir isotherm is centred on the hypothesis that adsorption only occur at specific homogeneous sites on the surfaces of an adsorbent and also, that no further adsorption can take place at these sites when an adsorbate molecule already occupies the site (Gupta *et al*., 2004). The linearized form of the Langmuir isotherm is expressed as:

$$\frac{1}{q_e} = \frac{1}{bQ_o} \cdot \frac{1}{C_e} + \frac{1}{Q_o} \qquad (3.13)$$

Where
q_e: amount of adsorbate adsorbed per unit weight of the adsorbent (mg/g)
Q_o: maximum amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)
b: Langmuir isotherm constant which indicates affinity of adsorption (mol/L)
C_e: equilibrium concentration of adsorbate in solution (mg/L)

The constants $\boldsymbol{Q_o}$ and ***b*** can be evaluated from intercept and slope in the linear plot of $\boldsymbol{1/q_e}$ against ***1/Ce***.

An important characteristic of Langmuir isotherm is the dimensionless separation parameter R_L (Ahmaruzzaman & Sharma, 2005) which is expressed as:

$$R_L = [1/ (1+bC_i)] \quad (3.14)$$

Where:
C_i: Initial concentration of adsorbate in solution (mg/L)

The values of $R_L = 1$: indicative that adsorption is linear;

$R_L > 1$: process of adsorption process is unfavourable;

when $R_L = 0$: this indicate irreversible adsorption;

and the values of R_L between 0 and 1 represent favourable adsorption (Mittal *et al*., 2007; Hameed *et al*., 2009).

3.9.2.2 Freundlich Adsorption Isotherm

The Freundlich isotherm is used to describe adsorption by heterogeneous surfaces. The empirical Freundlich isotherm equation (Ma *et al*., 2013) can be expressed as:

$$q_e = K_f C_e^{1/n} \quad (3.15)$$

Where
q_e: amount of adsorbate adsorbed per unit weight of the adsorbent (mg/g)
K_f: symptomatic adsorption capacity; the distribution coefficient indicative of relative adsorption capacity of the adsorbent $(mg/g)(L/mg)^{1/n}$
C_e: equilibrium concentration of adsorbate in solution (mg/L)
n: intensity of adsorption.

The magnitude of *n* indicates the favourability and intensity of adsorption. Values of *n* close to 1 and less than 10 represent favourable adsorption (Ma *et. al.*, 2013). The inverse (1/n) shows heterogeneity of adsorbent surfaces. The values of 1/n can range between 0 and 1. Adsorption process becomes more heterogeneous as the value of 1/n approaches zero; when $1/n < 1$, it represents a normal adsorption and for $1/n > 1$, this indicates the cooperative nature of adsorption (Ma *et. al*., 2013).

3.9.2.3 Temkin

The Temkin isotherm model can be used in evaluating characteristic energies of an adsorption process. The linearized Temkin equation (Ahmaruzzaman & Gayatri, 2011) can be expressed as:

$$q_e = B \ln K_{TEM} + B \ln C_e \quad (3.16)$$

Where:
B: heat of adsorption (kJ/mol)
K_{TEM}: Temkin equilibrium binding constant (L/g)
q_e: amount of adsorbate adsorbed per unit weight of the adsorbent (mg/g)
C_e: equilibrium concentration of adsorbate in solution (mg/L).

3.9.2.4 Dubunin-Radushkevich model

The Dubunin-Radushkevich (D-R) isotherm model was also used in evaluating the adsorption process. The linearized form of D-R equation (Soto *et al*., 2011) is represented as:

$$\ln q_e = \ln \Phi_D - \Psi_D (\ln [1+1/C_e])^2 \quad (3.17)$$

Where:
Φ_D: Dubunin-Radushkevich's maximum adsorption capacity (mg/g)
Ψ_D: characteristic energy of adsorption (J^2/mol^2)
q_e: amount of adsorbate adsorbed per unit weight of the adsorbent (mg/g)
C_e: equilibrium concentration of adsorbate in solution (mg/L).

3.9.3 Thermodynamic Parameters

Thermodynamic parameters such as the standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were determined.

The Gibbs free energy ΔG^0 ($kJmol^{-1}$) is used to determine spontaneity and thermodynamic favourability of adsorption (Aroguz, 2006). These parameters were evaluated using the Eq. 3.18 and Eq. 3.19.

$$\Delta G° = -RT \ln K_c \quad (3.18)$$

$$\ln K_c = - \Delta H^o/RT + \Delta S^o/R \quad (3.19)$$

Where:
K_c: thermodynamic equilibrium constant
R: universal gas constant (8.314 J/mol.K)
T: absolute temperature (K)

A linear graph of $ln\ K_c$ versus $1/T$ (Van't Hoff's plot) can be plotted from Eq. 3.19. The slope of the graph gives the standard enthalpy ΔH^0 (kJ/mol) while the intercept corresponds to the standard entropy change, ΔS^0 (J/K.mol) for the adsorption process (Aroguz, 2006).

3.10 Adsorption of phenols from environmental wastewaters

The levels of P, 2-NP, 4-NP and 2-CP in some collected wastewater samples were determined. The optimized conditions obtained from batch experiments on synthetic wastewater (contaminated with P, 2-NP, 4-NP and 2-CP) were applied for adsorption experiments on environmental wastewater samples.

3.11 Column studies

The potential industrial application of the prepared adsorbent can be projected through column studies. In fixed bed adsorption studies, same amount of adsorbent is in continuous contact with fresh concentration of adsorbate. This is in contrast to batch mode procedure, where same mass of adsorbent is in contact with fixed concentration of adsorbate for a specified contact time of adsorption.

In this study, 2.00 g of GLA was packed in a glass tube (15.0 cm long, internal diameter of 0.5 cm). Cotton wool was fixed at the bottom and above the adsorbent to prevent floatation. A total volume of 600 mL feed solution containing 500 mg/L of P, 4-NP, 2-NP and 2-CP was used for adsorption. The feed phenolic solution was passed through the packed column at a maintained flow rate of 2.0 mL/min using a peristaltic pump. Column effluents were collected at 50 cm^3 intervals. The resultant solutions were processed through SPE and analysis of residual phenol was done with HPLC.

3.12 Desorption studies

One of the advantages of adsorption is potential of reuse of the adsorbents. The rate of regeneration of the used carbons can be investigated through desorption studies.

In this study, 0.3 g, 0.5 g and 0.5 g of GLA, GLB and GL respectively was weighed into 25 mL solutions (500 mg/L) of phenols and equilibrated on an orbital shaker for 240 min. After adsorption of P, 4-NP, 2-NP and 2-CP onto the adsorbents, the aqueous solutions were filtered and analysed to determine the residual concentration of phenols which was not adsorbed by the adsorbents. The residue (adsorbent) thus contains known amounts of phenols.

A 25 mL solution of 0.1M HCl and 0.1 M NaOH was measured in separate 100 mL sized Erlenmeyer flasks. The loaded adsorbents were then added to the solutions and equilibrated on an orbital shaker for 240 min. All desorption experiments were carried out at room temperature. After equilibration, the solution was filtered. Recovered adsorbate was processed through SPE and analysed on HPLC.

The recovery of phenols (%) from the adsorbents was evaluated using equation 3.20.

$$\text{Recovery (\%)} = \frac{C_d}{C_0 - C_1} \text{ X } 100 \qquad 3.20$$

Where:
C_0: original concentration of P, 4-NP, 2-NP and 2-CP in solution
C_1: amount of P, 4-NP, 2-NP and 2-CP in solution after adsorption onto the adsorbents
C_d: amount of P, 4-NP, 2-NP and 2-CP desorbed from the adsorbents (mg/L)
C_0 – C1 gives the amount of P, 4-NP, 2-NP and 2-CP adsorbed onto the adsorbents

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Production yield and particle size distribution

At impregnation ratio of 2:1 and thermal treatment (500 ^{o}C for 90 min), the yield was 36% for GLA and 17% for GLB. Lower yield was obtained from alkaline activation. The percentage yield was evaluated from the weighed masses after washing and drying of the prepared active carbons (Table 4.1). In a similar study that used same impregnation ratio, Ahmed and Dhedan (2012) reported a yield of 40.46% after activation of date stones with $ZnCl_2$, at ratio of 2:1 and heat treatment at 500 ^{o}C for 1 h.

Table 4.1: Evaluation of yield for the prepared activated carbons

Activated carbon	Mass before activation (g)	Mass after activation, washing and drying (g)	Yield (%)
GLA	50	18	36
GLB	50	8.5	17

The particle size distribution of the adsorbents (GL, GLA & GLB) used in this study for adsorption of phenols are given in Table 4.2.

Table 4.2: Particle size distribution of prepared adsorbents

Particle size (µm)	GLA (%)	GLB (%)	GL (%)
≥ 500	28.08	25.78	0.00
$250 \leq x < 500$	10.43	21.05	66.76
$200 \leq x < 250$	34.79	0.12	11.87
$75 \leq x < 200$	26.69	42.47	18.37
< 75	0.00	10.59	3.01

The result revealed GLA had particle size ranged 75 – 500 µm, with most particles (34.8%) between 200 – 250 µm and 28.08% were ≥ 500 µm. In the case of GLB, 42.47% of the activated carbons were ranged 75 – 200 µm and 10.59% were < 75 µm. A higher percentage of GL (66.7%) had particle size ranged 250 – 500 µm. The non-treated adsorbent (GL) thus had more particles of higher sizes relative to those of the treated (GLA & GLB) adsorbents.

4.2 Moisture content results

The percentage moisture content of the prepared adsorbents is presented in Table 4.3. It is desirable to prepare adsorbents of low moisture level, because, moisture in these materials does not contribute to adsorption capacity. The amounts (%) of moisture in the prepared biomaterials are moderate (< 12 %). GL has higher moisture content than both GLA and GLB.

Table 4.3: Percentage moisture composition of GL, GLA and GLB

Carbon precursor	Moisture content (%)[1]
GL	11.65 ± 0.48
GLA	11.05 ± 1.28
GLB	9.30 ± 1.13

[1] Values indicate Mean ± SD of 3 determinations (n=3)

4.3 Inorganic matter (ash) content

The inorganic matter content of an activated carbon material plays no role in adsorption, and rather has limiting effects on adsorption potential of the AC. Therefore, assessing level of inactive matter in adsorbents is necessary. Inorganic composition can be determined in form of ash content. Lower levels of ash content in carbonaceous material indicate the quality of the material for adsorption purposes.

The ash content (%) of the precursors prepared from *Vitis vinifera* leaf litter is presented in Table 4.4. The results showed that the activated carbons had lower values of inorganic matter content. GLA and GLB had 96.64% and 99.53% organic components respectively.

Table 4.4: Inorganic matter (ash) content of GL, GLA and GLB

Carbon precursor	Ash content (%)[1]
GL	17.89 ± 0.13
GLA	3.36 ± 0.02
GLB	0.47 ± 0.02

[1] Values indicate Mean ± SD of 3 determinations (n=3)

4.4 pH

The results of pH measurements (Table 4.5) show the changes in pH of the adsorbents after chemical activation. GL and GLA were acidic while GLB was basic. GL and GLA lowered the pH of deionized water (6.85) and were characterised as L-type carbon materials, and GLB categorised as H-type carbon. The L-type activated carbons becomes ionised and are negatively charged upon hydration, resulting in acidic pH while the H-type materials are protonated when hydrated to yield basic solutions (Singh *et al*., 2008).

Table 4.5: pH of the adsorbent materials

Adsorbent	pH
GL	4.89
GLA	3.14
GLB	8.62

4.5 pH at point of zero charge

The determinations of pH at point of zero charge, (pHpzc), of the adsorbents were done using pH drift method. The pHpzc was taken as the pH where the initial pH equals the final pH. Figure 4.1 shows the drift in pH observed after the procedure while the corresponding pHpzc values are given in Table 4.6.

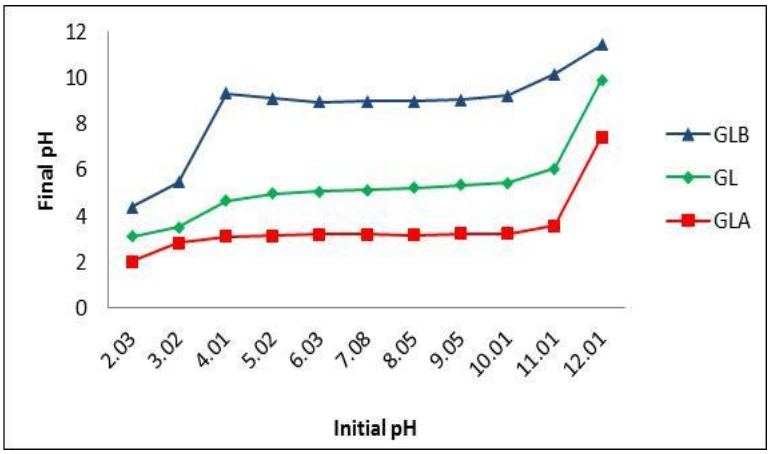

Figure 4.1: pH drift curve for determining pHpzc

Table 4.6: pHpzc of the adsorbent materials

Adsorbent	pHpzc
GL	5.02
GLA	2.04
GLB	9.05

Comparison of pH values of the adsorbents was made with the pH at point of zero charge values (Figure 4.2). The pH values of GL and GLB were slightly lower than their pHpzc values, while the pH of GLA was higher than the pHpzc. According to Moussavi and Barikbin (2010), the surface of an adsorbent is positively charged when the pH value is less than pHpzc value; such surfaces are more likely to attract anions, while on the other hand, when pH is above pHpzc values, the surfaces are negatively charged, thus, more probable to attract cations. Therefore, GL and GLB may be positively charged while surface of GLA may be negatively charged. The results are consistent with the characterization of carbon by Moussavi and Barikbin (2010) where the surface of carbon (from pistachio hull waste) was positive (pH < pHpzc) and was effective in adsorption of chromium species (in a dominant form of $HCrO_4^-$). However, the finding is in contrast with the classification for GL.

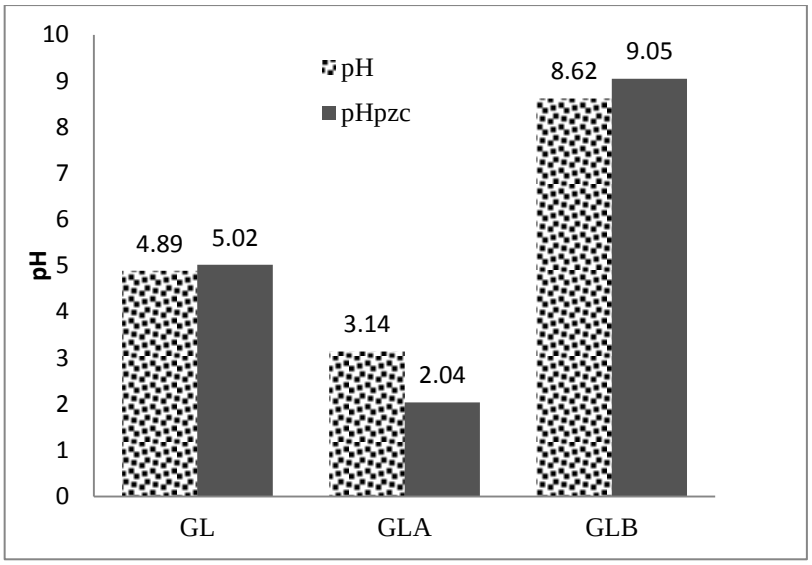

Figure 4.2: Comparison of pH with pHpzc values of the adsorbents

4.6 SEM micrographs of the adsorbents

The SEM micrographs obtained for non-activated (GL), acid-modified (GLA) and alkaline-modified (GLB) *Vitis vinifera* leaf litter before use in adsorption are represented in Figures 4.3a – 4.5a while the corresponding micrographs of the adsorbents after adsorption of phenols is shown in Figures 4.3b – 4.5b.

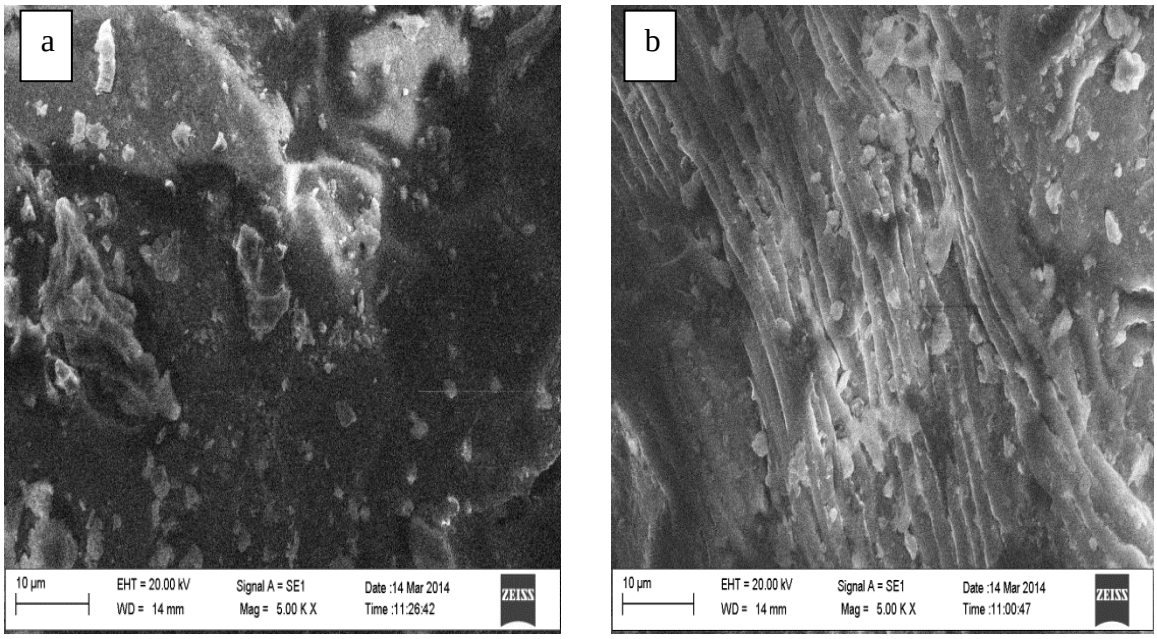

Figure 4.3: SEM of GL (a) before and (b) after adsorption of phenols

The SEM of GL before adsorption (Figure 4.3a) shows a moderately smooth surface which is devoid of defects (cracks and cavities) with presence of adhering particles which may be dust or salts (Dural *et al*., 2011), hence, proper and more vigorous washing of the leaf biomass is needed before application in adsorption. The micrograph of GL after adsorption of phenols (Figure 4.3b) shows depositions of adsorbed phenols in smooth regular formations on the surfaces.

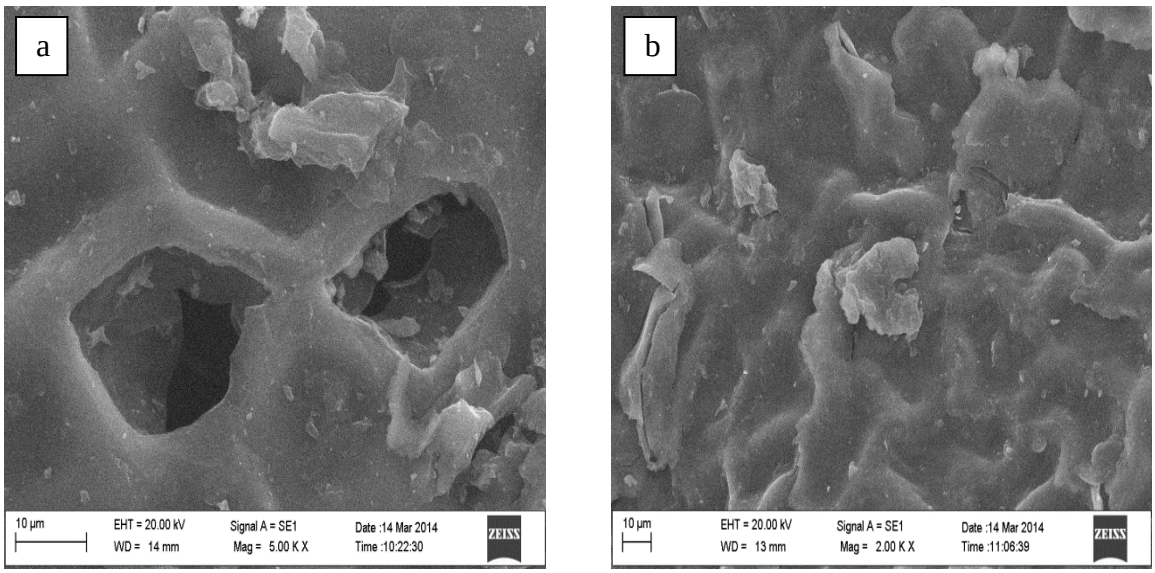

Figure 4.4: SEM of GLA (a) before and (b) after adsorption of phenols

Figure 4.4a shows the surface morphology of GLA after activation. It is clear that the surfaces of GLA are smooth and contains cavities and pores which may enhance biosorption and intra-particle diffusivity by ensuring infiltration of adsorbate solution into the 'non-crystalline' spaces in the adsorbent (Wahab *et al*., 2012). The porous structures have been filled after adsorption of phenols (Figure 4.4b).

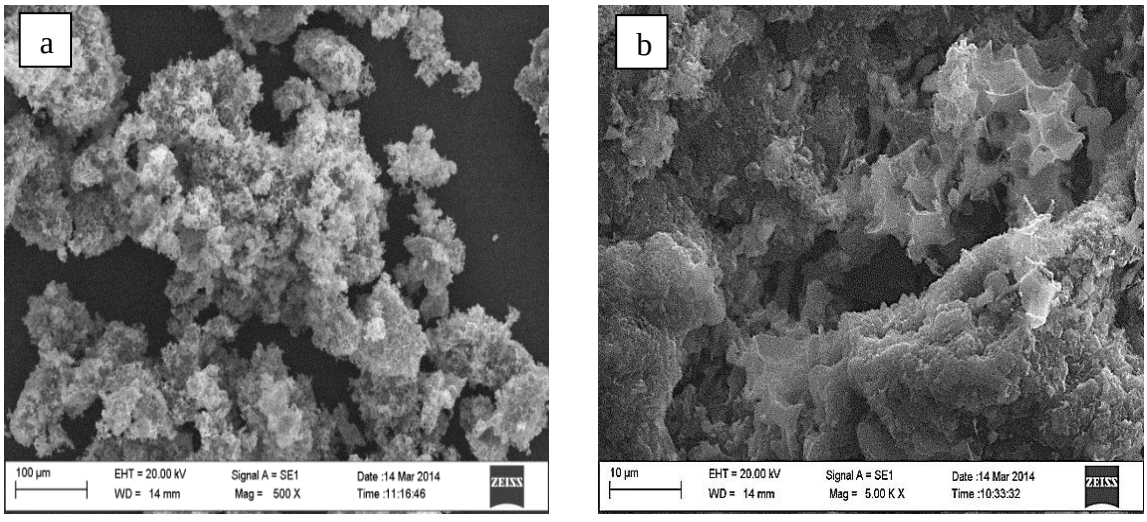

Figure 4.5: SEM of GLB (a) before and (b) after adsorption of phenols

The micrograph for the surfaces of GLB before adsorption (Figure 4.5a) shows the morphology of the surface to be rough, heterogeneous and irregular with crevices which enhances adsorption (Kumar & Min, 2011). Figure 4.5b shows formation of clusters on the adsorbent surfaces after adsorption of phenols.

4.7 EDX elemental microanalysis

Micro-beams from Energy-Dispersive X-ray instruments were used for determining the elements in the adsorbents and their composition. The results for elemental phase compositions of non-activated leaf litter (GL), phosphoric acid – activated carbon (GLA); and sodium hydroxide - activated carbon (GLB) is represented in Figure 4.6 – 4.8 respectively.

The adsorbents prepared in this study were shown to contain surface oxygen, which is essential in adsorption process to enable chemical interactions such as hydrogen and –OH bond formation between adsorbent – adsorbate species. The precursors from *Vitis vinifera* leaves may thus, be a good source of adsorbent; and investigating the potential adsorption capacity is the vital aim of this research.

Figure 4.6 shows that GL contains 60.34% carbon and 37.86% oxygen; and other elements were in trace amounts. This result indicates that although surfaces of GL lacks porous network (Chapter 4.1), there is available C – O groups and possibility of other interactions with the surface oxygen moieties in adsorption process.

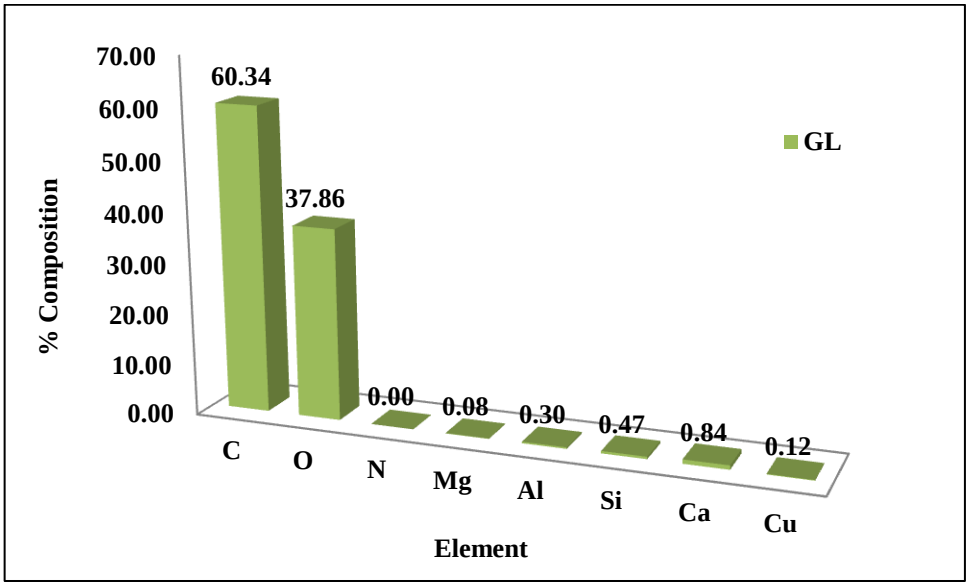

Figure 4.6: Elemental composition of GL

Upon chemical activation, the phase composition of elements in GLA (Figure 4.7) revealed that the activated carbon material is mostly composed of carbon (67.98%) and oxygen (28.34%), as well as significant amount of phosphorous (2.04%) which may have resulted from activation with phosphoric acid.

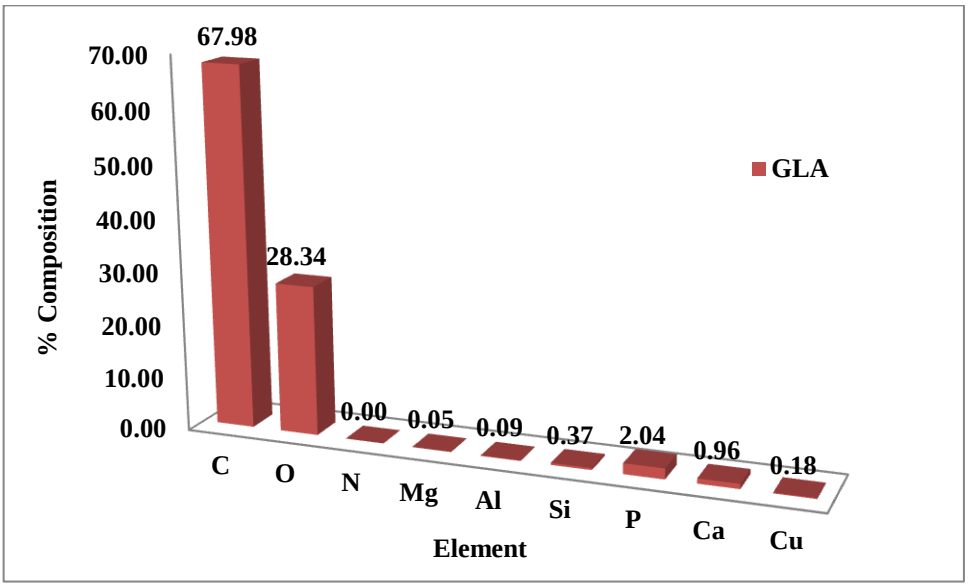

Figure 4.7: Elemental composition of GLA

GLB contained 65.64% carbon and 27.45% oxygen (Figure 4.8). The amounts of Ca (3.75%), Na (0.30%) and other inorganics are also significant. The Ca may have been introduced from the alkaline solution used for activation, however, a general change in composition of the adsorbents after chemical activation was observed.

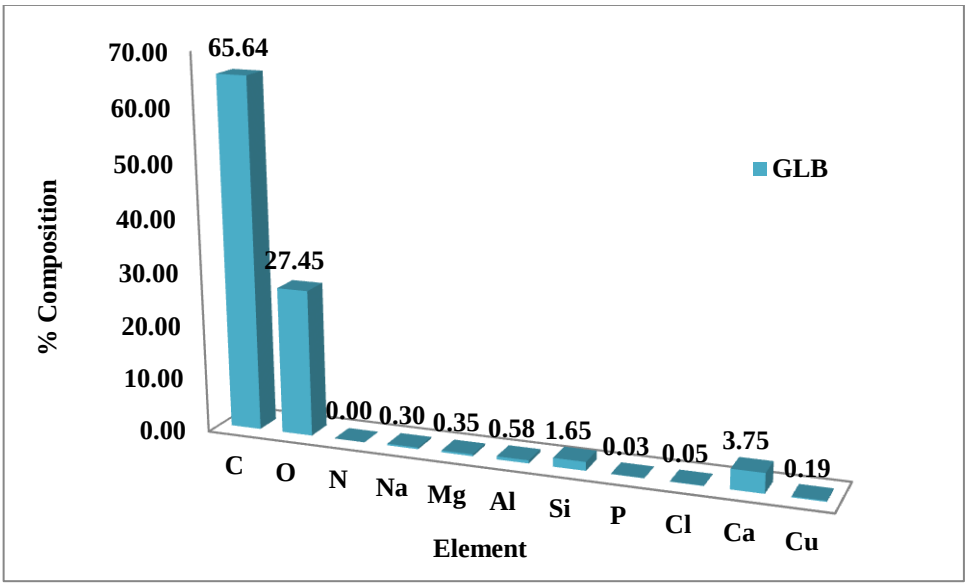

Figure 4.8: Elemental composition of GLB

These results revealed that GLA has the highest percentage carbon content (67.98%) relative to GL (60.34%) and GLB (65.64%). On the basis of carbon-framework support for sorption, higher carbon content in GLA may be suggestive of higher adsorption capacity of GLA as there will be more active sites for catenation in adsorption; this claim will be scrutinised in subsequent adsorption experiments.

4.8 FTIR analysis

The prominent functional groups on the surfaces of the adsorbents were determined with FTIR. The shift and/or changes in spectra bands which resulted from chemical activation and adsorption processes were also assessed. Figure 4.9a - c shows the changes in spectra scan and adsorption bands of *Vitis vinifera* leaf litter before and after chemical activation. The spectra of the adsorbents before and after use in adsorption of phenols are presented in Figures 4.10 – 4.12 a - b.

In the FTIR spectrum of GL (Figure 4.9a), there is a distinct broad adsorption band at 3419 cm^{-1} which is assigned to –OH of hydroxyls, and also prominent peaks at 2851 and 2922 cm^{-1} assigned to C – H bonds of methyl and methylene groups (Wahab *et al*., 2012). These wave bands were less observed after chemical activation as shown in the overlapped spectra of GLA (Figure 4.9b) and GLB (Figure 4.9c). This may be attributed to significant loss in lignin, as well as degradation reactions (such as dehydration, depolymerisation and decarboxylation) upon thermal treatment (Demirbas, 2004). These reactions may account for reduced functional groups on GLA and GLB after activation.

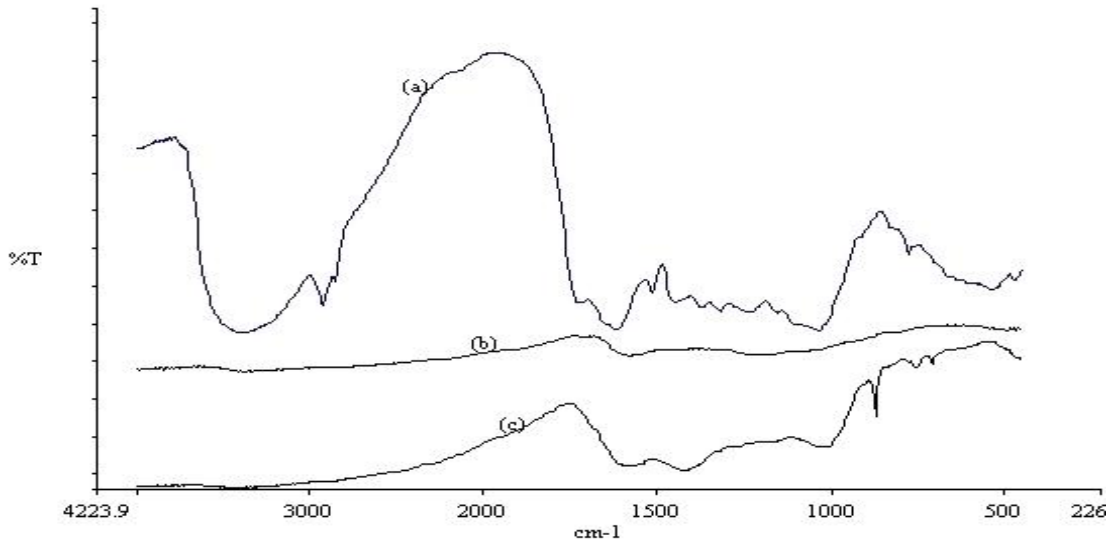

Figure 4.9: FTIR spectra of (a) GL (b) GLA and (c) GLB

The FTIR spectrum of GL before and after adsorption of phenols is shown in Figure 4.10 a-b and the observed shift in adsorption bands is presented in Table 4.7.

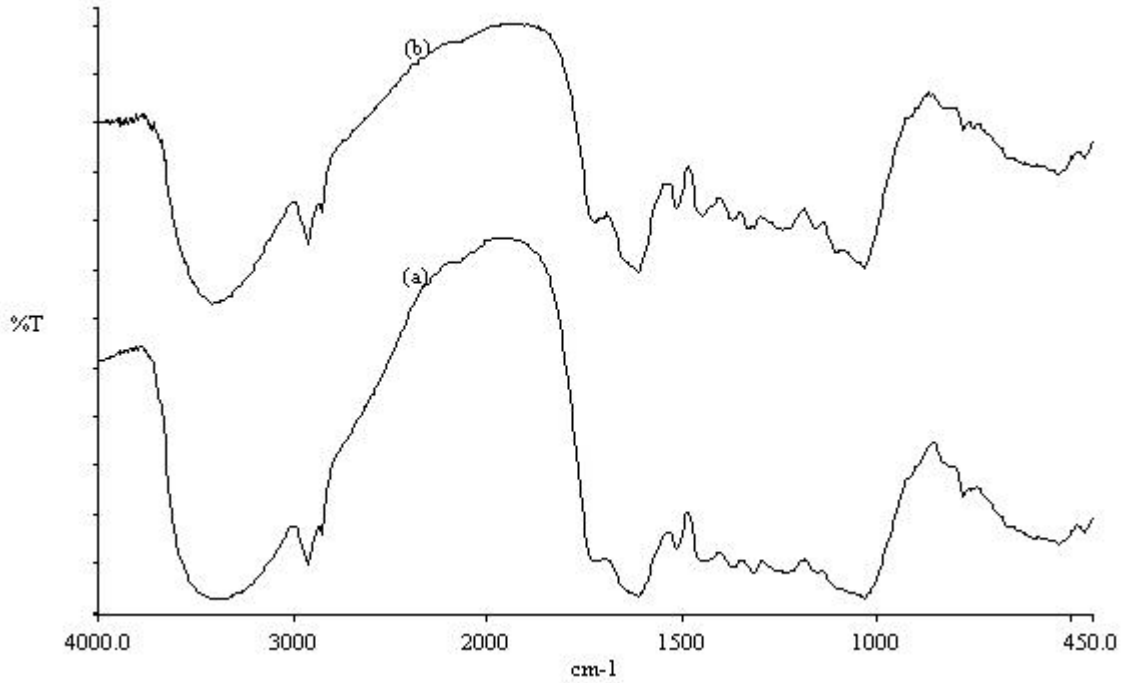

Figure 4.10: FTIR spectra of GL (a) before and (b) after adsorption of phenols

Table 4.7: FTIR spectra characterisation of GL before and after adsorption of phenol

Wavelength class range (cm^{-1})	Band assignment	GL			
		Before adsorption	After adsorption	Difference	Remark
3500 – 3200	-OH of hydroxyl groups	3411	3417	+6	Less broad
2950 – 2850	C – H of Alkyl groups	2921	2921	0	More intense
1700 – 1500	C = C of aromatics	1617	1614	-3	More prominent
1300 – 1000	C – O of alcohols, ethers, carboxylic, esters	1035	1035	0	More intense

Adsorption reactions such as ion exchange and complexation are justified by bond formation between adsorbed species and – OH of phenol, carboxyl, or hydroxyl groups on the surface of the adsorbent (Wahab *et al*., 2012), thus the –OH group on GL may be responsible for adsorption onto GL.

FTIR spectra of GLA before and after adsorption of phenols are presented in Figure 4.11 a-b. The corresponding adsorption wavelengths are summarised in Table 4.8.

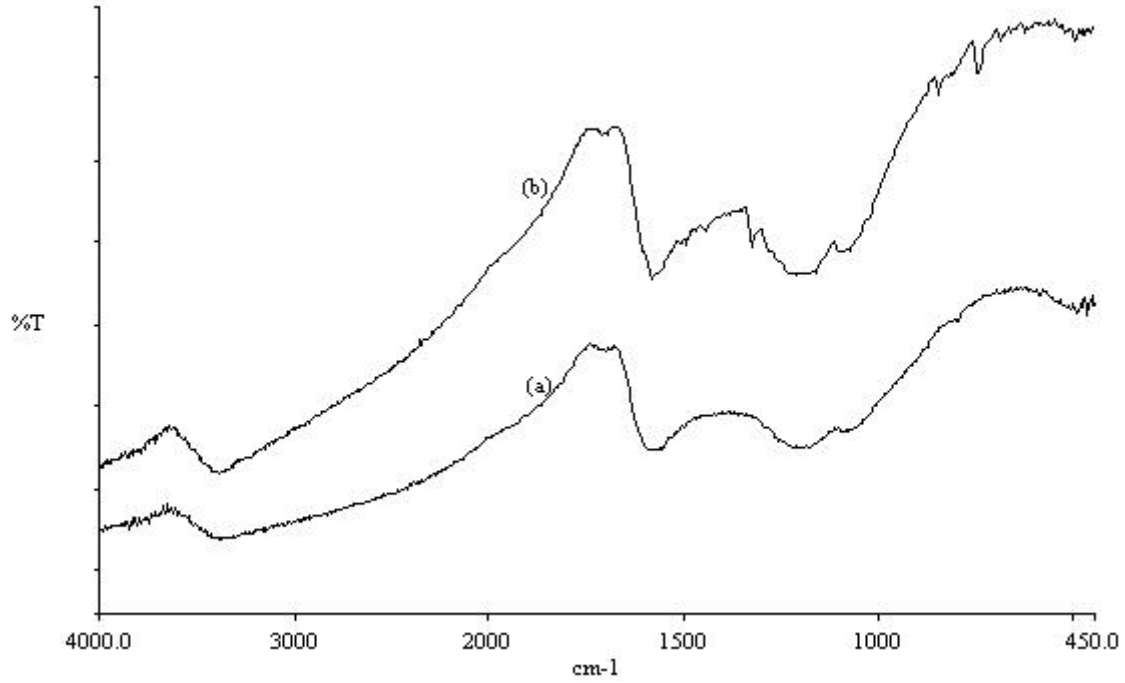

Figure 4.11: FTIR spectra of GLA (a) before and (b) after adsorption of phenols

Table 4.8: FTIR spectra characterisation of GLA before and after adsorption of phenol

Wavelength class range (cm^{-1})	Band assignment	GLA			
		Before adsorption	After adsorption	Difference	Remark
3500 – 3200	-OH of hydroxyl groups	3383	3393	+10	Very weak
1700 – 1500	C = C of aromatics	1582	1585	+3	Prominent
1300 – 1000	C – O of alcohols, ethers, carboxylic, esters	1219	1210	-9	Medium
900 – 600	C –H of aromatics	Absent	749	-	Weak

Figure 4.12 a – b shows the FTIR spectrum of GLB before and after adsorption of phenols. The corresponding adsorption wavelengths are given in Table 4.9.

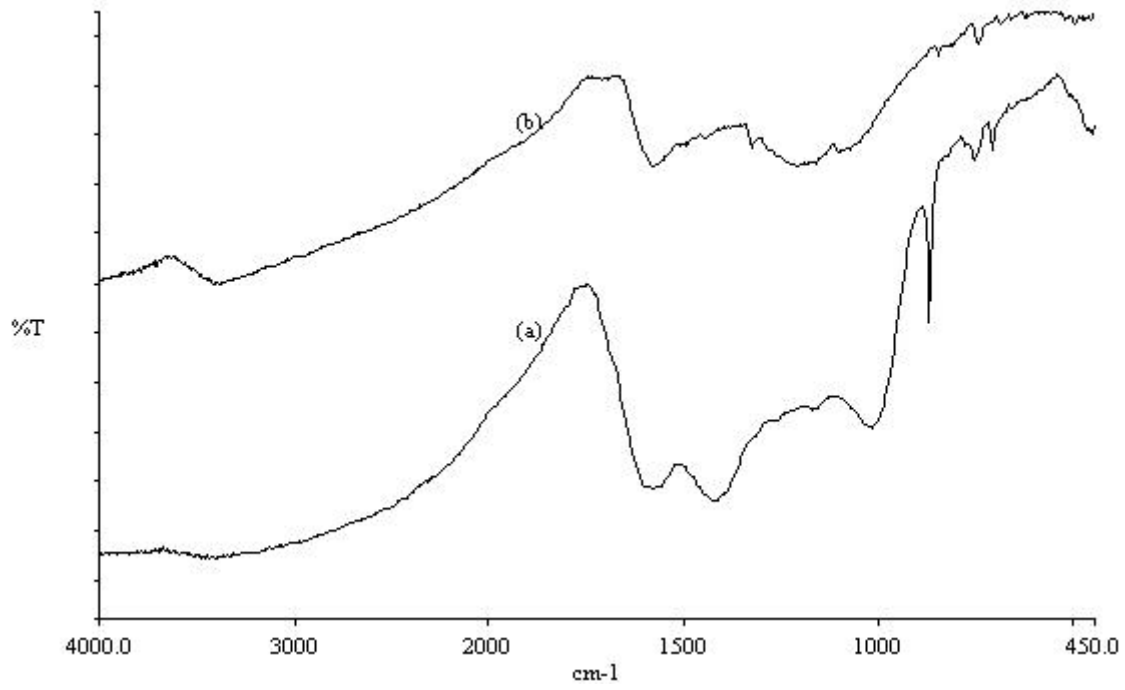

Figure 4.12: FTIR spectrum of GLB (a) before and (b) after adsorption of phenols

Table 4.9: FTIR spectra characterisation of GLB before and after adsorption of phenol

Wavelength class range (cm^{-1})	Band assignment	GLB			
		Before adsorption	After adsorption	Difference	Remark
1700 – 1500	C = C of aromatics	1575	1589	+14	Medium
1300 – 1000	C – O of alcohols, ethers, carboxylic, esters	1018	1026	+8	Medium
900 – 600	C –H of aromatics	872	872	0	Prominent

4.9 Iodine number

From Table 4.10, it can be deduced that activated carbons prepared via chemical activation using phosphoric acid exhibit higher iodine number (1065.96 mg/g) when compared to activated carbon prepared using sodium hydroxide (571.05 mg/g) and non-activated biomass (342.63 mg/g). Based on an impregnation ratio of 2:1 used in this study for the determination of iodine number values, GLA was seen to be more efficient than GL and GLB.

Table 4.10: Iodine number of the prepared adsorbents

Adsorbent	Iodine number (mg/g)
GL	342.63
GLA	1065.96
GLB	571.05

In a similar study by Benadjemia *et al*. (2011), globe artichoke leaves were impregnated with phosphoric acid in different ratios. The reported iodine number values were 852, 1134 and 931 mg/g for impregnation ratios of 1:1, 2:1 and 3:1 respectively indicating activated carbons exhibiting higher iodine number were prepared with ratio of 2:1. The ease of iodine sorption was linked to the surface areas of the active carbons. The carbons with ratio 2:1 had the highest surface areas relative to those with ratios 1:1 and 3:1. In this study, the pores and crevices present on GLA may have influenced the accessibility of iodine molecules onto the adsorbent, thus having higher iodine number value, while the absence of pore structure may explain the lower iodine value of GL.

4.10 Methylene blue adsorption

Prior to the utilization of the adsorbents in sorption of phenolic compounds, their potential to adsorb and decolourise methylene blue (MB) dye was assessed. The ability to remediate and decolourise coloured compounds is one of the main characteristics of a good adsorbent. The results obtained from batch adsorption experiments when different masses of GL, GLA and GLB were weighed into 25 mL solutions of MB (1000 mg/L) are presented in Figure 4.14.

An equilibrium mass of 0.1 g of GLA removed 99.94% of MB in 25 mL. Also, at an adsorbent dosage of 0.2 g per 25 mL solution, the percent MB removal by GLB was 99.71%. GL showed the lowest adsorption capacity as 90.07% of MB was removed by 0.4 g of the adsorbent. This result shows that the efficiency of the adsorbents in adsorption of MB is in the order GLA > GLB > GL.

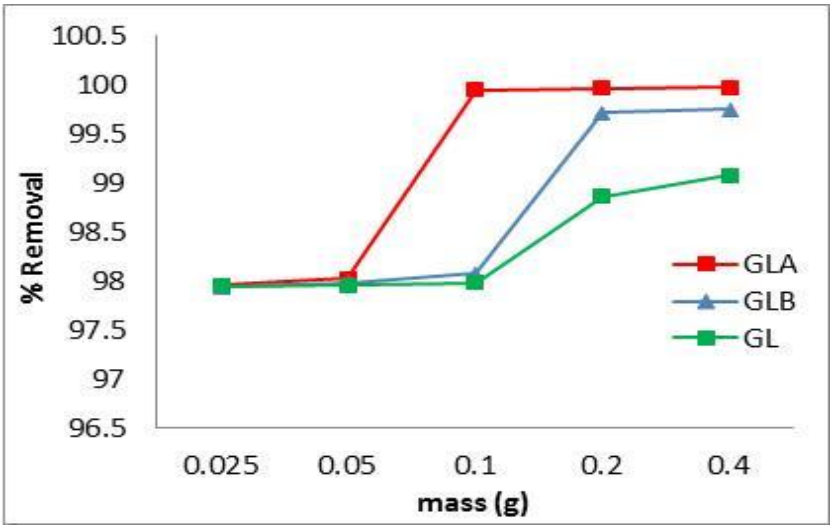

Figure 4.13: Methylene blue adsorption capacity of the adsorbents

Adsorption conditions: Concentration of MB = 1000 mg/L; Volume of MB solution = 25 mL; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

4.11 HPLC analysis

The peak absorbance areas from the LC system were plotted against concentrations of P, 2-NP, 4-NP and 2-CP (µg/mL) to evaluate linearity range for quantification. The obtained results were evaluated for linearity using least squares linear regression. A linearity range of 1 – 1000 µg/mL was recorded for the phenols. Table 4.11 shows the values from standard curve analysis. (The graphical representations are presented in Appendices 1 – 4). A representative LC chromatogram for P, 2-NP, 4-NP and 2-CP is shown in Figure 4.14. The absorbance wavelengths for quantitation of the phenols using photodiode array detector are presented in Table 4.12.

Table 4.11: Linear regression assessment of P, 4-NP, 2-CP and 2-NP standards

Standards	Linear regression equation	R^2
Phenol	y = 11.46x + 30.917	0.9994
4-Nitrophenol	y = 37.794x + 681.97	0.9982
2-Chlorophenol	y = 8.314x + 21.682	0.9998
2-Nitrophenol	y = 26.759x + 338.68	0.9980

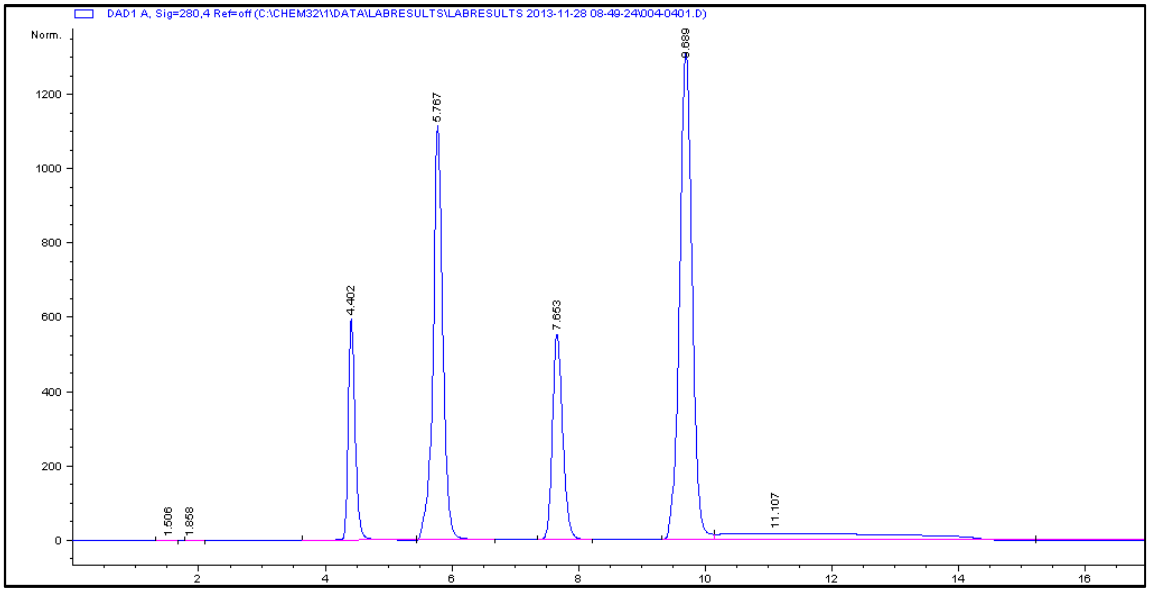

Figure 4.14: HPLC chromatogram for P, 4-NP, 2-CP and 2-NP

Table 4.12: Maximum absorption wavelengths

Compounds	λ_{max}
Phenol	270
4_Nitrophenol	320
2_Chlorophenol	275
2_Nitrophenol	275

4.12 Recovery of phenols

Solid phase extraction technique was employed for pre-concentration of phenols in this study. The optimal performance of the polymeric sorbent material and extraction procedure was assessed. Excellent recoveries were obtained for all phenols and results are presented in Table 4.13.

From the data, the average recovery expressed as percentage for P is ranged 97.40 – 102.40%; 4-NP is ranged 94.20 – 101.51%; 2-CP is ranged 92.60 – 102.85% and 2-NP is ranged 99.64 – 102.04%.

Table 4.13: Average recovery of P, 4-NP, 2-CP and 2-NP

Standards	Expected Concentration (µg/mL)	Measured Concentration (µg/mL)[1]	%RSD	Average Recovery (%)
Phenol				
	1	0.97 ± 0.044	4.51	97.40
	10	10.02 ±0.192	1.92	100.16
	50	49.82 ±0.172	0.35	99.64
	100	100.50 ±0.697	0.69	100.50
	300	307.21 ±3.929	1.28	102.40
4-Nitrophenol				
	1	0.94 ±0.120	12.77	94.20
	10	10.03 ±0.040	0.39	100.32
	50	49.67 ±0.364	0.73	99.33
	100	101.51 ±1.892	1.86	101.51
	300	299.50 ±2.457	0.82	99.83
2-Chlorophenol				
	1	0.93 ±0.035	3.79	92.60
	10	10.05 ±0.079	0.79	100.52
	50	49.67 ±0.345	0.69	99.34
	100	100.22 ±0.119	0.12	100.22
	300	308.54 ±0.917	0.30	102.85
2-Nitrophenol				
	1	1.02 ±0.056	5.50	102.00
	10	10.18 ±0.074	0.73	101.82
	50	49.82 ±0.104	0.21	99.64
	100	99.98 ±0.370	0.37	99.98
	300	306.11 ±4.129	1.35	102.04

[1] Values indicates Mean ± SD of 5 determinations (n=5). RSD, relative standard deviation

4.13 Adsorption studies

4.13.1. Effect of adsorbent dosage on removal efficiency

The initial masses of GLA, GLB and GL were varied from 0.05 – 0.7 g to determine the effect of increasing dose on simultaneous adsorption of P, 2-NP, 4-NP and 2-CP from solution. The initial concentration of the phenolic system was fixed at 100 mg/L (P, 2-NP, 4-NP and 2-CP), and all other adsorption parameters were kept constant. The effective removal (%) of P, 2-NP, 4-NP and 2-CP adsorbed from solution increased as the masses of the adsorbents increased (Figure 4.15 – 4.17) up to a point of equilibrium. This is attributed to an increase in surface area of the adsorbent and the availability of more active sites for adsorption on the surfaces of the adsorbent (Kumar & Min, 2011).

Removal was 92.70%, 99.92%, 99.98% and 99.90% of P, 2-NP, 4-NP and 2-CP respectively using 0.3 g of GLA. A further increase in adsorbent dose showed no significant difference on sorption efficiency; therefore 0.3 g of GLA was used in further adsorption experiments.

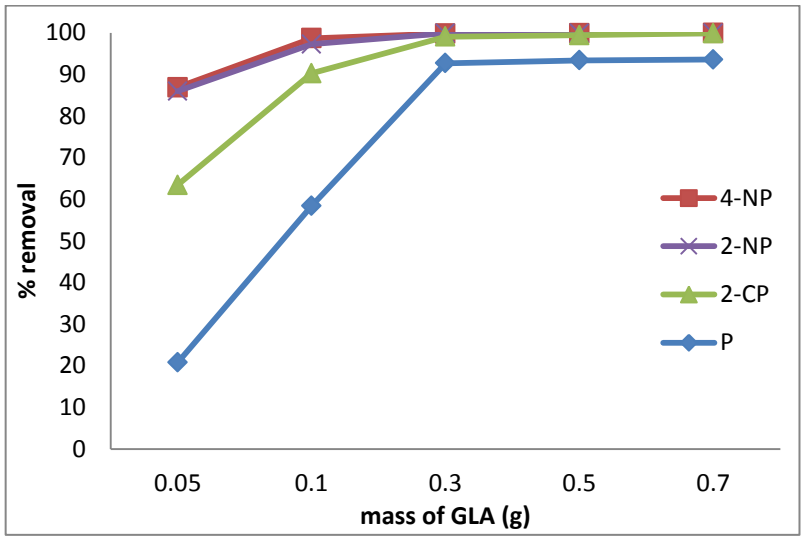

Figure 4.15: Effect GLA dosage on adsorption of P, 2-NP, 4-NP and 2-CP

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

At a dose of 0.5 g of GLB, percentage removal was 86.89%, 89.69%, 84.05% and 93.23% for P, 2-NP, 4-NP and 2-CP respectively. Hence, an optimal mass of 0.5 g GLB was used in subsequent adsorption experimentation involving GLB.

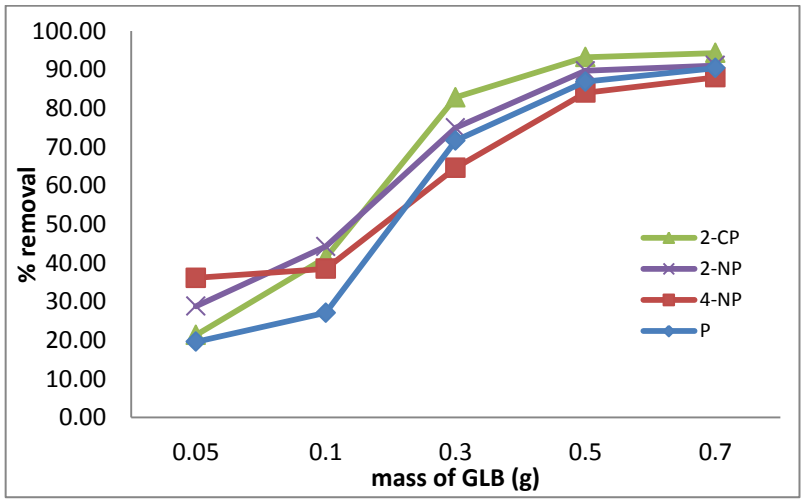

Figure 4.16: Effect of GLB dosage on adsorption of P, 2-NP, 4-NP and 2-CP

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

From Figure 4.17, even at higher dose of GL, the maximum adsorption was 52% for 2-NP, while the amount of 4-NP, 2-CP and P removed (42.89%, 38.78% and 15.20% respectively) were lower. The non-activated biomass was therefore seen not to be very effective in adsorption of phenols of interest; however, further investigation of the adsorbent under different adsorption conditions was carried out. A mass of 0.5 g of GL was chosen for further experiments.

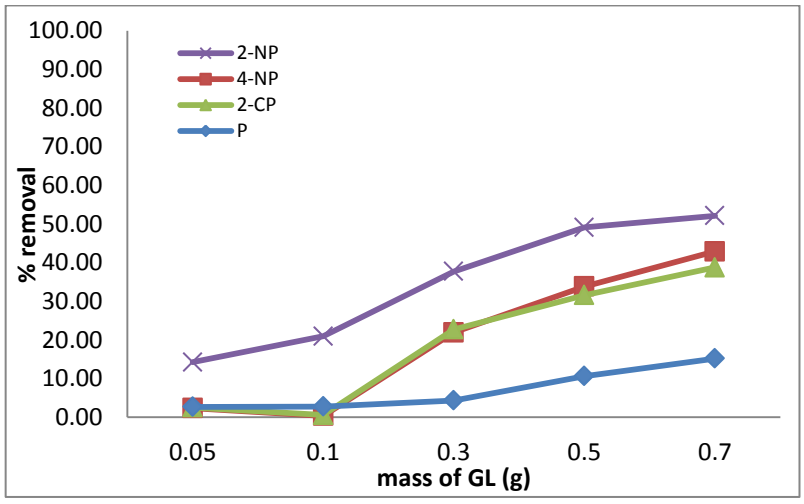

Figure 4.17: Effect of GL dosage on adsorption of P, 2-NP, 4-NP and 2-CP

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

4.13.2 Effect of contact time

The effect of contact time on adsorption efficiency of GLA, GLB and GL was assessed by varying the contact time from 15 – 240 min with other parameters held constant. Increased adsorption was observed with increases in contact time. The initial rise in adsorption observed for GLA, GLB and GL is due to bulk diffusion of P, 2-NP, 4-NP and 2-CP from solution onto the surfaces of the adsorbents.

Equilibrium was attained in 30 minutes for adsorption of 4-NP and 2-NP by GLA (Figure 4.18); however, maximum adsorption of 2-CP and P was not recorded at 30 min, rather at 240 min. Highest equilibrium adsorption of all phenols, 4-NP (20.0 mg/g, 99.99% removal), 2-NP (20.0 mg/g, 99.99% removal), 2-CP (19.52 mg/g, 97.59% removal) and P (16.85 mg/g, 80.23% removal) occurred after 240 min. GLA adsorbed the nitrophenols with nearly same efficiency, thus, their trend lines overlapped. A contact time of 240 min was used in other sorption experiments onto GLA.

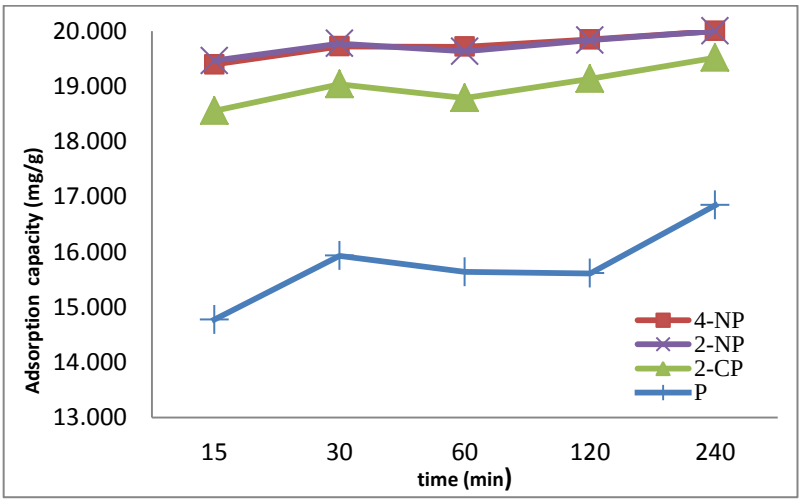

Figure 4.18: Effect of contact time on adsorption of P, 2-NP, 4-NP and 2-CP using GLA

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Mass of GLA = 0.3 g; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

In adsorption using GLB, P attained equilibrium in 30 min, and beyond, a less significant variation in adsorption was observed (Figure 4.19). As phenol cannot be singled out of the phenol system, thus, the optimal contact time for sorption by GLB required considering all four phenols in the system. At 240 min, the equilibrium adsorption onto GLB was 13.14 mg/g (32.16 %) of P; 17.02 mg/g (47.54 %) of 2-NP; 14.97 mg/g (28.48 %) of 4-NP; and 21.13 mg/g (64.89 %) of 2-CP. Optimal contact time used in subsequent adsorption by GLB was 240 min.

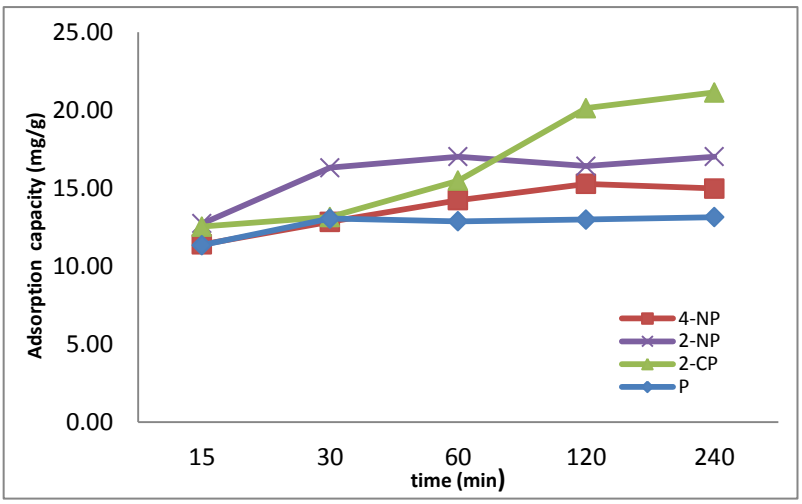

Figure 4.19: Effect of contact time on adsorption of P, 2-NP, 4-NP and 2-CP using GLB

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Mass of GLA = 0.3 g; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

For GL, the adsorption of 2-NP and 2-CP increased with increases in contact time (Figure 4.20). In case of P and 4-NP, sorption was fast in first 30 min, maintained equilibrium and thereafter, an increase in adsorption of these species onto GLB was observed at 240 min. Removal was 6.46 mg/g (19.02 %) of P; 16.66 mg/g (83.32 %) of 2-NP; 4.53 mg/g (22.66 %) of 4-NP; and 13.05 mg/g (65.27 %) of 2-CP at 240 min. A distinct equilibrium cannot be determined within the tested contact times; however, other experiments for optimization of phenols removal using GL were carried out at 240 min.

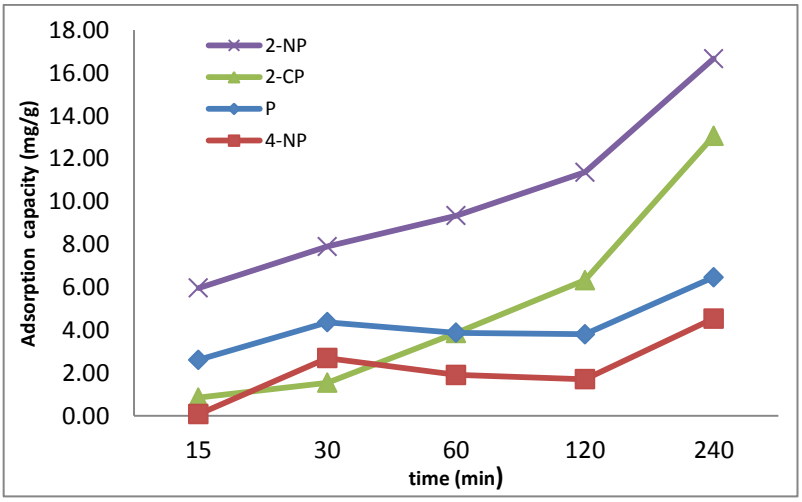

Figure 4.20: Effect of contact time on adsorption of P, 2-NP, 4-NP and 2-CP using GL

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Mass of GL = 0.5 g; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

4.13.2.1 Adsorption kinetics

The mechanism and the rate determining step of an adsorption reaction can be determined by modelling into kinetic models. The pseudo-first order, pseudo-second order, Elovich and fractional power models were used to determine the rate constants for adsorption of P, 4-NP, 2-NP and 2-CP onto GLA, GLB and GL. The effect of diffusion on rate of reaction was determined with intra-particle diffusion model equation.

GLA

Pseudo-second order kinetic model best describes the adsorption of P, 4-NP, 2-NP and 2-CP onto GLA ($R^2 > 0.99$) (Table 4.14). The plots of the kinetic model that best describes the adsorption process for P, 4-NP, 2-NP and 2-CP using GLA are presented in Figures 4.21 – 4.24 respectively.

Table 4.14: Kinetic parameters for adsorption of P, 4-NP, 2-CP and 2-NP onto GLA

Kinetic models				
Pseudo-first order		**K_1 (min^{-1})**	**q_e (mg/g)**	**R^2**
	P	0.0009	1.33	0.0563
	4-NP	0.0032	0.27	0.1681
	2-NP	0.0039	0.26	0.0454
	2-CP	0.0009	0.61	0.2385
Pseudo-second order		**K_2 (g/(mg.min)**	**qe (mg/g)**	**R^2**
	P	0.0123	16.95	0.9977
	4-NP	0.0690	20.04	1
	2-NP	0.0664	20.04	0.9999
	2-CP	0.0320	19.61	1
Intra-particle diffusion		**K_3 (mg/(g.$min^{1/2}$)**	**C (mg/g)**	**R^2**
	P	0.0935	14.946	0.3384
	4-NP	0.0437	19.356	0.8258
	2-NP	0.0383	19.409	0.8052
	2-CP	0.0706	18.393	0.7673
Elovich		**α_ε (g min^2/mg)**	**β (g min/mg)**	**R^2**
	P	2.48×10^{21}	3.31	0.1985
	4-NP	3.40×10^{42}	5.20	0.8971
	2-NP	5.11×10^{51}	6.15	0.7726
	2-CP	9.94×10^{26}	3.42	0.7740
Fractional Power		**v (min^{-1})**	**k (mg/g)**	**R^2**
	P	0.019	14.60	0.1865
	4-NP	0.0098	18.96	0.8953
	2-NP	0.0082	19.09	0.7725
	2-CP	0.015	17.85	0.7733

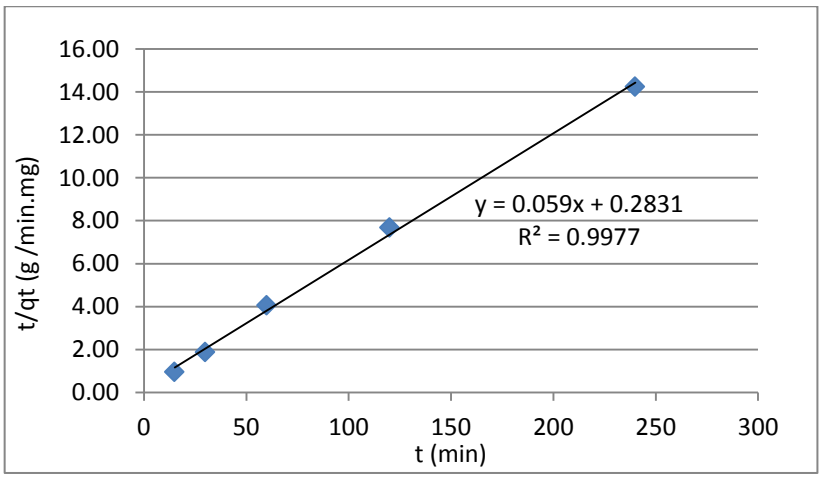

Figure 4.21: Pseudo-second order linear plot for adsorption of P onto GLA

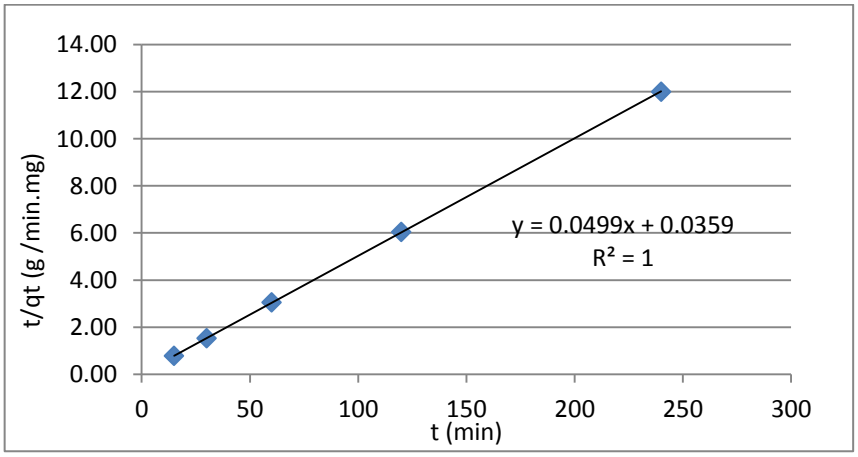

Figure 4.22: Pseudo-second order linear plot for adsorption of 4-NP onto GLA

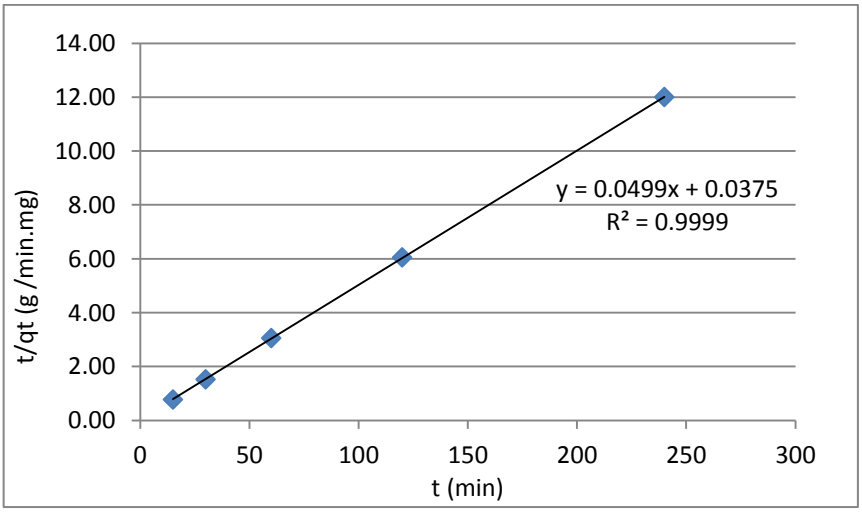

Figure 4.23: Pseudo-second order linear plot for adsorption of 2-NP onto GLA

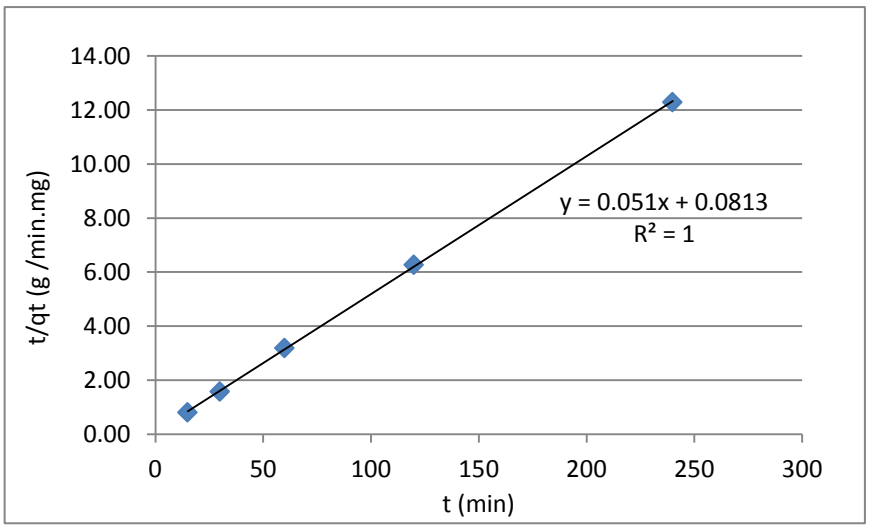

Figure 4.24: Pseudo-second order linear plot for adsorption of 2-CP onto GLA

The intra-particle diffusion is seen to be more involved in adsorption of 4-NP and 2-NP while it is less correlated in adsorption of P. This explains the increased adsorption of 4-NP and 2-NP relative to 2-CP and P. The pseudo-second order kinetic model gives the best description for adsorption process of the phenolic compounds onto GLA. This suggests the dependence of adsorption of P, 4-NP, 2-NP and 2-CP on the number of available active sites on the adsorbent surface (Dural *et al*., 2011).

The pseudo- second order rate constant for adsorption of P, 4-NP, 2-NP and 2-CP were 0.0123, 0.0690, 0.0664 and 0.0320 g/mg/min; and the amount adsorbed at equilibrium per unit weight of GLA were 16.95, 20.04, 20.04 and 19.61 mg/g respectively. The nitrophenols were more effectively removed than phenol and chlorophenol.

GLB

From the kinetic parameters (Table 4.15), pseudo-second order kinetic model gives the highest correlation coefficient ($R^2 > 0.99$) for the adsorption of P, 4-NP, and 2-NP onto GLB. Adsorption of 2-CP using GLB did not fit into pseudo-second order model ($R^2 = 0.1648$), rather, the adsorption is best described by pseudo-first order kinetic model ($R^2 = 0.9784$). The data also fitted well into Elovich model ($R^2 = 0.94$).

The pseudo-second order plots for the adsorption of P, 4-NP, and 2-NP using GLB are presented in Figures 4.25 – 4.27 respectively; while the pseudo-first order plot for 2-CP onto GLB is presented in Figure 4.28.

Table 4.15: Kinetic parameters for adsorption of P, 4-NP, 2-CP and 2-NP onto GLB

Kinetic models				
Pseudo-first order		**K_1 (min^{-1})**	**q_e (mg/g)**	**R^2**
	P	0.0044	3.01	0.7852
	4-NP	0.0078	0.6	0.5250
	2-CP	0.0131	24.37	0.9784
	2-NP	0.0060	4.32	0.7064
Pseudo-second order		**K_2 (g/(mg.min)**	**qe (mg/g)**	**R^2**
	P	0.0073	15.22	0.9940
	4-NP	0.0092	11.12	0.9960
	2-CP	4.19×10^{-5}	69.97	0.1648
	2-NP	0.0054	19.38	0.9943
Intra-particle diffusion		**K_3 (mg/(g.$min^{1/2}$)**	**C (mg/g)**	**R^2**
	P	0.2512	10.861	0.7993
	4-NP	0.3085	16.428	0.7832
	2-CP	1.8236	0.633	0.8621
	2-NP	0.4112	12.715	0.7002
Elovich		**α_ε (g min^2/mg)**	**β (g min/mg)**	**R^2**
	P	4056.4	0.954	0.7789
	4-NP	1.14×10^{-7}	0.85	0.6315
	2-CP	0.014	0.124	0.9416
	2-NP	66.45	0.546	0.7785
Fractional Power		**v (min^{-1})**	**k (mg/g)**	**R^2**
	P	0.08	9.36	0.7838
	4-NP	0.089	19.69	0.6454
	2-CP	0.878	0.30	0.7212
	2-NP	0.117	10.01	0.7577

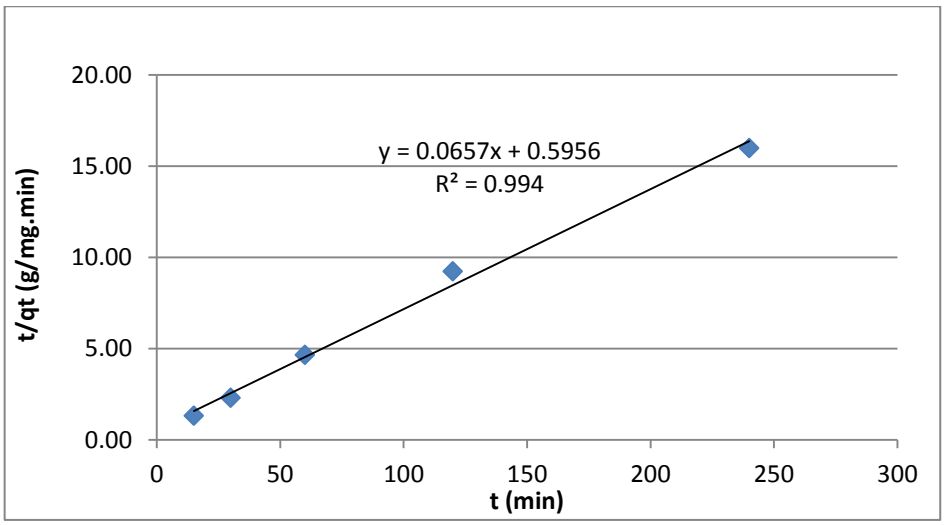

Figure 4.35: Pseudo-second order linear plot for adsorption of P onto GLB

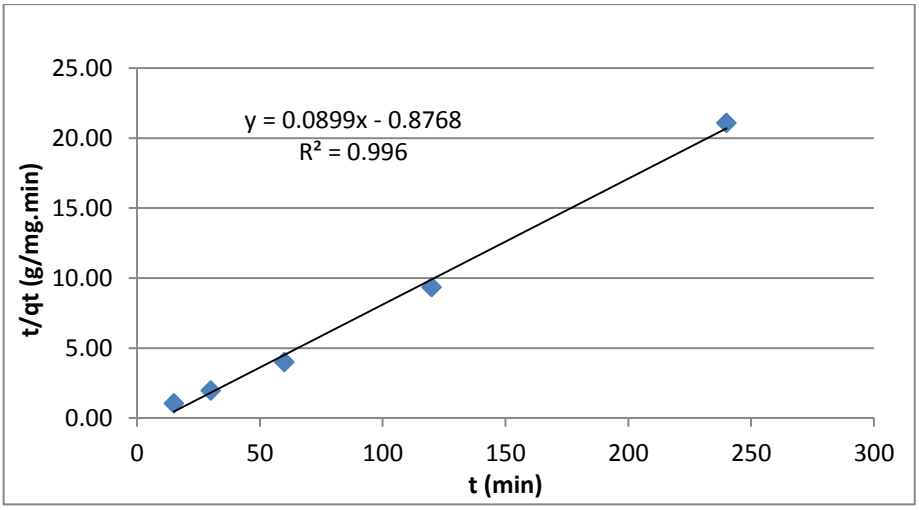

Figure 4.36: Pseudo-second order linear plot for adsorption of 4-NP onto GLB

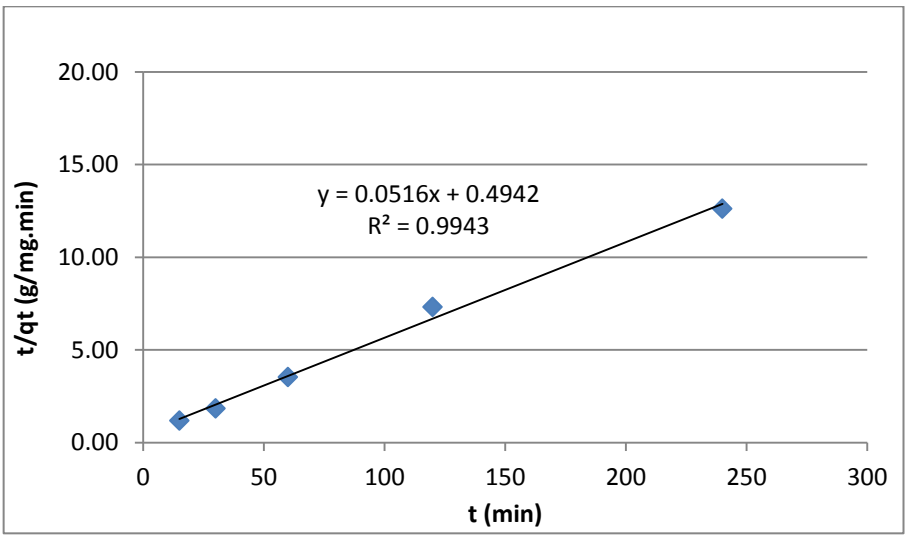

Figure 4.37: Pseudo-second order linear plot for adsorption of 2-NP onto GLB

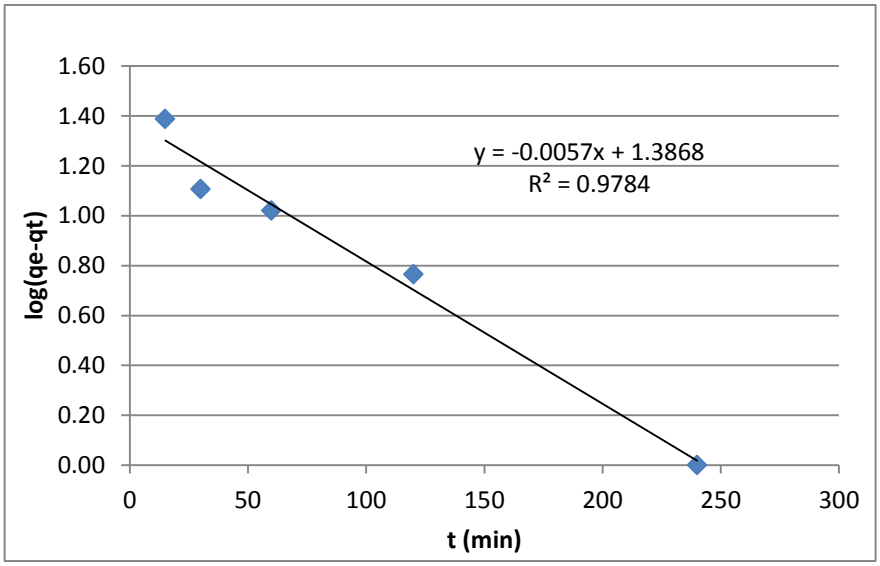

Figure 4.38: Pseudo-first order linear plot for adsorption of 2-CP onto GLB

The calculated pseudo-second order adsorption capacity of GLB was 15.22 mg/g, 11.12 mg/g and 19.38 mg/g for P, 4-NP and 2-NP respectively. Also, the capacity of GLB to adsorb 2-CP (24.37 mg/g) was evaluated with pseudo-second order model. Intra-particle diffusion model depicts that particle diffusivity may be involved for sorption of the phenols (P, 4-NP, 2-NP and 2-CP) onto GLB. The model gave fairly high correlation values, and gave a better fit and/or description of 2-CP adsorption relative to other species (P, 4-NP, and 2-NP).

GL

The adsorption of 4-NP and 2-CP onto GL does not at all fit into pseudo-second order kinetic model. All tested models showed poor correlation for adsorption of 4-NP; pseudo-first order model also poorly described P and 4-NP adsorption (Table 4.16).

The adsorption process of P & 4-NP using GL are best described by pseudo-second order (R^2 = 0.88) and intra-particle diffusion model (R^2 = 0.62) respectively. The fractional power model gave the highest correlation (R^2 > 0.98) for adsorption of both 2-CP and 2-NP relative to other models (Table 4.16).

Linear plot of the models showing best correlation are presented, thus the pseudo-second order and intra-particle diffusion model plots for adsorption of P and 4-NP respectively are represented (Figures 4.29 – 4.30). Fractional power model plots for adsorption of 2-NP and 2-CP onto GL are presented in Figures 4.31 – 4.32.

Table 4.16: Kinetic parameters for adsorption of P, 4-NP, 2-CP and 2-NP onto GL

Kinetic models				
Pseudo-first order		**K_1 (min^{-1})**	**q_e (mg/g)**	**R^2**
	P	0.0046	3.46	0.7385
	4-NP	0.0048	3.54	0.6099
	2-CP	0.0110	17.19	0.9480
	2-NP	0.0100	13.35	0.9645
Pseudo-second order		**K_2 (g/(mg.min)**	**qe (mg/g)**	**R^2**
	P	0.0038	6.812	0.8802
	4-NP	6.29×10^{-4}	4.030	0.0850
	2-CP	4.10×10^{-7}	370.4	0.0254
	2-NP	0.0010	19.08	0.9509
Intra-particle diffusion		**K_3 (mg/(g.$min^{1/2}$)**	**C (mg/g)**	**R^2**
	P	0.2561	1.999	0.7079
	4-NP	0.2764	0.2277	0.6223
	2-CP	1.0486	4.0082	0.9718
	2-NP	0.8769	2.6057	0.9823
Elovich		**α_ε (g min^2/mg)**	**β (g min/mg)**	**R^2**
	P	0.962	0.969	0.6642
	4-NP	0.098	0.870	0.5986
	2-CP	1.06×10^{-23}	0.237	0.8783
	2-NP	0.080	0.279	0.9212
Fractional Power		**v (min^{-1})**	**k (mg/g)**	**R^2**
	P	0.242	1.500	0.6655
	4-NP	1.13	0.012	0.5751
	2-CP	0.994	0.057	0.9936
	2-NP	0.3492	2.230	0.9785

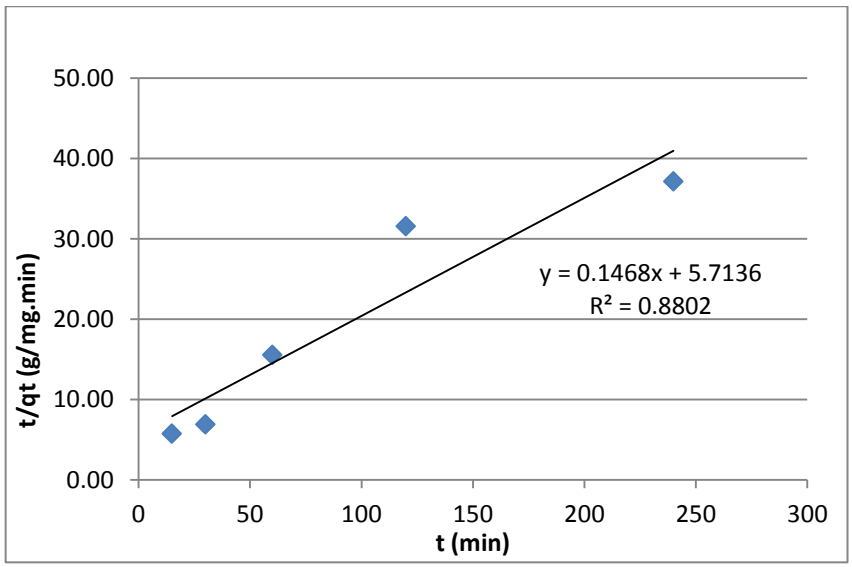

Figure 4.29: Pseudo-second order linear plot for adsorption of P onto GL

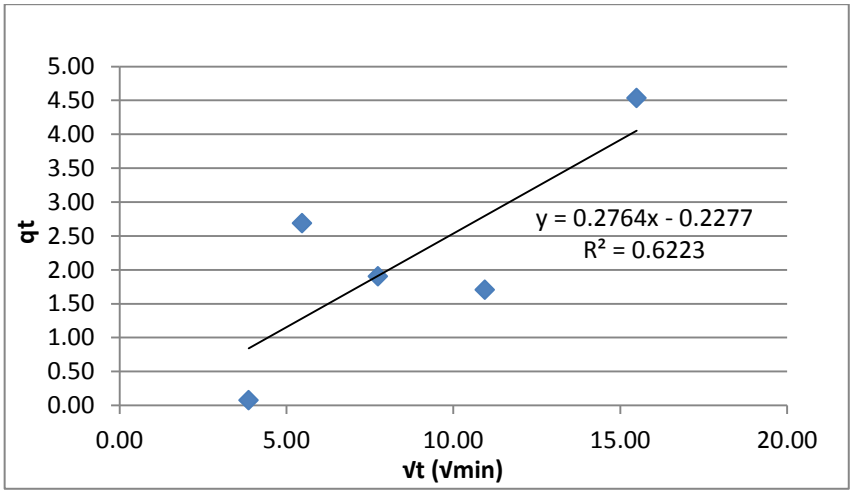

Figure 4.30: Intra-particle diffusion linear plot for adsorption of 4-NP onto GL

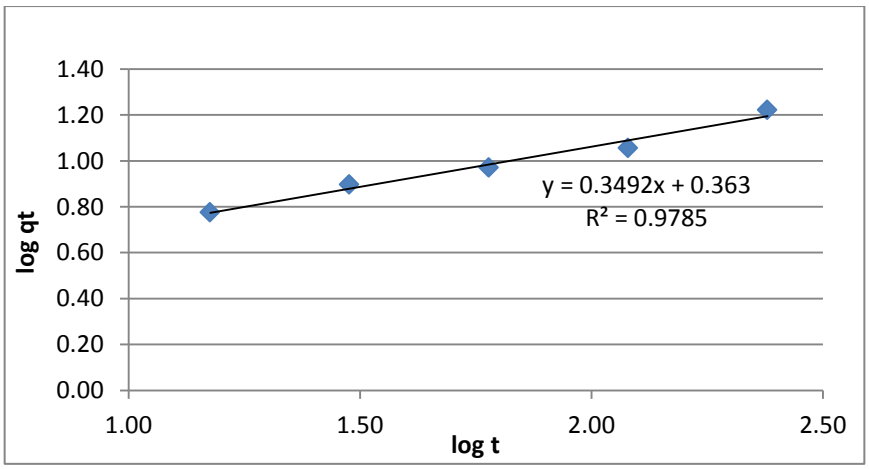

Figure 4.31: Fractional power linear plot for adsorption of 2-NP onto GL

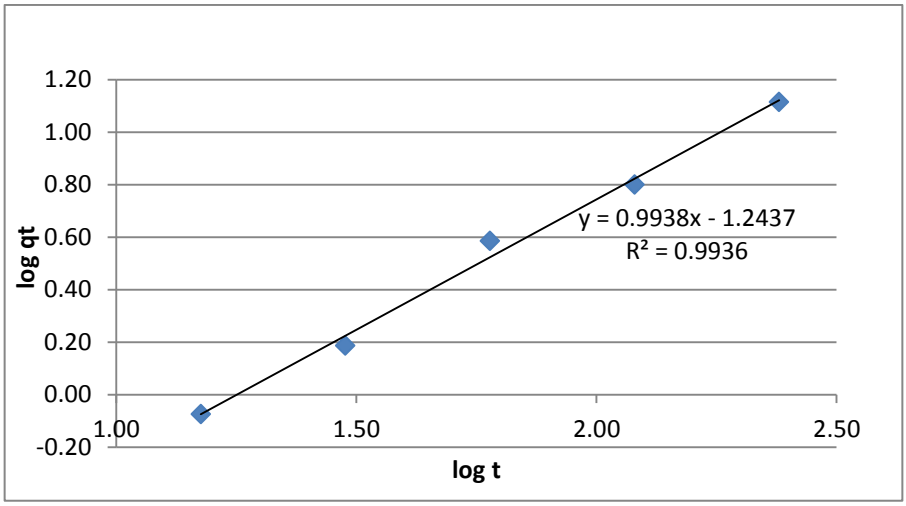

Figure 4.32: Fractional power plot for adsorption of 2-CP onto GL

The adsorption of P, 4-NP, 2-NP and 2-CP onto GL was influenced by intra-particle diffusivity. Diffusion seems to be an integral part of the adsorption process of these phenols onto GL.

4.13.3 Effect of pH

The initial pH of P, 4-NP, 2-NP and 2-CP solutions were varied from pH 4 – 9. Solution pH affects the functional groups present on the adsorbents' (GLA, GLB, GL) surfaces and the existence of P, 4-NP, 2-NP and 2-CP in solution.

The target phenols, P, 4-NP, 2-NP and 2-CP have pKa values of 9.89, 7.15, 7.17 and 8.52 respectively at 25 ^{o}C (Dabrowski *et al.,* 2005). Phenols tend to remain in molecular form when the pH value of the solution is less than pKa, due to availability of protons. They exist as phenolate ions in solutions with pH above their pKa values (Li *et al*., 2009).

Adsorption efficiency of GLA was fairly constant (Figure 4.33) between pH 4 - 5 for 4-NP, 2-NP and 2-CP, thereafter, the effective removal of P, 4-NP, 2-NP and 2-CP by GLA increased as the pH increased up to equilibrium point. The maximum adsorption efficiencies occurred in the pH 7 – 8 region. The adsorption of 4-NP, 2-NP and 2-CP reached equilibrium at neutral pH 7 (pH lower than pKa for all species) with 99.24, 99.72 and 95.72 % removal respectively. There was no significant change (increase or decrease) in adsorption at pH 8 but adsorption efficiency decreased beyond pH 8.

However, maximum adsorption of P (79.21%) was at a pH value of 8 (pH lower than pKa). Since there was no change in adsorption of 4-NP, 2-NP and 2-CP at pH 7 – 8 and sorption of P is maximal at pH 8, an equilibrium pH of 8 was selected for optimal adsorption using GLA.

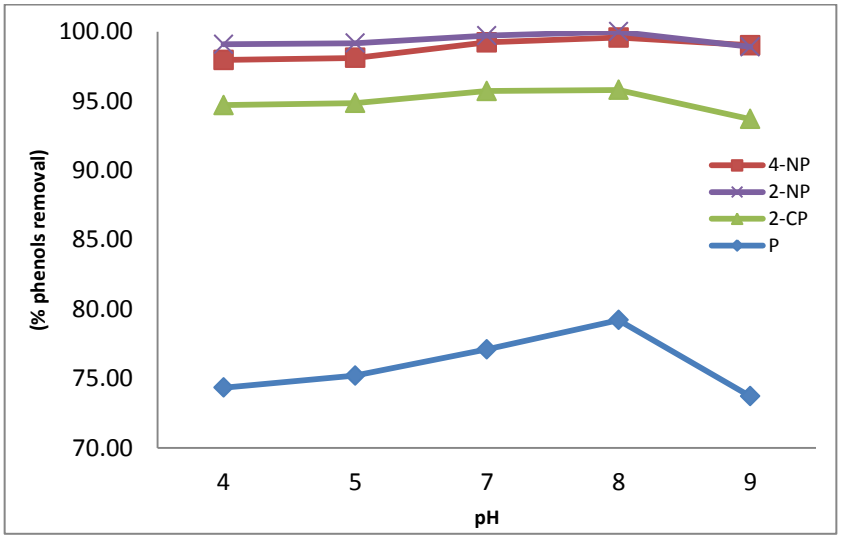

Figure 4.33: Effect of pH on adsorption of P, 2-NP, 4-NP and 2-CP onto GLA

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Mass of GLA = 0.3 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

Thus, P, 4-NP, 2-NP and 2-CP were efficiently adsorbed onto GLA in their molecular forms. These results are consistent with those reported by Li *et al*. (2009) for the adsorption of p-nitrophenol, p-chlorophenol and phenol where the optimal pH was reported as 7, 9 and 9 respectively. Intermolecular interactions such as hydrophobic, Van der Waals and hydrogen bonds may be responsible for efficient adsorption of P, 4-NP, 2-NP and 2-CP onto GLA.

GLB

The initial pH of the solutions containing P, 4-NP, 2-NP and 2-CP were varied from pH 4 – 9 using GLB as adsorbent. Adsorption of P, 4-NP, 2-NP and 2-CP onto GLB decreased with increasing pH for all adsorbates (Figure 4.34). Since the pKa values of P, 4-NP, 2-NP and 2-CP at 25 ^{o}C are 9.89, 7.15, 7.17 and 8.52 respectively (Dabrowski *et al*., 2005), the results therefore revealed that removal of P, 4-NP, 2-NP and 2-CP was achieved in the adsorbates' molecular forms onto GLB (pH < pKa).

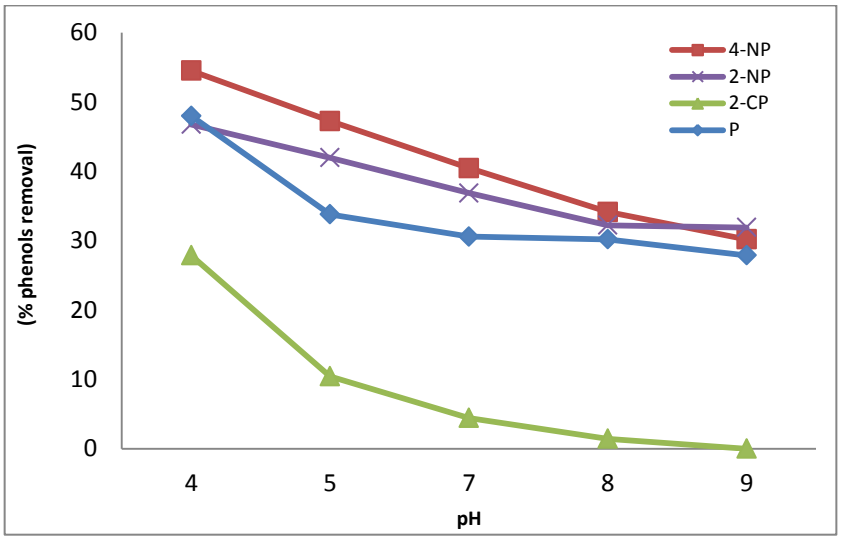

Figure 4.34: Effect of pH on adsorption of P, 2-NP, 4-NP and 2-CP onto GLB

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Mass of GLB = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

The observed optimal adsorption of the phenols in acidic medium suggests that the surface of GLB may have become partially negative and the phenols are in their molecular form, producing ease of chemical interaction between the negative functional moieties on GLB and the phenols. However, in alkaline medium and at pH > pKa values, the surface of GLB becomes positively charged (protonated), and the phenols exist in ionised forms, a considerable energy will be needed to break the –OH bond on GLB in order for chemical bonding to occur between the adsorbent and adsorbate in solution. A pH of 4 is subsequently used for adsorptions onto GLB.

GL

The initial pH of P, 4-NP, 2-NP and 2-CP solutions were varied from pH 4 – 9 to investigate the effect of pH on adsorption of the phenols onto GL. The result of varying pH on adsorption efficiency of GL is shown in Figure 4.35.

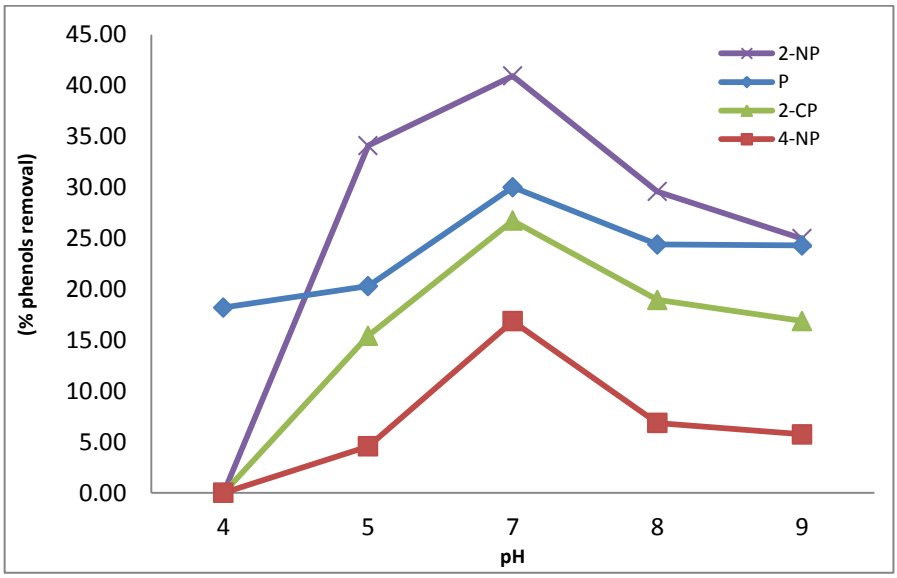

Figure 4.35: Effect of pH on adsorption of P, 2-NP, 4-NP and 2-CP onto GL

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP = 100 mg/L; Volume of solution = 25 mL; Mass of GL = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

Adsorption of P, 4-NP, 2-NP and 2-CP onto GL increased with increase in pH with optimal efficiency at pH 7. Beyond the optimal pH value, a decrease in adsorption for all adsorbates was observed. An optimal pH (7) was selected for further adsorption experiments using GL.

4.13.4 Effect of initial adsorbates' concentration

The initial concentration of the adsorbates was varied from 47 – 940 mg/L of P, 4-NP, 2-NP and 2-CP for the evaluation of adsorption isotherms and for assessment of adsorption efficiency. Adsorption conditions (stirring speed and temperature) were kept constant and the optimal pH, contact time and masses of the adsorbents were applied. The isotherm equations of Langmuir, Freundlich, Temkin and D-R were used for modelling the equilibrium data.

The result for removal of P, 4-NP, 2-NP and 2-CP at higher concentrations using 0.3 g of GLA is presented in Figure 4.36. Adsorption of the phenols onto GLA was fairly constant from 50 - 200 mg/L for 4-NP and 2-NP, and 50 – 100 mg/L for 2-CP and P. Afterwards, there was a decrease in percentage removal. The decrease in adsorption can be attributed to saturation of available adsorption sites on the surfaces of GLA. At a high adsorbate loading of 1000 mg/L (P, 4-NP, 2-NP and 2-CP), 0.3 g of GLA adsorbed 40.09, 64.39, 79.49 and 54.78% of P, 4-NP, 2-NP and 2-CP respectively.

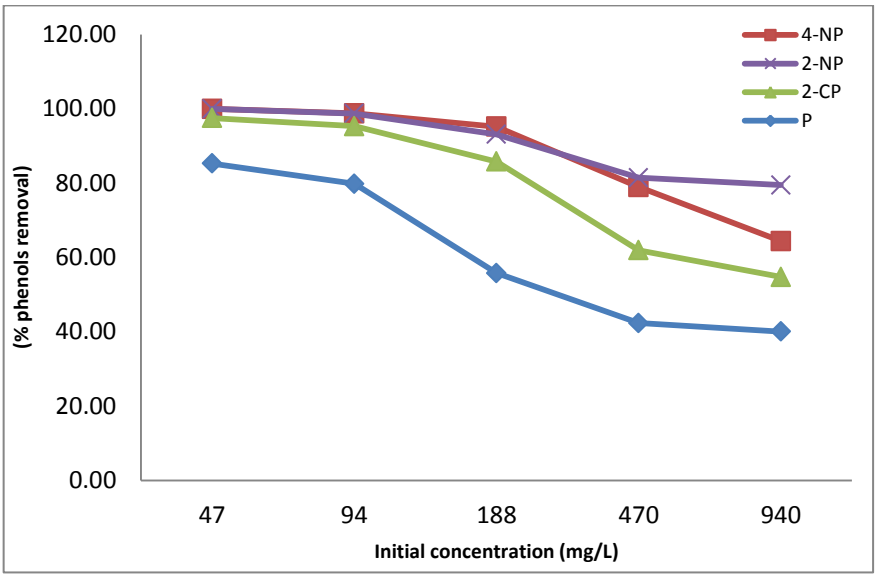

Figure 4.36: Removal of P, 2-NP, 4-NP and 2-CP using GLA at increasing adsorbate concentrations

Adsorption conditions: pH of solution = 8; Volume of solution = 25 mL; Mass of GLA = 0.3 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

Using GLB, the efficiency of removal of P, 4-NP, 2-NP and 2-CP at increasing adsorbate concentration is presented in Figure 4.37. The adsorption of the P, 2-CP and 2-NP decreased with increase in concentration. The decrease in adsorption of P, 2-CP and 2-NP can be attributed to saturation of available adsorption sites on the surfaces of GLB. In contrast, the adsorption of 4-NP increased with increasing initial concentration, suggestive of increased driving forces resulting from the increased concentration gradient between the surface of GLB and 4-NP in bulk solution.

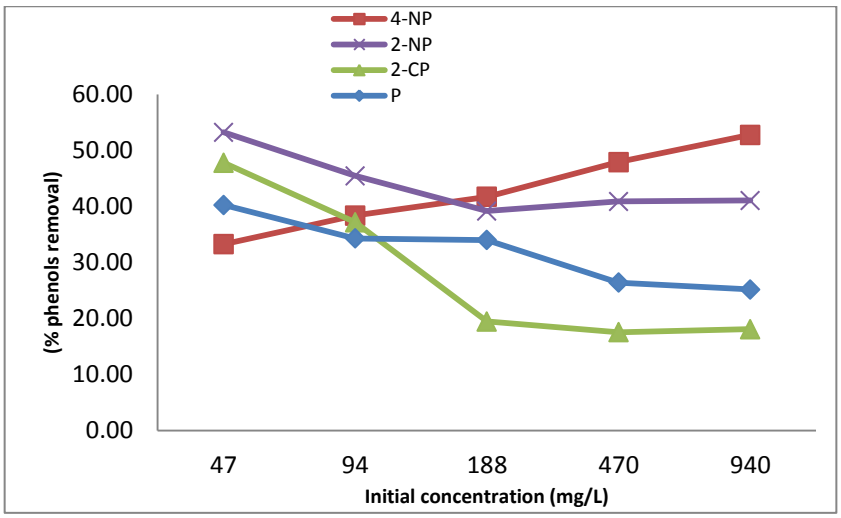

Figure 4.37: Removal of P, 2-NP, 4-NP and 2-CP using GLB at increasing adsorbate concentrations

Adsorption conditions: pH of solution = 4; Volume of solution = 25 mL; Mass of GLB = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

Data on percentage removal of P, 4-NP, 2-NP and 2-CP by GL (Figure 4.38) shows there was an initial increase in adsorption of 2-NP, 2-CP and 4-NP due to increased driving force of the concentration of the adsorbate towards the surface of GL. At higher concentration, there was decrease in adsorption capacity, attributed to the saturation of active sites available for adsorption. This observation and/or result are similar to the findings of Babu and Gupta (2008); in the study, percentage removal of chromium from solution decreases with an increase in initial solution concentration due to increased adsorbate ions on surfaces of a fixed amount of adsorbent.

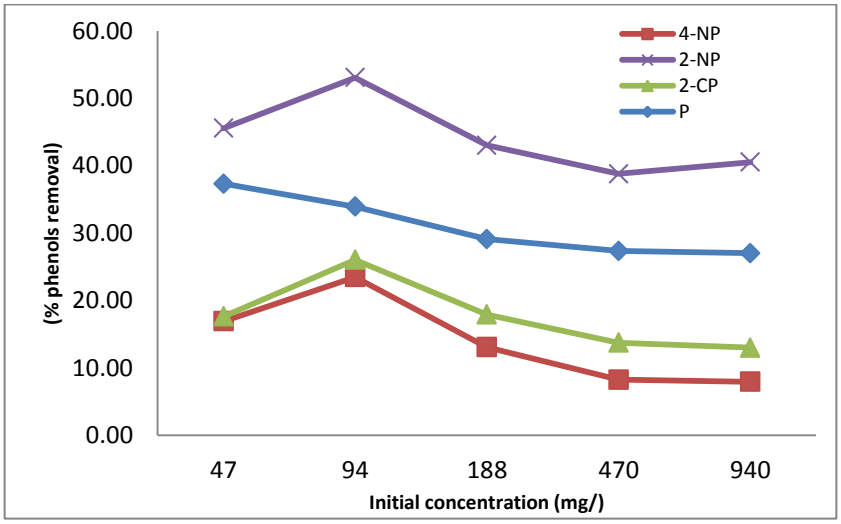

Figure 4.38: Percent removal of P, 2-NP, 4-NP and 2-CP by GL at increasing adsorbate concentrations

Adsorption conditions: pH of solution = 7; Volume of solution = 25 mL; Mass of GL = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C.

4.13.4.1 Adsorption isotherms

The equilibrium adsorption data obtained after adsorption P, 4-NP, 2-NP and 2-CP onto the adsorbents (GLA, GLB, and GL) were fitted into isotherm models to assess the model which best describe the adsorption process.

The Freundlich adsorption isotherm best describes the adsorption processes of P, 4-NP, 2-NP and 2-CP onto GLA as it gives the highest correlation coefficient ($R^2 > 0.95$) relative to other isotherm models (Table 4.17). The evaluated adsorption isotherm parameters are given in Table 4.17 and the Freundlich isotherm plots for adsorption of P, 4-NP, 2-NP and 2-CP onto GLA are presented in Figures 4.39 – 4.42.

Table 4.17: Isotherm parameters for adsorption of P, 4-NP, 2-CP and 2-NP onto GLA

Equilibrium models					
FREUNDLICH		**K_F (mg/g)(L/g)$^{1/n}$**		**n**	**R^2**
	P	3.24		2.13	0.9466
	4-NP	18.15		2.69	0.9683
	2-NP	16.53		2.33	0.9648
	2-CP	11.12		2.61	0.9881
LANGMUIR		**Q_o (mg/g)**	**b (L/g)**	**R_L**	**R^2**
	P	39.37	0.036	0.801 – 0.049	0.9456
	4-NP	103.09	0.213	1.000 – 0.009	0.9087
	2-NP	103.10	0.210	1.000 – 0.0164	0.8660
	2-CP	67.11	0.140	0.8194 – 0.0122	0.9514
TEMKIN		**B (J/mol)**	**K_{TEM} (L/g)**		**R^2**
	P	13.698	0.151		0.7558
	4-NP	24.213	1.36		0.9356
	2-NP	30.421	1.01		0.8145
	2-CP	19.374	0.646		0.8637
DUBUNIN-RADUSHKEVICH		**Ψ_D (J^2/mol^2)**	**Φ_D(mg/g)**		**R^2**
	P	83.707	33.77		0.5704
	4-NP	5.998	102.92		0.6496
	2-NP	6.7304	110.05		0.5854
	2-CP	6.9879	62.56		0.6042

Heterogeneous adsorption processes are best described by Freundlich isotherm models (Ma *et al*., 2013); therefore the adsorption of P, 4-NP, 2-NP and 2-CP onto GLA is heterogeneous in nature. In this study, the values of '*n'* ranged 1 – 10 indicate favourable adsorption (Singh *et al*., 2008). Although the Langmuir model does not give the highest correlation for the adsorption process, the evaluation of the dimensionless separation parameter R_L also gives insight into the favourability of an adsorption process (Hameed *et al*., 2009). The values of R_L for adsorption of P, 4-NP, 2-NP and 2-CP onto GLA all lies within the range 0 – 1 which is also indicative of favourable adsorption. The result conforms to the findings of Karabacakoglu *et al*. (2008)

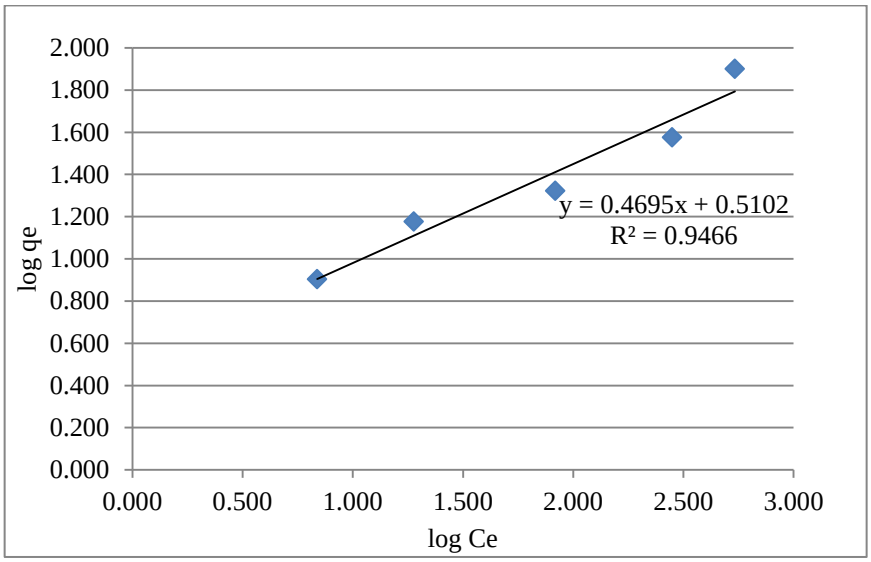

Figure 4.39: Freundlich isotherm for adsorption of P onto GLA

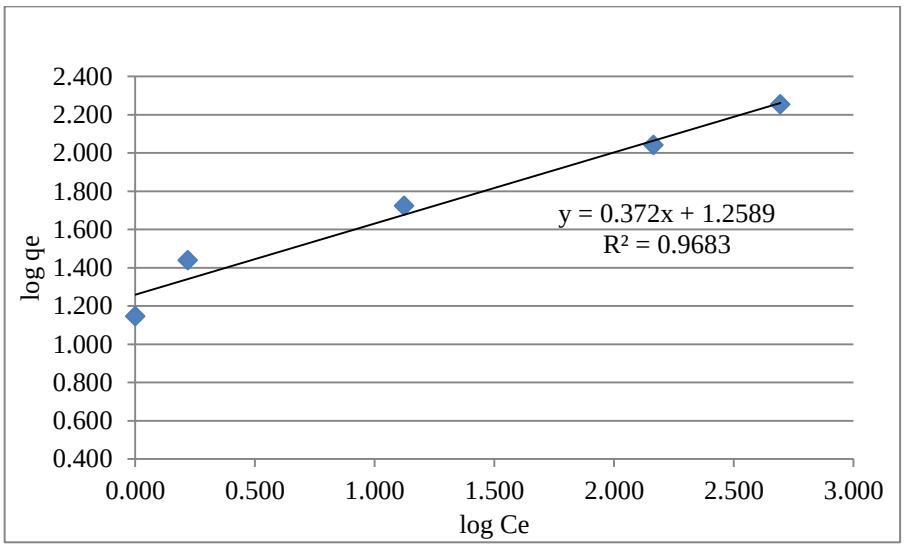

Figure 4.40: Freundlich isotherm for adsorption of 4-NP onto GLA

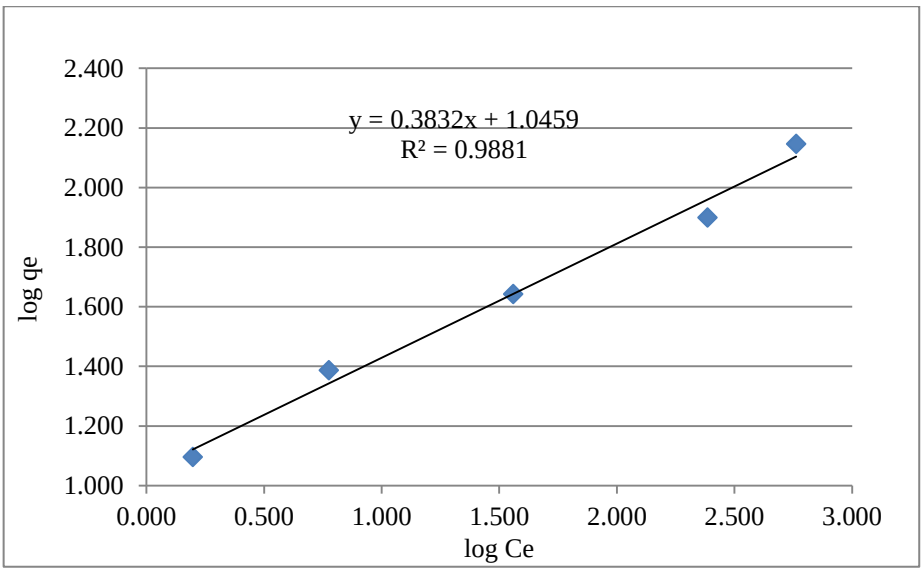

Figure 4.41: Freundlich isotherm for adsorption of 2-CP onto GLA

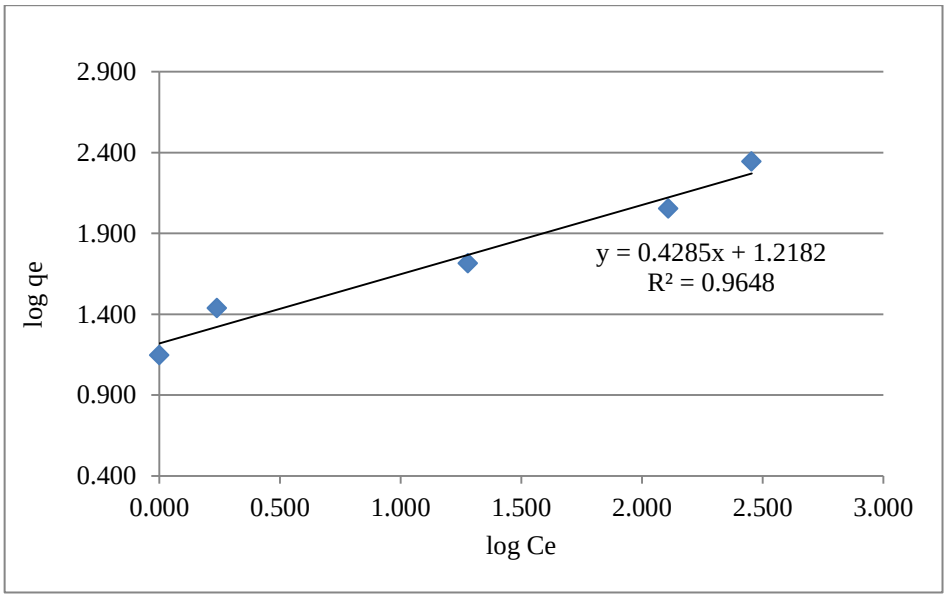

Figure 4.42: Freundlich isotherm for adsorption of 2-NP onto GLA

GLB

Both Freundlich and Langmuir isotherm models showed good correlation for the adsorption of P, 4-NP, 2-NP and 2-CP on GLB (Table 4.18). While 4-NP, 2-NP and 2-CP were best described by Freundlich model; P had a higher correlation with Langmuir isotherm model.

The evaluated adsorption isotherm parameters are given in Table 4.18. The Freundlich and Langmuir isotherm plots for the adsorption processes of P, 4-NP, 2-NP and 2-CP using GLB are presented in Figures 4.43 – 4.50.

Table 4.18: Isotherm parameters for adsorption of P, 4-NP, 2-CP and 2-NP onto GLB

Equilibrium models				
FREUNDLICH		**K_F (mg/g)(L/g)$^{1/n}$**	**n**	**R^2**
	P	0.34	1.14	0.953
	4-NP	0.03	0.77	0.999
	2-CP	0.77	1.81	0.905
	2-NP	0.33	1.17	0.985
LANGMUIR		**Q_o (mg/g)**	**b (L/g)**	**R_L**	**R^2**
	P	70.42	0.004	0.899 – 0.287	0.956
	4-NP	60.98	0.002	0.915 – 0.432	0.990
	2-CP	22.32	0.010	0.750 – 0.087	0.826
	2-NP	78.74	0.003	0.911 – 0.289	0.967
TEMKIN		**B (J/mol)**	**K_{TEM} (L/g)**	**R^2**
	P	34.027	0.026	0.728
	4-NP	50.715	0.016	0.836
	2-CP	10.367	0.031	0.757
	2-NP	31.318	0.023	0.823
DUBUNIN-RADUSHKEVICH		**Ψ_D (J^2/mol^2)**	**Φ_D(mg/g)**	**R^2**
	P	1449.4	41.42	0.508
	4-NP	6375.4	57.75	0.725
	2-CP	6752.9	19.42	0.449
	2-NP	2132.4	42.91	0.556

The values of '*n'* from Freundlich model (Table 4.18) ranged 1 – 10 which suggests that the adsorption process for P, 2-NP and 2-CP onto GLB is favourable ($1 < n < 10$). The exception was 4-NP.

The dimensionless separation parameter R_L from Langmuir isotherm also provided insight into the favourability of the adsorption process. The values of R_L for adsorption of P, 4-NP, 2-NP and 2-CP onto GLB ranged 0 – 1 which is indicative of favourable adsorption (Hameed *et al.*, 2009).

The adsorption of P, 4-NP, 2-NP and 2-CP onto GLB can be described as both monolayer and heterogeneous due to the strong positive values of both Freundlich and Langmuir isotherm models. This finding is not rare; similar results were reported by Mohd Din *et al.* (2009) where the adsorption of phenol onto activated coconut shell fitted reasonably well into Freundlich and Langmuir isotherm models.

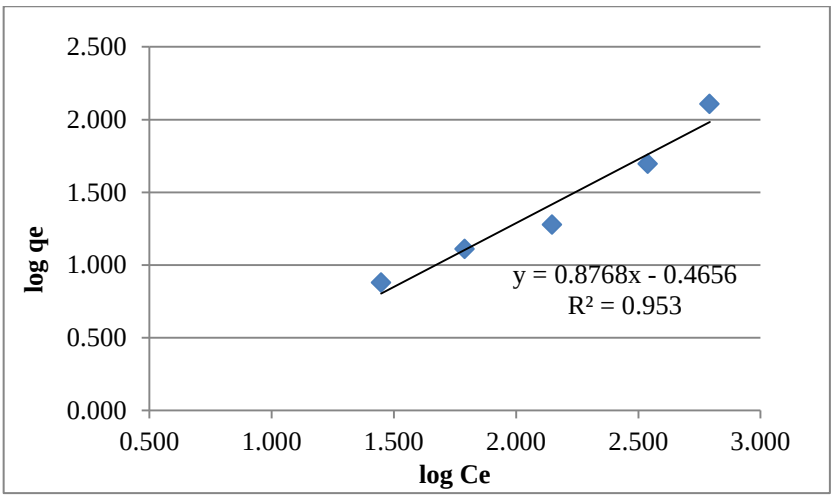

Figure 4.43: Freundlich isotherm for adsorption of P onto GLB

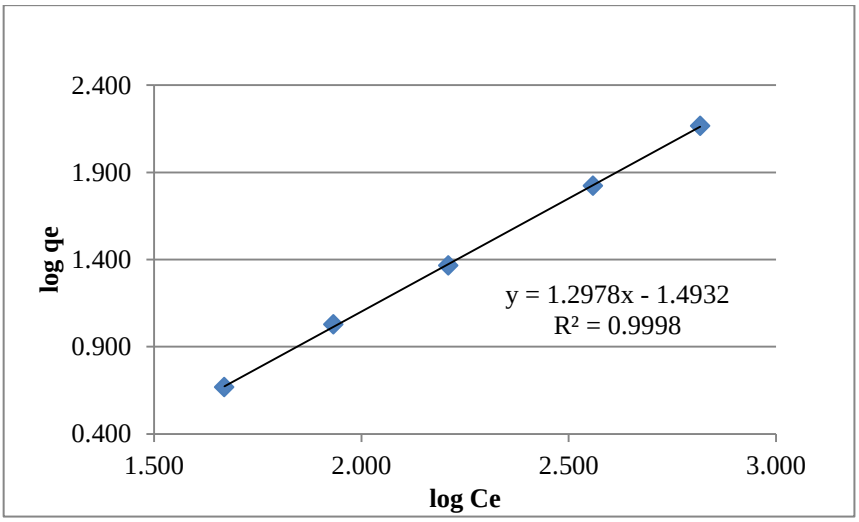

Figure 4.44: Freundlich isotherm for adsorption of 4-NP onto GLB

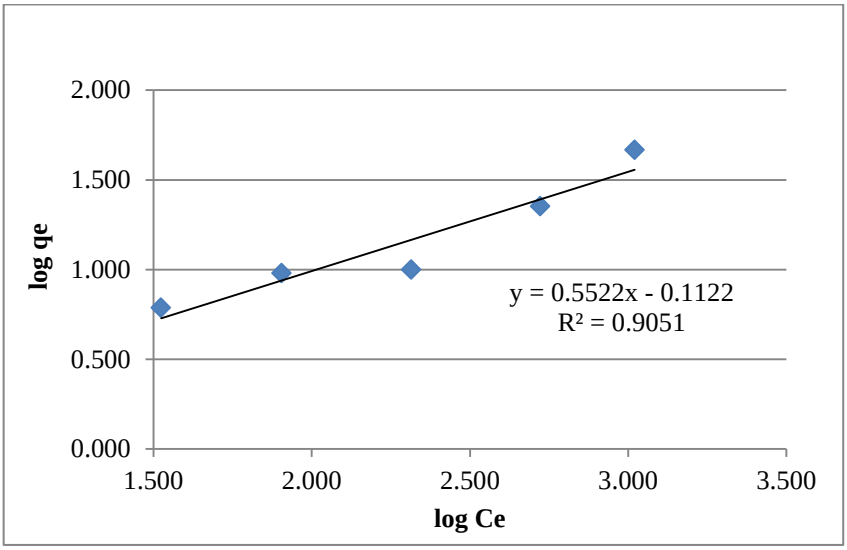

Figure 4.45: Freundlich isotherm for adsorption of 2-CP onto GLB

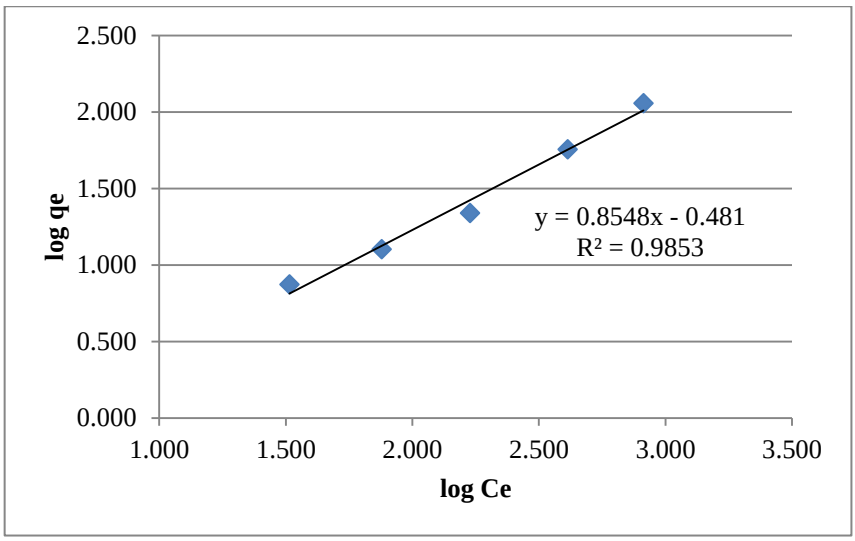

Figure 4.46: Freundlich isotherm for adsorption of 2-NP onto GLB

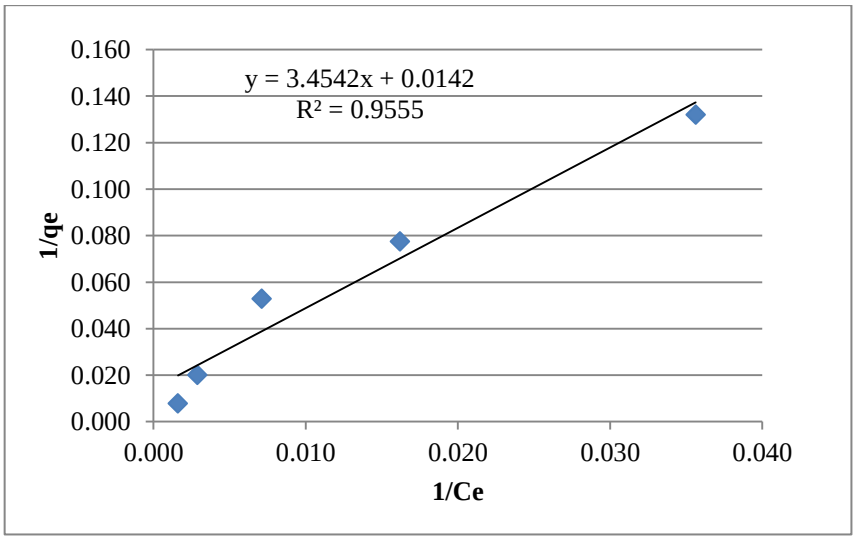

Figure 4.47: Langmuir isotherm for adsorption of P onto GLB

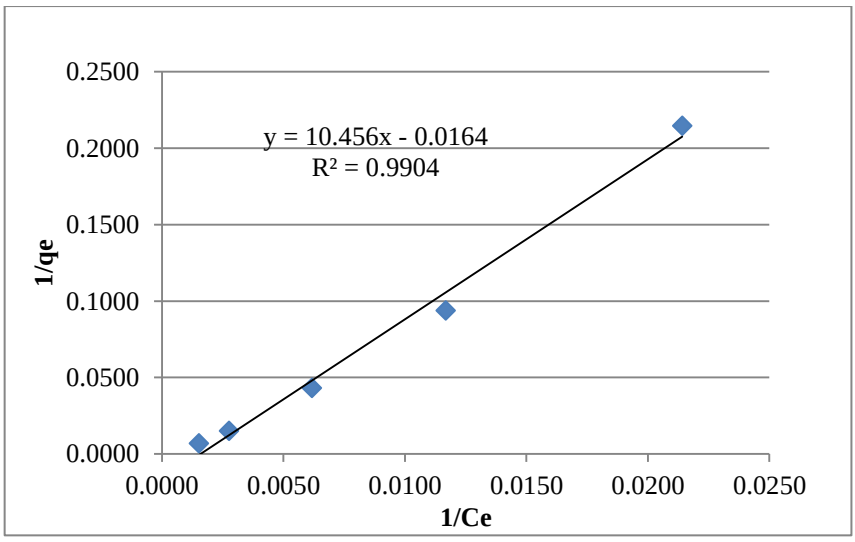

Figure 4.48: Langmuir isotherm for adsorption of 4-NP onto GLB

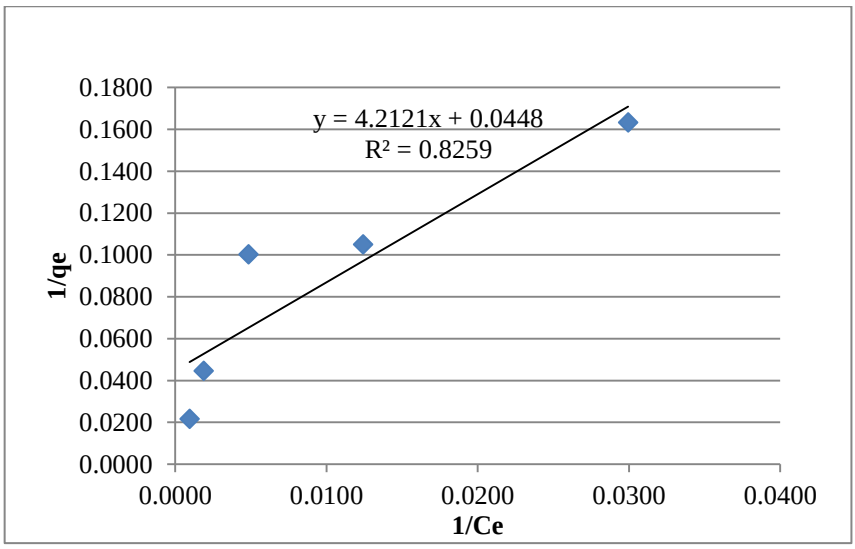

Figure 4.49: Langmuir isotherm for adsorption of 2-CP onto GLB

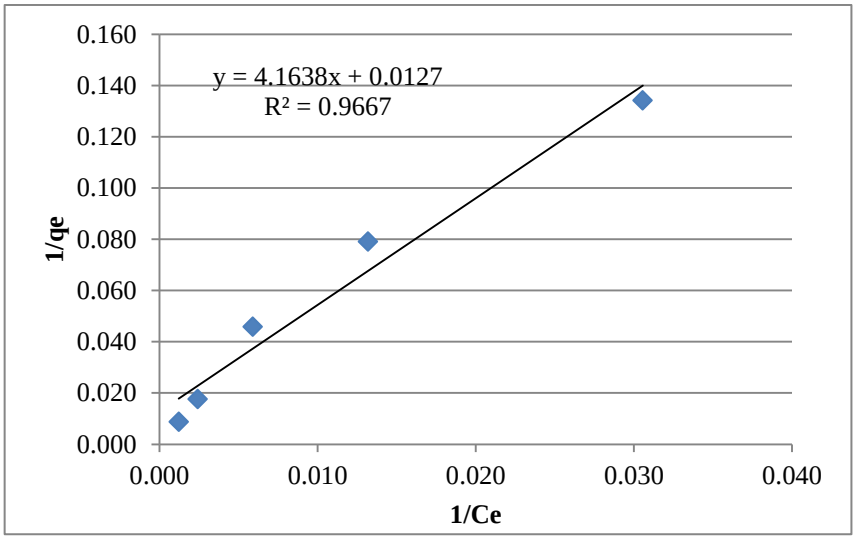

Figure 4.50: Langmuir isotherm for adsorption of 2-NP onto GLB

GL

The equilibrium adsorption data obtained after adsorption of P, 4-NP, 2-NP and 2-CP onto GL were fitted into isotherm models for proper description of adsorption process. In the adsorption processes of P, 4-NP, 2-NP and 2-CP using GL, both Freundlich and Langmuir isotherm models displayed excellent correlation for describing the adsorption process. However, the Freundlich adsorption isotherm (Figures 4.51 – 4.53) had a higher regression coefficient for the adsorption of P, 2-NP and 2-CP onto GL relative to other models; and on the other hand, Langmuir model (Figure 4.54) best described adsorption of 4-NP (Table 4.19).

Table 4.19: Isotherm parameters for adsorption of P, 4-NP, 2-CP and 2-NP onto GL

Equilibrium models				
FREUNDLICH		**K_F (mg/g)(L/g)$^{1/n}$**	**n**	**R^2**
	P	0.06	0.93	0.9781
	4-NP	0.05	1.06	0.8051
	2-CP	0.06	1.04	0.9350
	2-NP	0.23	1.08	0.9736
LANGMUIR		**Q_o (mg/g)**	**b (L/g)**	**R_L**	**R^2**
	P	79.37	9.53×10^{-4}	0.968 – 0.640	0.9728
	4-NP	57.8	0.0008	0.956 – 0.551	0.9115
	2-CP	140.85	0.0003	0.984 – 0.772	0.9343
	2-NP	1111.1	0.00002	0.987 – 0.871	0.9655
TEMKIN		**B (J/mol)**	**K_{TEM} (L/g)**	**R^2**
	P	20.544	0.022	0.7562
	4-NP	18.452	0.012	0.5360
	2-CP	15.939	0.015	0.7015
	2-NP	35.784	0.022	0.7872
DUBUNIN-RADUSHKEVICH		**Ψ_D (J^2/mol^2)**	**Φ_D(mg/g)**	**R^2**
	P	3055.3	25.37	0.7006
	4-NP	7516.3	17.81	0.5296
	2-CP	1443.8	20.77	0.6997
	2-NP	3455.4	52.93	0.7195

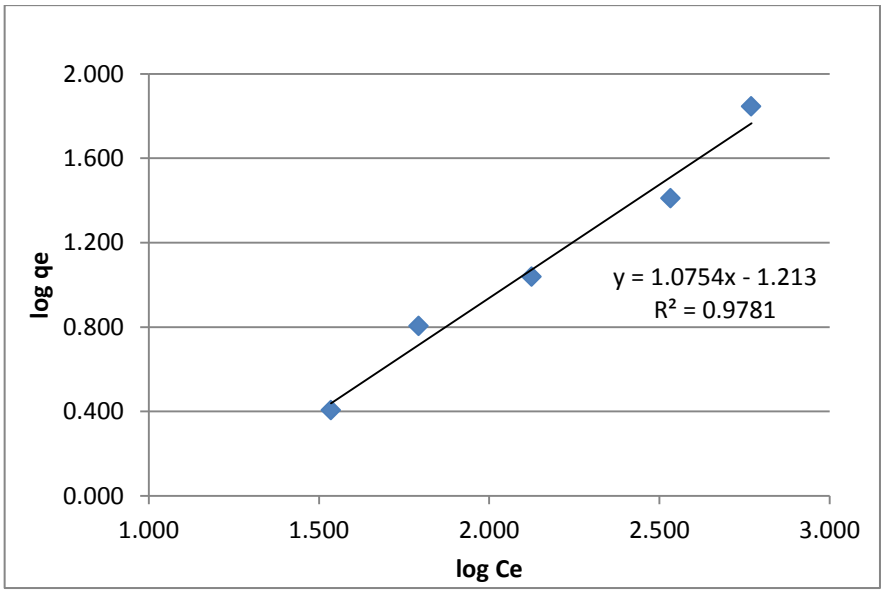

Figure 4.51: Freundlich isotherm for adsorption of P onto GL

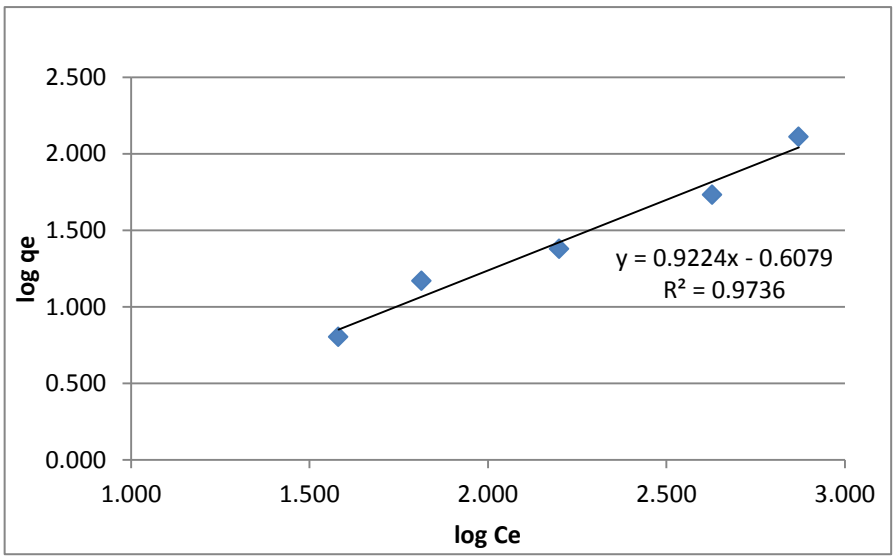

Figure 4.52: Freundlich isotherm for adsorption of 2-NP onto GL

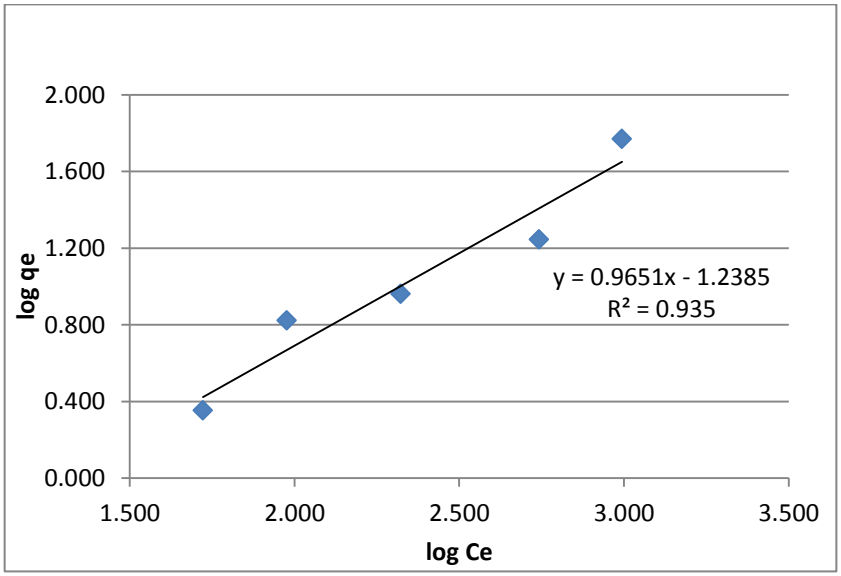

Figure 4.53: Freundlich isotherm for adsorption of 2-CP onto GL

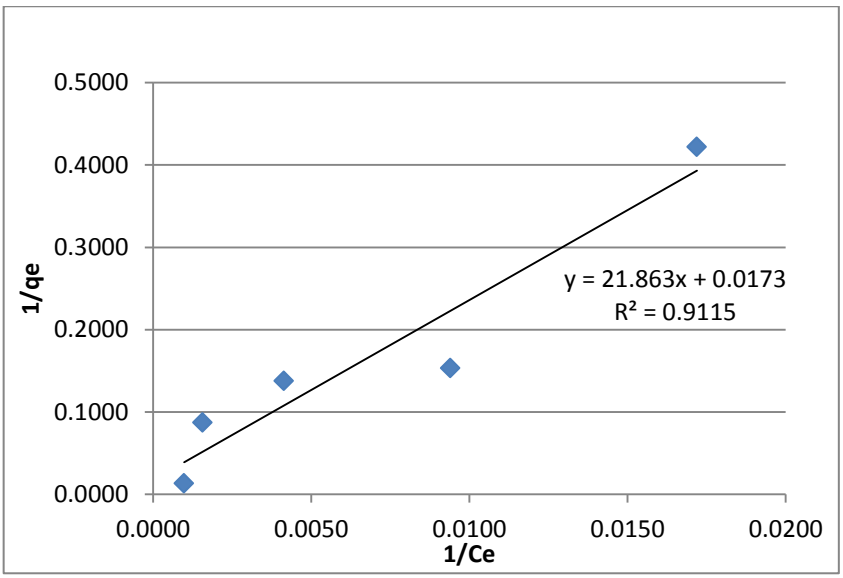

Figure 4.54: Langmuir isotherm for adsorption of 4-NP onto GL

The adsorption of P, 4-NP, 2-NP and 2-CP using GL were well described by both Freundlich and Langmuir isotherm models. This revealed that the adsorption process was governed by monolayer, and at same time heterogeneous adsorption. The finding is same as those reported by Li *et al*. (2009), where adsorption of phenol, p-chlorophenol and p-nitrophenol were well described by both Freundlich and Langmuir isotherm models. Although both models showed good correlation for P, 2-NP and 2-CP, sorption of 4-NP was best fitted into Langmuir isotherm.

The evaluated dimensionless separation parameter, $R_{L,}$ from Langmuir isotherm for adsorption of P, 4-NP, 2-NP and 2-CP onto GL ranged 0 – 1, and were closer to 1 at lower phenolic concentrations. This showed that the adsorption process was favourable. According to karabacakoglu *et al*. (2008), a high R_L value at lower phenol concentration shows that adsorption is more favourable at lower solution (phenol) concentration; this is correlated with this study.

The values of '*n'* from Freundlich model (Table 4.18) ranged 1 – 10 which suggests that the adsorption process for P, 2-NP and 2-CP onto GLB is favourable. The values of 'n' are greater than 1 (except 4-NP) indicating molecular interaction between GL and the phenols. These results are in agreement with Li *et al*. (2009).

4.13.5 Effect of temperature

GLA

The results from batch adsorption experiments (Figure 4.55) on effect of temperature revealed that the efficiency of adsorption of P, 4-NP, 2-NP and 2-CP onto GLA decreased with increase in temperature; thus, adsorption process was favourable at low temperatures. An increase in temperature tends to weaken and break predominant adsorptive forces (such as hydrogen, hydrophobic, $\pi - \pi$ and –OH bonds) between active sites, adsorbed species and adjacent molecules in adsorbed phase. This result is consistent with Li *et al*. (2009) who reported that adsorption of phenol, p-chlorophenol and p-nitrophenol onto chitosan decreased with increased temperatures.

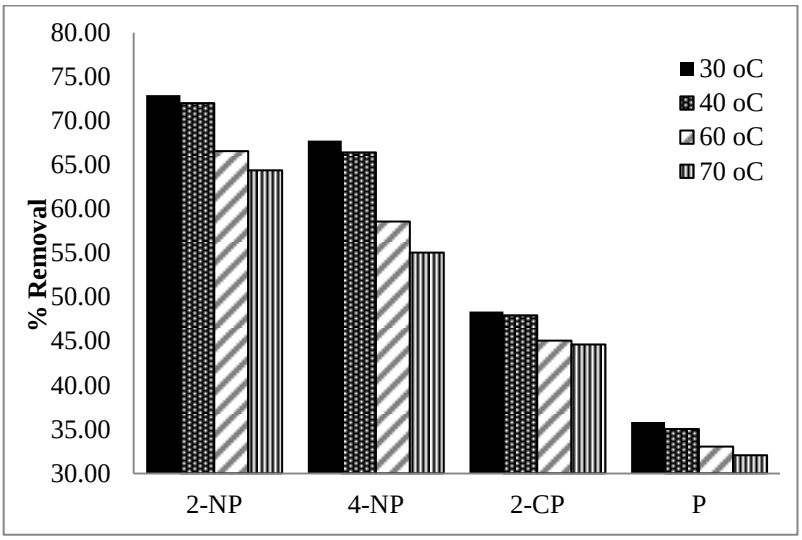

Figure 4.55: Effect of temperature on adsorption of 2-NP, 4-NP, 2-CP and P onto GLA

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP in solution = 100 mg/L; Volume of solution = 25 mL; Mass of GLA = 0.3 g; Contact time = 240 min; Stirring speed = 200 rpm, pH of solution = 8

For all phenols, adsorption onto GLA was highest at 30 ^{o}C. At same temperatures, highest adsorption was observed in 2-NP while the least adsorbed compound was P. The Van't Hoff's plot for the adsorption of P, 4-NP, 2-NP and 2-CP onto GLA are presented in Figure 4.56 – 4.59. Thermodynamic parameters are given in Table 4.20.

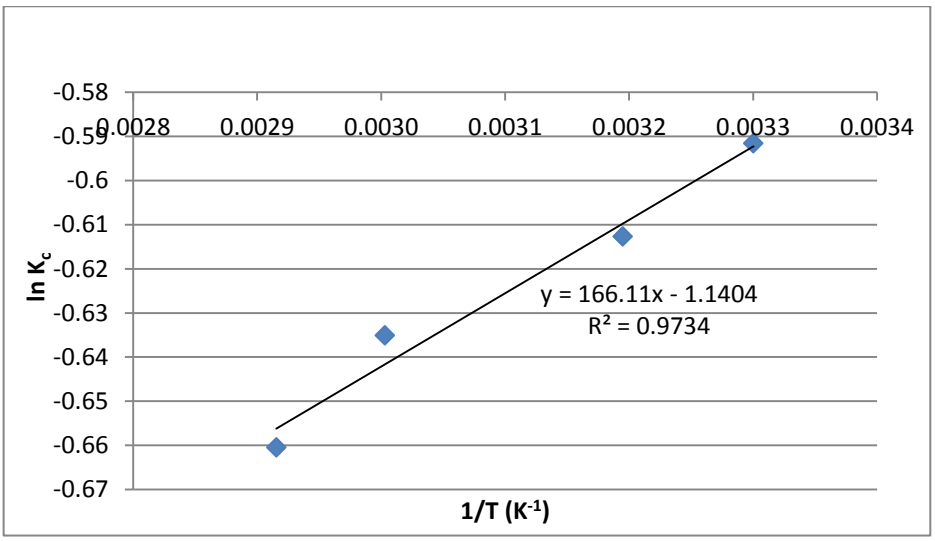

Figure 4.56: Van't Hoff plot for adsorption of P onto GLA

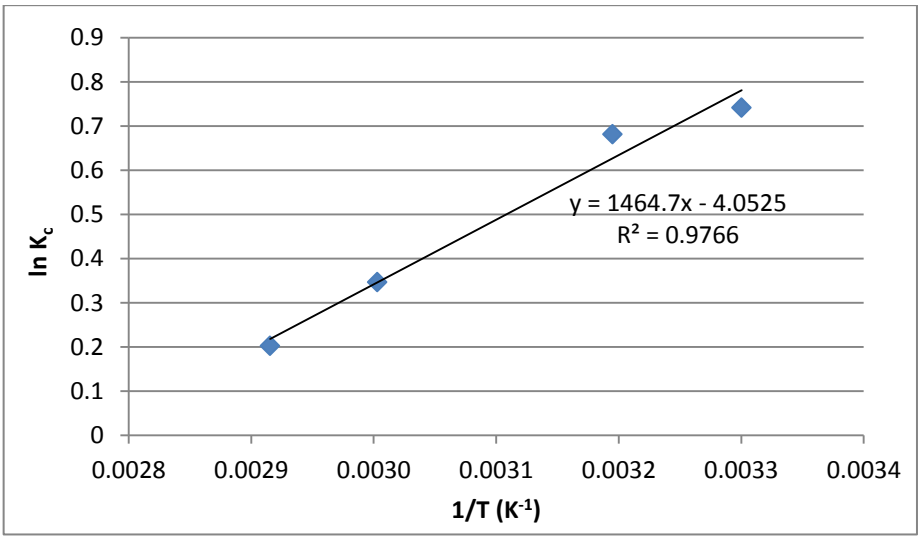

Figure 4.57: Van't Hoff plot for adsorption of 4-NP onto GLA

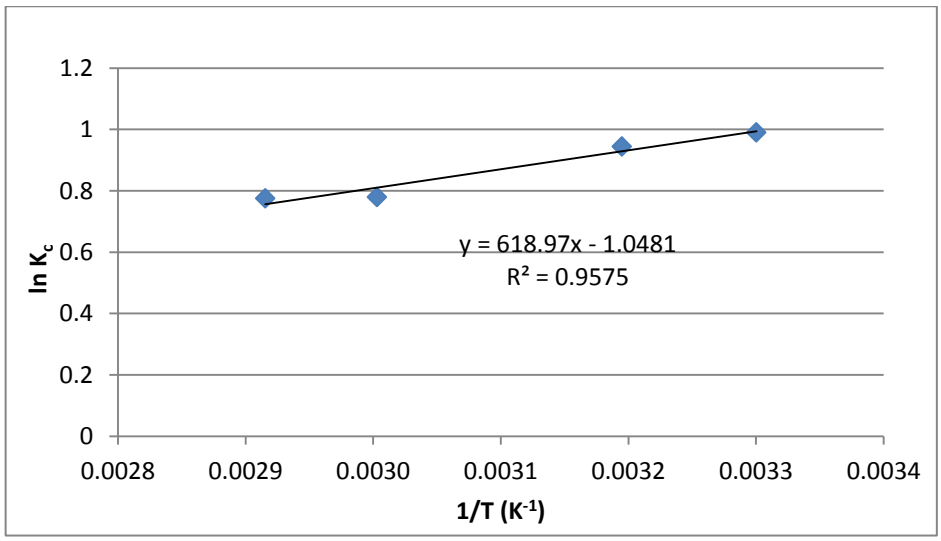

Figure 4.58: Van't Hoff plot for adsorption of 2-NP onto GLA

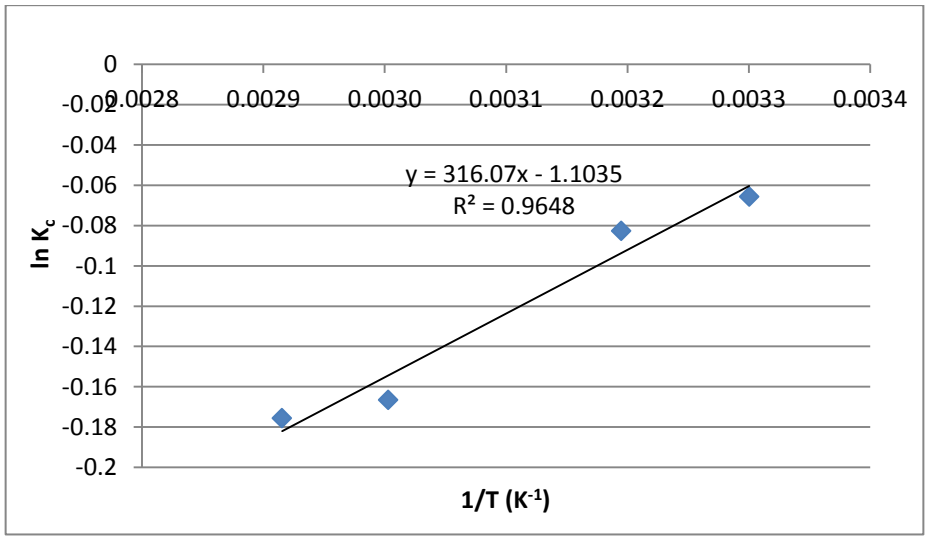

Figure 4.59: Van't Hoff plot for adsorption of 2-CP onto GLA

Table 4.20: Thermodynamic parameters for sorption of P, 4-NP, 2-CP and 2-NP onto GLA

	ΔH^o (kJ/mol)	ΔS^o (J/mol.K)	ΔG° (kJ/mol)			
			303 K	**313 K**	**333 K**	**343 K**
P	- 1.381	- 9.48	1.490	1.594	1.758	1.883
4-NP	- 12.177	- 33.69	- 1.869	- 1.773	- 0.959	- 0.577
2-NP	- 5.146	- 8.71	- 2.495	- 2.458	- 2.212	- 2.159
2-CP	- 2.628	-9.15	0.165	0.215	0.461	0.500

The negative values of ΔH^0 (Table 4.20) indicate that the adsorption process is exothermic, thus, the adsorption of P, 4-NP, 2-NP and 2-CP onto GLA will be unfavourable at high temperatures. The corresponding values of ΔS^0 are negative for the entire adsorption process, indicating a decrease in degree of freedom. This can be attributed to the decrease in amount of adsorbate on the surfaces of GLA due to high temperature. Furthermore, the adsorption of 4-NP and 2-NP onto GLA is spontaneous (negative ΔG^0 values) whereas the adsorption process for P and 2-CP onto GLA is not spontaneous (positive ΔG^0 values) (Aroguz, 2006).

The standard enthalpy values may reasonably explain the trend and efficiency of adsorption with increased temperature. A lower ΔG^0 value is indicative of favourable adsorption. 2-NP may have been more effectively removed by GLA than other phenols due to lesser energy required; while P, (higher ΔG^0 values) was least removed relative to other phenols at same temperature.

GLB

The results (Figure 4.60) from batch adsorption experiments on effect of temperature revealed that removal efficiency of P, 4-NP, 2-NP and 2-CP onto GLB increased with increasing temperature. GLB had earlier been characterised as an H-typed carbon (protonated), hence an increase in temperature will tend to weaken and break the –OH bond on GLB in order to create electrostatic attraction, and create more adsorptive forces for bonding with the adsorbate.

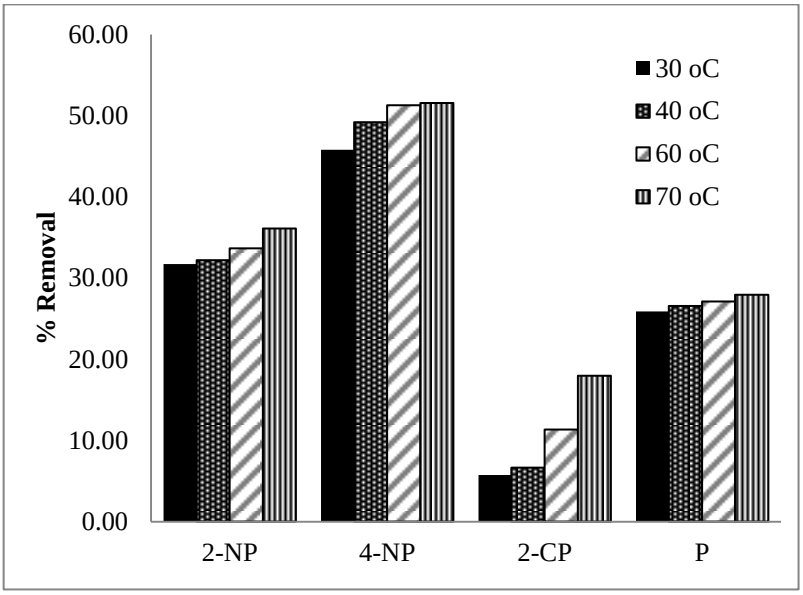

Figure 4.60: Effect of temperature on adsorption of 2-NP, 4-NP, 2-CP and P onto GLB

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP in solution = 100 mg/L; Volume of solution = 25 mL; Mass of GLB = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, pH of solution = 4

From the graph above, it can be observed that 4-NP was more adsorbed onto GLB with increase in temperature relative to other phenols, and the least removal efficiency was seen for 2-CP. The Van't Hoff's plot for the adsorption of P, 4-NP, 2-NP and 2-CP onto GLB are presented in Figure 4.61 – 4.64 respectively and thermodynamic parameters in Table 4.21.

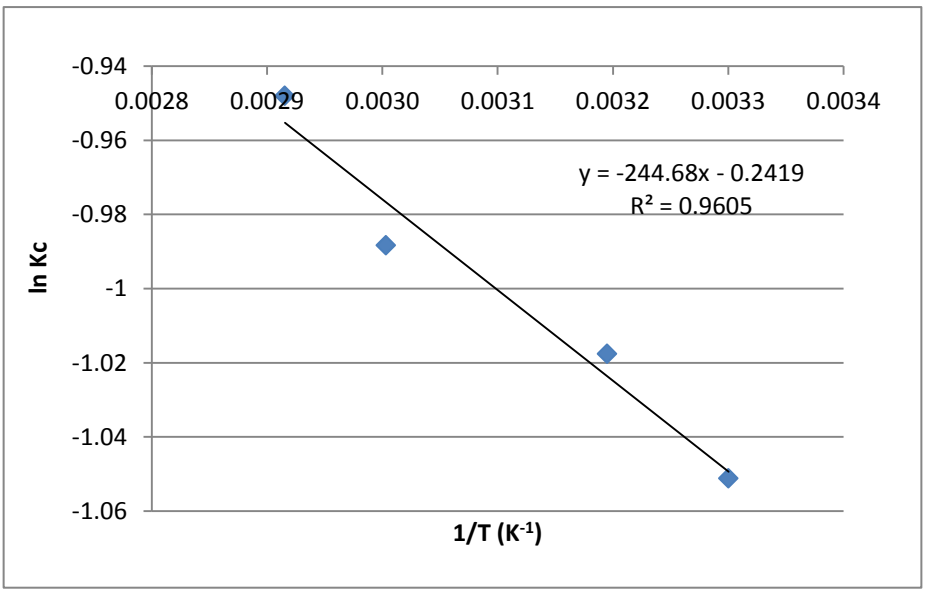

Figure 4.61: Van't Hoff plot for adsorption of P onto GLB

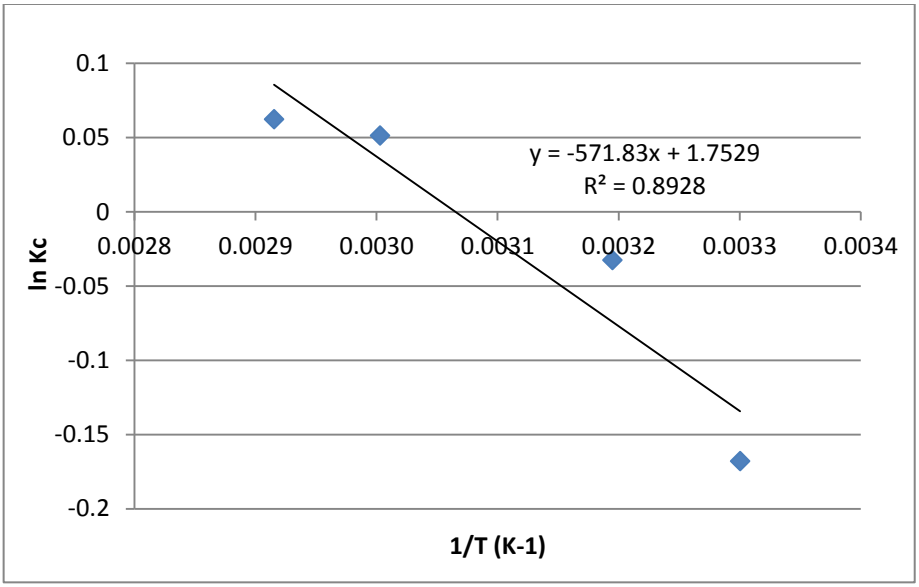

Figure 4.62: Van't Hoff plot for adsorption of 4-NP onto GLB

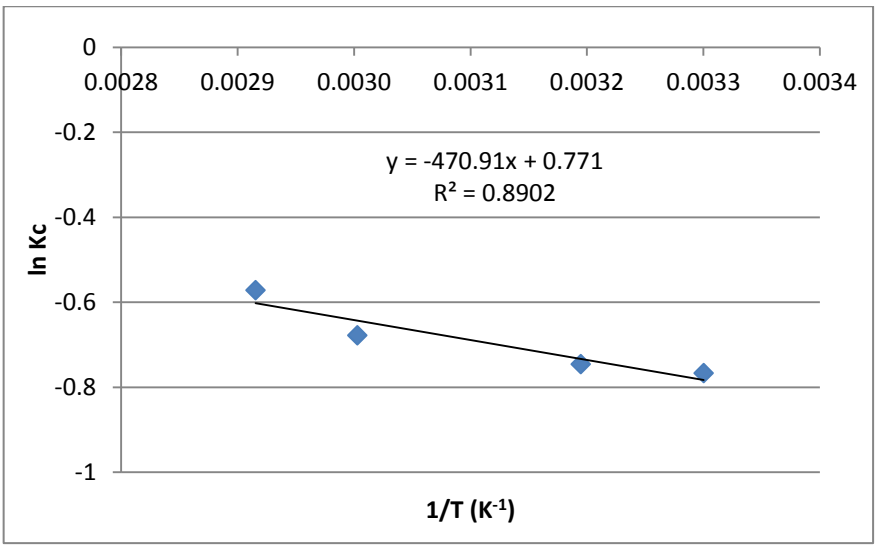

Figure 4.63: Van't Hoff plot for adsorption of 2-NP onto GLB

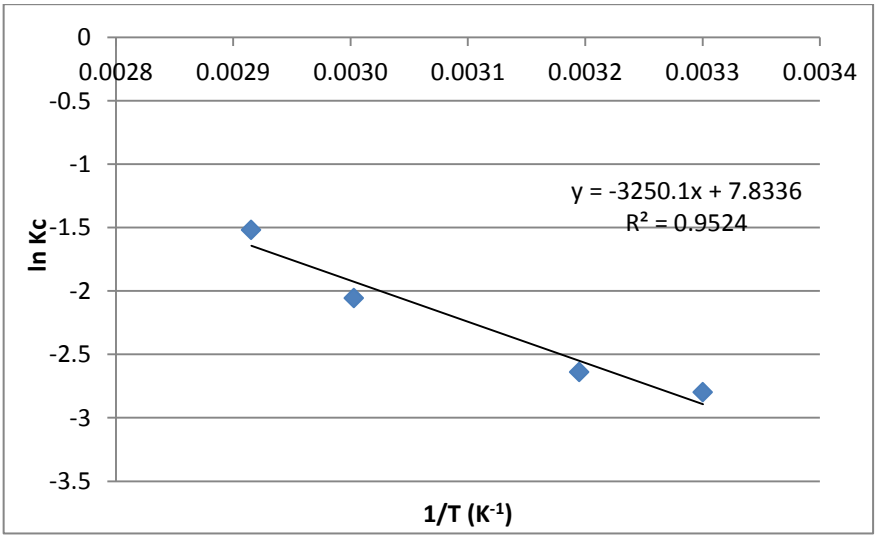

Figure 4.64: Van't Hoff plot for adsorption of 2-CP onto GLB

Table 4.21: Thermodynamic parameters for sorption of P, 4-NP, 2-CP and 2-NP onto GLB

	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)	ΔG° (kJ/mol)			
			303 K	**313 K**	**333 K**	**343 K**
P	2.034	- 2.01	2.648	2.650	2.703	2.736
4-NP	4.754	14.57	0.423	0.085	- 0.142	- 0.178
2-CP	27.02	65.13	7.049	6.870	5.688	4.329
2-NP	3.915	6.41	1.931	1.909	1.876	1.630

The positive values of ΔH^0 (Table 4.21) indicate that the adsorption process is endothermic and adsorption of P, 4-NP, 2-NP and 2-CP onto GLB will be favourable at high temperatures.

These positive values of ΔH^0 are better described with physisorption (< 41.8 kJ/mol). Chemisorption is involved in reactions with enthalpy values ranged 41.8 – 125.4 kJ/mol (Aroguz, 2006). The corresponding value of ΔS^0 is negative for adsorption of P indicating a decrease in degree of freedom, while the values are positive for adsorption of 4-NP, 2-NP and 2-CP implying an increase in randomness of the solid – adsorbate interphase in solution. The ΔG^0 values are positive for all phenols except 4-NP which had negative ΔG^0values at higher temperatures. The decreasing values imply increasing driving force of adsorption, spontaneity and thermodynamically favourable adsorption (Aroguz, 2006). The lower ΔG^0 values of 4-NP may justify the higher efficiency of GLB towards the removal. 2-CP with highest ΔG^0 was least adsorbed from solution at all temperatures.

GL

The results from batch adsorption experiments on effect of temperature on adsorption of P, 4-NP, 2-NP and 2-CP using GL is presented in Figure 4.65. The results showed that percentage removal of phenols using GL increased with increase in temperature. The increasing temperature creates more driving force (kinetic energy) and increases the collision between the phenols and the adsorbent, and also caused more bond breakage on GL for the adsorption process to take place (Wahab *et al*., 2011).

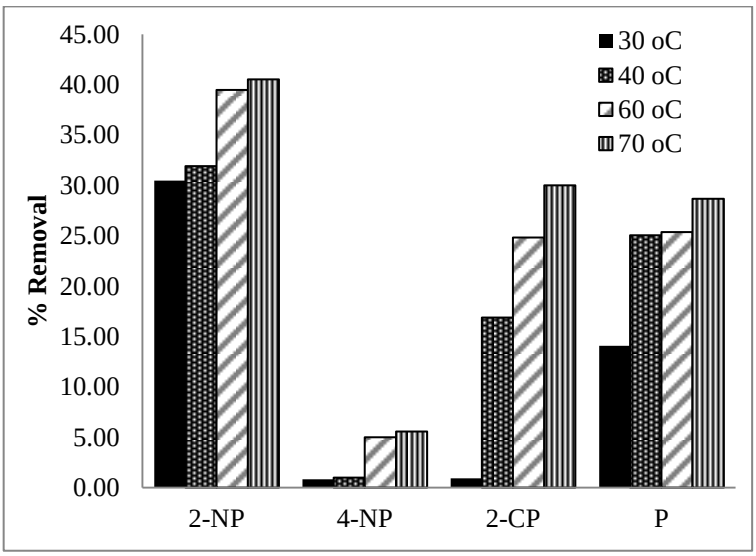

Figure 4.65: Effect of temperature on adsorption of 2-NP, 4-NP, 2-CP and P onto GL

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP in solution = 100 mg/L; Volume of solution = 25 mL; Mass of GL = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, pH of solution = 7

With an increase in temperature, the order of efficient removal of the phenols by GL was 2-NP > 2-CP > P > 4-NP. The Van't Hoff's plot for the adsorption of P, 4-NP, 2-NP and 2-CP onto GL are presented in Figures 4.66 – 4.69, respectively, and thermodynamic parameters are given in Table 4.22.

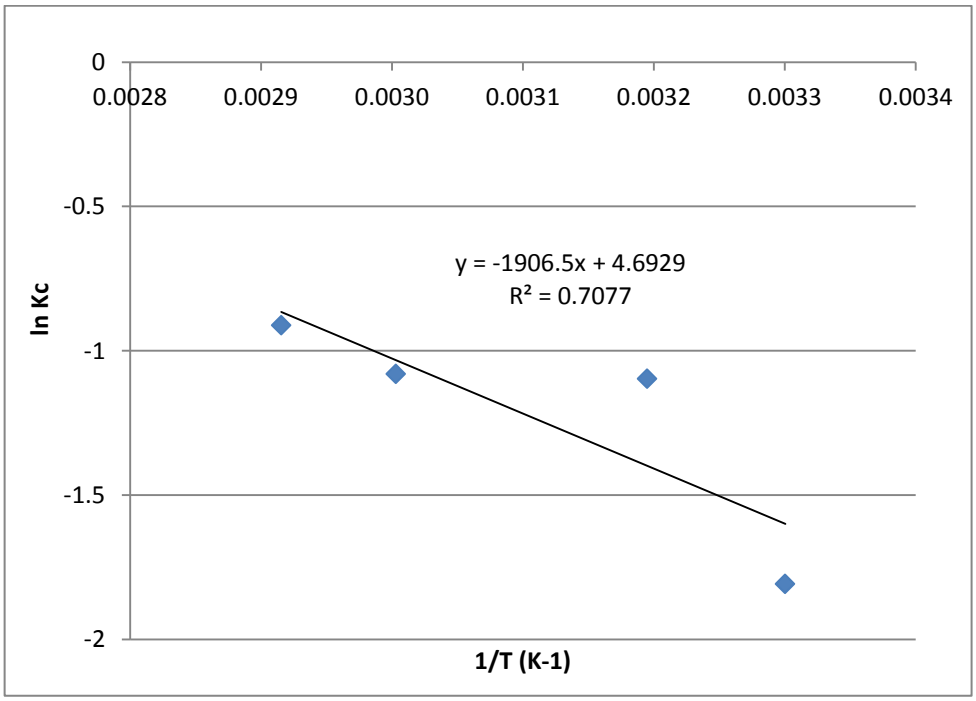

Figure 4.66: Van't Hoff plot for adsorption of P onto GL

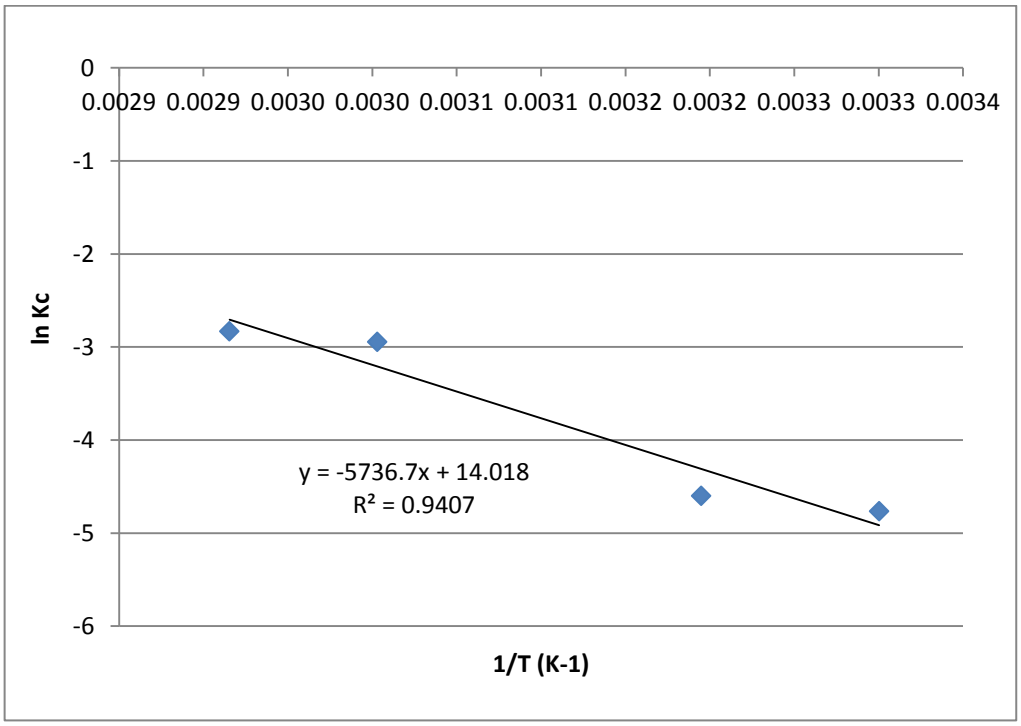

Figure 4.67: Van't Hoff plot for adsorption of 4-NP onto GL

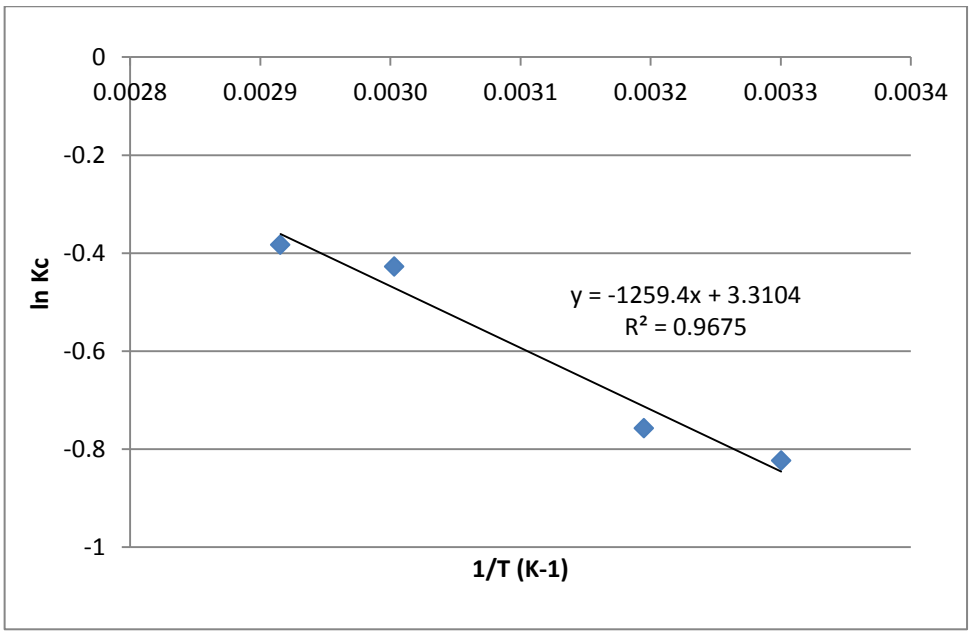

Figure 4.68: Van't Hoff plot for adsorption of 2-NP onto GL

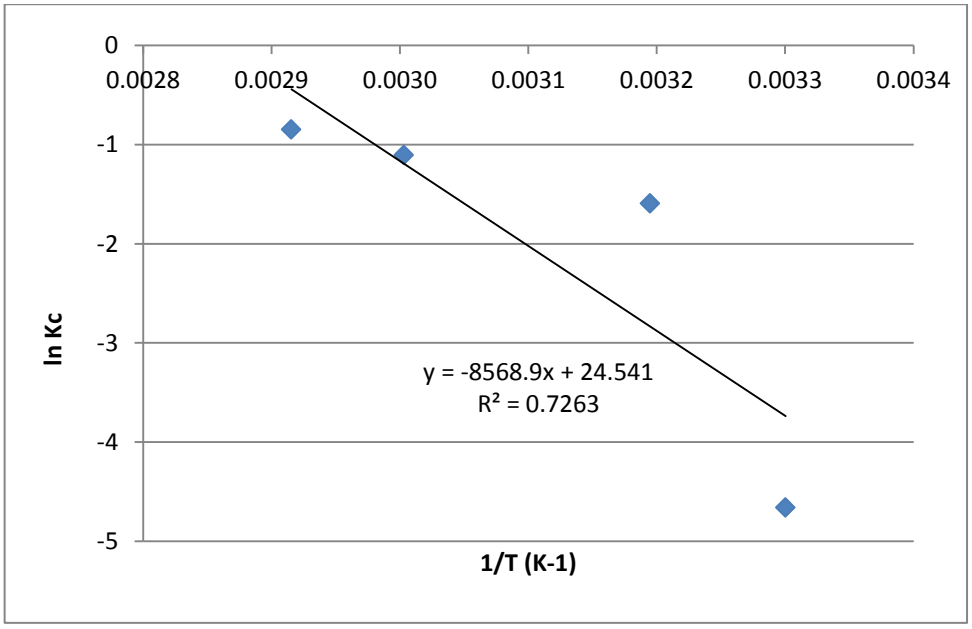

Figure 4.69: Van't Hoff plot for adsorption of 2-CP onto GL

Table 4.22: Thermodynamic parameters for sorption of P, 4-NP, 2-CP and 2-NP onto GL

	ΔH^o (kJ/mol)	ΔS^o (J/mol.K)	ΔG° (kJ/mol)			
			303 K	**313 K**	**333 K**	**343 K**
P	15.850	39.02	4.553	2.988	2.852	2.599
4-NP	47.694	116.55	12.005	11.969	8.152	8.078
2-CP	71.241	204.03	11.739	4.149	3.064	2.416
2-NP	10.470	27.52	2.074	1.971	1.182	1.092

The adsorption of P, 4-NP, 2-NP and 2-CP using GL was endothermic, as indicated by positive enthalpy (ΔH^0) values (Table 4.22). P and 2-NP adsorption was governed by physical adsorption (ΔH^0 < 41.8 kJ/mol) while in the cases of 4-NP and 2-CP, chemisorption was involved. Adsorption processes with positive ΔH^0 values ranged 41.8 – 125.4 kJ/mol are characterised as chemisorption (Aroguz, 2006).

The phenols exhibited increased degree of freedom. This was shown by the positive values of standard entropy (ΔS^0). Spontaneity and thermodynamic favourability of adsorption can be determined with standard free energy (ΔG^0). Negative and lower values of ΔG^0 can be linked to spontaneous and thermodynamically favourable adsorption (Aroguz, 2006). In this study, the decreasing values of $\Delta G^0$for adsorption of phenols onto GL imply that adsorption will be more spontaneous and favoured at high temperature. 2-NP had lowest ΔG^0 values relative to other phenols; this may suggest the more effective removal of 2-NP by GLA at increasing temperature. Other phenols with higher ΔG^0 values were less adsorbed.

Assessing correlation between Van't Hoff plot and thermodynamic nature of the adsorption processes, a Van't Hoff plot with positive slope indicates exothermic nature of a thermodynamic system. This was observed for GLA (Figures 4.56 – 4.59). Since for exothermic processes, $\Delta H < 0$, thus, the slope of the plot is greater than zero ($-\Delta H/R > 0$). This implies decrease in equilibrium constant with an increase in temperature. In contrast, plots with negative slope depict endothermic reactions as seen in plots for adsorption of phenols onto GLB (Figures 4.61 – 4.64) and GL (Figures 4.66 – 4.69). The slope of Van't Hoff plots for endothermic reactions are less than zero ($-\Delta H/R < 0$).

4.13.6 Adsorption of phenols from influent of wastewater treatment plant

The adsorption experiments (Chapter 4.13.1 – 4.13.5) had shown GLA is more effective for adsorption of P, 4-NP, 2-CP and 2-NP in comparison to the capacities of GLB and GL. Therefore, GLA was used for removal of phenols from industrial wastewater samples.

Wastewater samples from two sources were collected (as detailed in Section 3.4). The measured phenolic compositions and some properties of the wastewater samples are given in Table 4.23.

Table 4.23: Characteristics of collected industrial wastewater samples

	Wastewater samples			
Properties	W1		W2	
pH	7.27		8.28	
TDS (mg/L)	147		483	
Conductivity (µS/cm)	224		735	
Salinity (mg/L)	111		386	
Phenolic content (µg/L)		%RSD		%RSD
P	5.2	2.07	72.3	0.70
4-NP	35.7	0.69	40.1	1.10
2-CP	7.5	1.68	61.2	0.47
2-NP	45.5	0.32	51.9	1.86

The optimal adsorption conditions of stirring speed of 200 rpm, contact time of 240 min, 0.3 g of GLA were applied on adsorption of 25 mL sample of the wastewaters. Adsorption was carried out at 23 ^{o}C. The wastewater samples exhibited pH values (7.27 & 8.28) which are close to the optimal pH for the adsorption of P, 4-NP, 2-CP and 2-NP onto GLA. After adsorption and analysis with HPLC, none of the phenolic compounds was detected in the filtrates. Conclusively, at concentrations of 72.3 µg/L of P, 40.1 µg/L of 4-NP, 61.2 µg/L of 2-CP and 51.9 µg/L of 2-NP in some treatment plant influents, 0.3 g of GLA successfully remediated the phenols.

4.14 Column study

A 600 mL synthetic water contaminated with 500 mg/L of P, 2-CP, 4-NP and 2-NP was passed through a fixed column packed with 2 g of GLA at a flow rate of 2.0 mL/min.
The efficiency of removal of the phenols in fixed bed mode is presented in Figure 4.70.

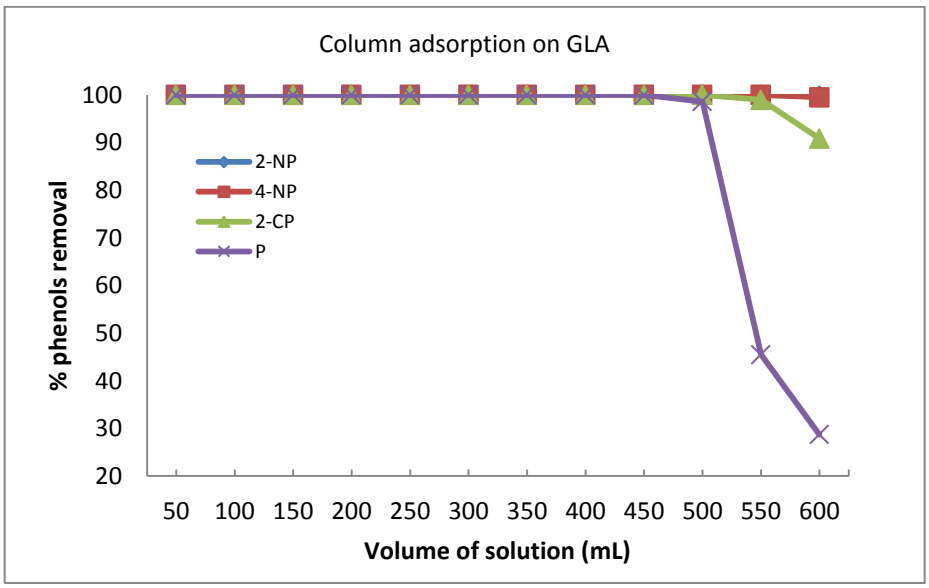

Figure 4.70: Adsorption of P, 2-CP, 4-NP and 2-NP onto GLA in fixed bed mode

Adsorption conditions: Concentration of P, 2-NP, 4-NP and 2-CP in solution = 500 mg/L; Total volume of solution = 600 mL; Flow rate = 2 mL/min; Mass of GLA = 2.0 g; Temperature = 23 ^{o}C

Removal of 2-NP and 4-NP was > 99.9% when 600 mL stock solution was passed through the column. The nitrophenols were adsorbed at same rate and their results overlap (Figure 4.70) Efficiency of P and 2-CP removal was > 99.9% at 500 mL and 450 mL respectively; a decreased removal was observed afterwards.

The column study was carried out at room temperature; implying simplicity and reduced cost of the process. These results that GLA is effective and may be applied in treatment of phenolic contaminated waters, even at high concentrations.

4.15 Desorption studies

This section outlines the desorption studies carried out in order to investigate the potential of reuse of the adsorbents after they have been utilized in adsorption of P, 2-CP, 2-NP and 4-NP. Figures 4.71 – 4.73 represent results of desorption of phenols from GLA, GLB and GL, respectively, using 0.1 M HCl and 0.1 M NaOH.

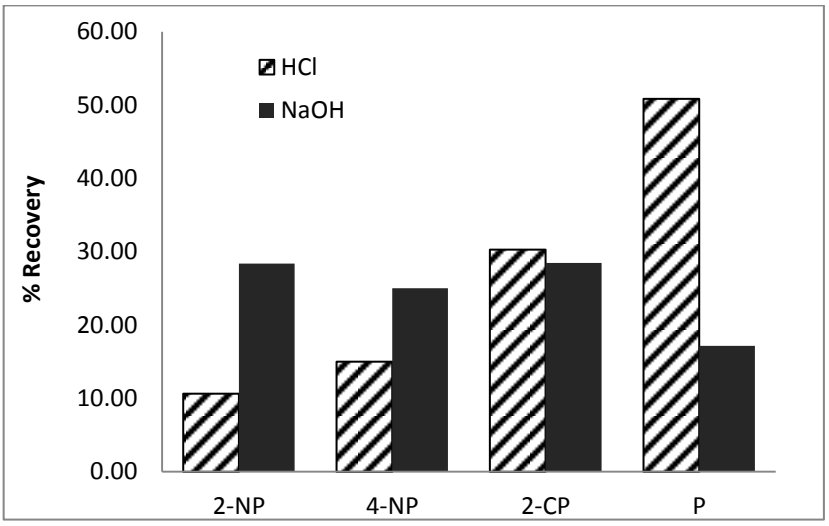

Figure 4.71: Percentage desorption of P, 2-CP, 4-NP and 2-NP from GLA

Desorption conditions: Volume of 0.1 M HCl = 25 mL; Volume of 0.1 M NaOH = 25 mL; Mass of GLA = 0.3 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

The phenols, P, 2-CP, 4-NP and 2-NP were desorbed from GLA using 0.1 M HCl and 0.1 M NaOH. A recovery of 28.67% of 2-NP and 25.02% of 4-NP was achieved using NaOH. These values are higher relative to the recovery when HCl was used (10.66 and 15.03% for 2-NP and 4-NP respectively).

In contrast, the recovery of 2-CP (30.28%) and P (50.85%) from GLA was more efficient using HCl relative to values of NaOH (28.48 and 17.14% for 2-CP and P, respectively).

Table 4.24: Desorption of phenols from GLA

	Recovery efficiency (%) using HCl	Recovery efficiency (%) using NaOH
2-NP	10.66	28.67
4-NP	15.03	25.02
2-CP	30.28	28.48
P	50.85	17.14

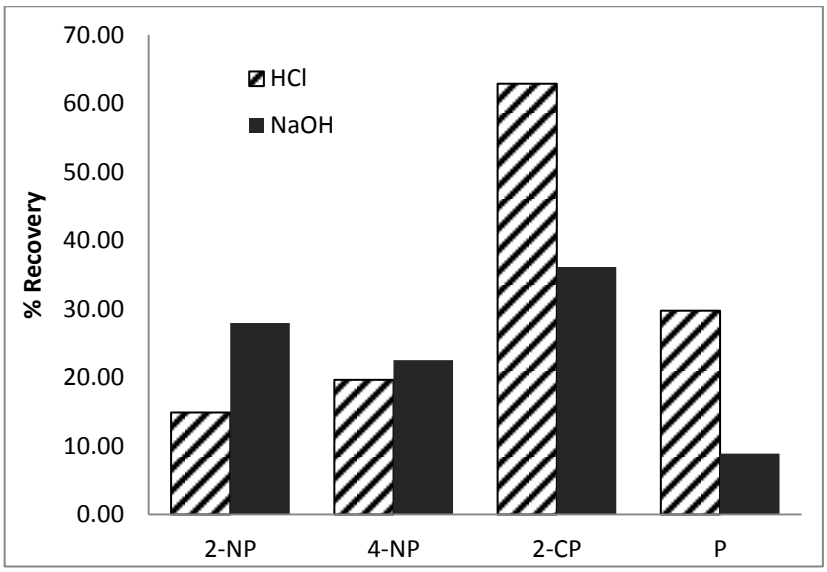

Figure 4.72: Percentage desorption of P, 2-CP, 4-NP and 2-NP from GLB

Desorption conditions: Volume of 0.1 M HCl = 25 mL; Volume of 0.1 M NaOH = 25 mL; Mass of GLB = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

Results from adsorbate desorption experiments using NaOH as desorbent showed a higher desorption of 2-NP (27.94%) and 4-NP (22.52%) from GLB (Figure 4.72). On the other hand, desorption values using HCl were 14.89 and 19.55% for 2-NP and 4-NP, respectively.

Efficiency of recovery of 2-CP (62.91%) and P (29.76%) from GLB was higher using HCl relative to NaOH values (36.12 and 8.86% for 2-CP and P, respectively).

Table 4.25: Desorption of phenols from GLB

	Recovery efficiency (%) using HCl	Recovery efficiency (%) using NaOH
2-NP	14.89	27.94
4-NP	19.55	22.52
2-CP	62.91	36.12
P	29.76	8.86

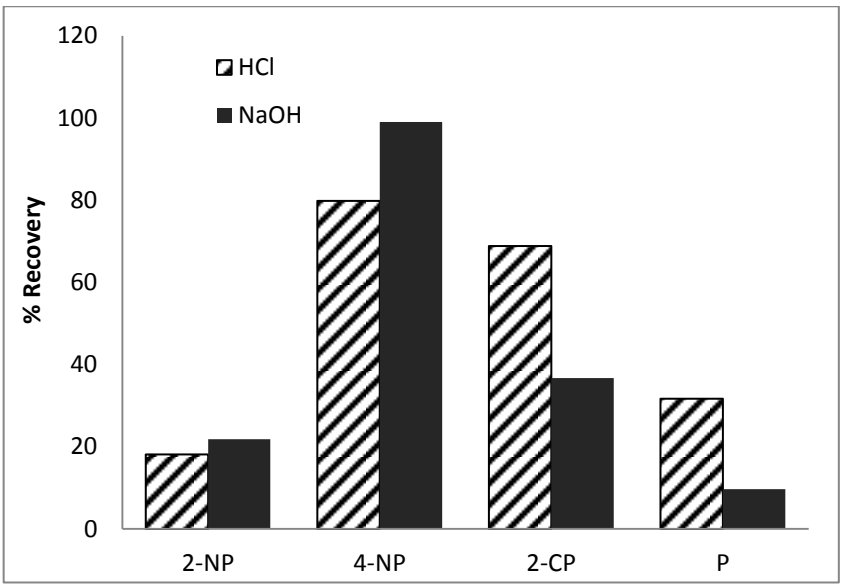

Figure 4.73: Percentage desorption of P, 2-CP, 4-NP and 2-NP from GL

Desorption conditions: Volume of 0.1 M HCl = 25 mL; Volume of 0.1 M NaOH = 25 mL; Mass of GL = 0.5 g; Contact time = 240 min; Stirring speed = 200 rpm, Temperature = 23 ^{o}C

In the recovery of P, 2-CP, 4-NP and 2-NP from GL, results from adsorbate desorption experiments showed a higher desorption of 2-NP (21.79%) and 4-NP (99.01%) from GL (Figure 4.73) was achieved using NaOH. In contrast, desorption values using HCl were lower; 18.15 and 79.86% for 2-NP and 4-NP, respectively.

Efficiency of recovery of 2-CP (68.88%) and P (31.72%) was higher using HCl relative to NaOH values (36.69 and 9.69% for 2-CP and P, respectively).

Table 4.26: Desorption of phenols from GL

	Recovery efficiency (%) using HCl	Recovery efficiency (%) using NaOH
2-NP	18.15	21.79
4-NP	79.86	99.01
2-CP	68.88	36.69
P	31.72	9.69

Overall, results showed similar trends in terms of solvents' effectiveness for adsorbent regeneration. HCl was found to be more effective for desorption of P and 2-CP from the adsorbents while NaOH was more efficient for desorption of the two nitrophenols. Since NaOH is a strong base, it abstracts proton from the nitrophenols resulting in formation of nitrophenoxide ion and water.

In case of using HCl on the nitrophenols, the conjugate base of HCl (chloride ion) can also remove their protons, however, the formed nitrophenoxide ions will accept protons released from the acid and return to nitrophenols, hence no relative effect with HCl. The results were vice versa for phenol and 2-Chlorophenol, where HCl was effective as desorbent. These effects and reactions of acid and base on structure of the phenols may explain the observed variation in desorption efficiency of the solvents.

CHAPTER FIVE

CONCLUSIONS

The study on characterisation of the untreated and activated materials from *Vitis vinifera* leaf litter provided useful information on the surface morphology of the adsorbents. SEM analysis showed presence of large pores and cavities in phosphoric acid – activated carbons. This may suggest reasoning for observed higher adsorption efficiency of these carbons due to crevices for active adsorption and intra-particle diffusion possibilities. Similarly, the rough irregular and heterogeneous surfaces of sodium hydroxide – activated carbons may have enhanced the uptake of phenols. Lack of porous network may explain the poor adsorption potential of non-activated biomass.

The presence of surface oxygen on the adsorbents was revealed by EDX spectroscopy. The oxygen moieties provided adsorbents with enhanced sorption potential. The adsorbents also had high carbon content (> 60%), an essential characteristic of adsorbent materials. Based on FTIR analysis, the –OH group which was predominant on GL became less observed in GLA and was absent in GLB. However, these adsorbents had prominent C –O, C – C and C – H groups responsible for adsorption. The low ash content of the adsorbents also facilitated their adsorption potential.

A lower unit mass (0.3 g) of GLA was required to attain equilibrium in adsorption of 100 mg/L solution of the phenolic compounds. On the other hand, 0.5 g of GLB and > 0.5 g of GL was required for optimal equilibrium adsorption of phenols from 100 mg/L stock solution. GLA, 0.3 g adsorbed 92.27%, 99.92%, 99.98% and 99.90% of P, 2-NP, 4-NP and 2-CP respectively from 100 mg/L phenolic solution. The affinity of the adsorbate for adsorbent and ease of removal by GLA is 4-NP > 2-NP > 2-CP > P. At same initial phenolic concentration, GLB and GL had lower adsorption capacities relative to GLA.

The adsorption of phenols onto GLA and GLB depends on available adsorption sites because adsorption processes were best described by pseudo-second order kinetic model. High correlation value of intraparticle diffusion model also showed that diffusion of phenols from bulk of solution onto the adsorbents played a significant role in adsorption process. The intra-particle and fractional power model had the best fit for adsorption of phenols onto GL; thus, particle diffusion and higher energy were involved in the adsorption.

The adsorption of P, 4-NP, 2-CP and 2-NP onto the adsorbents (GL, GLA and GLB) were at pH values lesser than the respective pKa values, thus the phenols were adsorbed onto the adsorbents in their molecular forms.

Freundlich isotherm best described the adsorption process using GLA & GL. The sorption of GLB was well correlated with Freundlich and Langmuir isotherm models, indicating GLB adsorption is heterogeneous and monolayer in nature.

The ΔH^o values for the adsorption of P, 4-NP, 2-CP and 2-NP onto GLA were negative and positive for GL and GLB experiments. Therefore, the adsorption process is exothermic for GLA and endothermic for both GL and GLB. Furthermore, the standard enthalpy change suggests that adsorption of P, 4-NP, 2-CP and 2-NP onto GLA is primarily governed by physisorption while chemisorption is involved in adsorption of 4-NP and 2-CP onto GLB. Considering thermodynamic parameters, adsorption process onto GLA was spontaneous and favourable, unlike for GL and GLB. For economic considerations, GLA will be a better choice of adsorbent. The order of efficiency and desired attributes of the adsorbents is GLA > GLB > GL.

The use of 0.3 g of GLA and optimal sorption parameters on wastewater influents containing 72.3 µg/L, 40.1 µg/L, 61.2 µg/L and 51.9 µg/L of P, 4-NP, 2-CP and 2-NP respectively resulted in significant remediation. After the adsorption process, target phenols were not detected upon analysis.

GLA can be efficiently applied in fixed bed mode for biosorption processes; this was confirmed from the results of column study. At a feed solution concentration of 500 mg/L, a removal efficiency of >99.9% was achieved in fixed bed mode using 2 g of GLA and passing 450 mL phenols solution at 2 mL/min. Thereafter, there was a decrease in adsorption of 2-CP and P to 90.82 & 28.69% respectively. The adsorbent can therefore be effectively utilised in fixed beds for wastewater treatment processes.

Adsorbed 2-CP and P were effectively recovered from the three adsorbents (GL, GLA and GLB) using HCl while the recovery of 2-NP and 4-NP were best using NaOH. This implies the possibility of reuse and /or regeneration of the adsorbents.

The results of this study led to general conclusion that activated carbons can in fact, be prepared from *Vitis vinifera* (grape) leaf litter, and these carbons were efficient in removal of some priority list phenolic compounds from wastewaters, at environmental and elevated levels in both batch and column mode processes.

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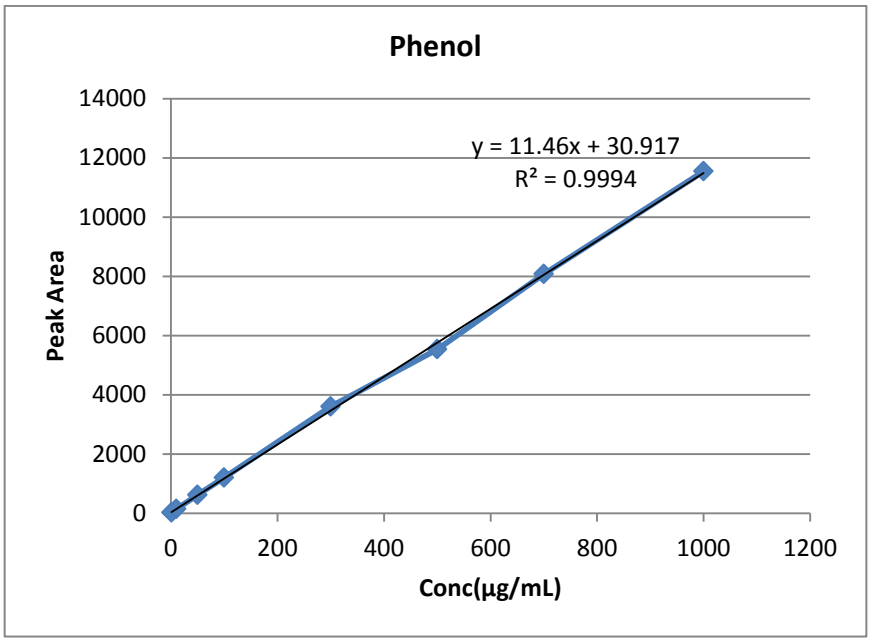
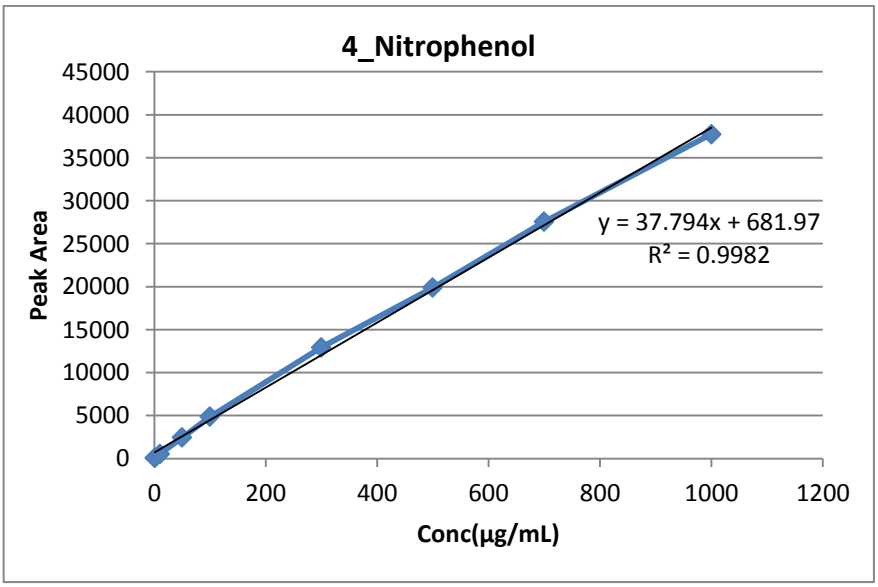
APPENDICES

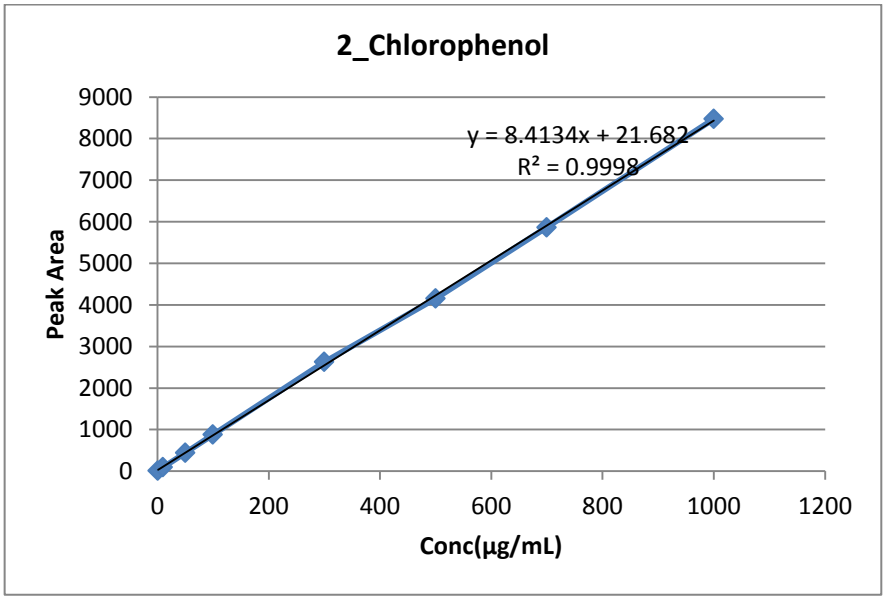
Appendix A: Linear standard curve for Phenol



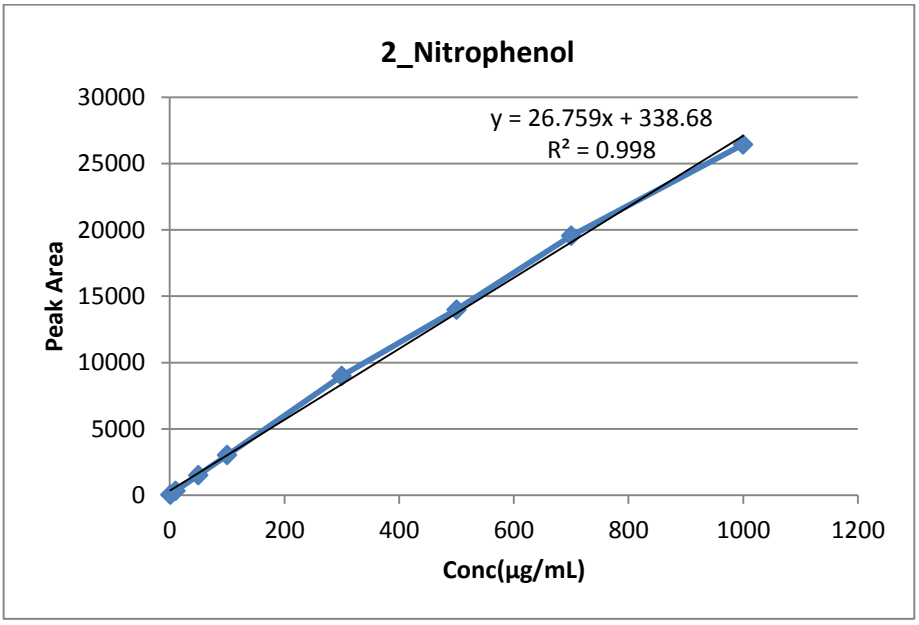
Appendix B: Linear standard curve for 4-Nitrophenol



Appendix C: Linear standard curve for 2-Chlorophenol



Appendix D: Linear standard curve for 2-Nitrophenol



Appendix E: EDX microanalysis of GL

Electron-Dispersive/Wavelength-Dispersive (EDX/WDS) X-ray Microanalysis results for non-treated precursors from *Vitis vinifera* leaf litter								
GL	Elemental composition (%)							
	C	O	N	Mg	Al	Si	Ca	Cu
Spectrum 1	60.517	37.830	0.000	0.070	0.255	0.368	0.826	0.134
Spectrum 2	60.369	37.959	0.000	0.067	0.292	0.430	0.776	0.108
Spectrum 3	60.148	37.779	0.000	0.090	0.345	0.601	0.904	0.132
Mean	60.34	37.86	0.00	0.08	0.30	0.47	0.84	0.12
SD	0.19	0.09	0.00	0.01	0.05	0.12	0.06	0.01
%RSD	0.31	0.24	0.00	16.84	15.24	25.90	7.74	11.67

Appendix F: EDX microanalysis of GLA

Electron-Dispersive/Wavelength-Dispersive (EDX/WDS) X-ray Microanalysis results for phosphoric acid - activated carbons from *Vitis vinifera* leaf litter									
GLA	Elemental composition (%)								
	C	O	N	Mg	Al	Si	P	Ca	Cu
Spectrum 1	68.936	27.776	0.000	0.046	0.159	0.385	1.811	0.766	0.122
Spectrum 2	68.139	28.138	0.000	0.035	0.060	0.389	2.006	1.006	0.227
Spectrum 3	66.854	29.101	0.000	0.075	0.041	0.327	2.309	1.098	0.195
Mean	67.98	28.34	0.00	0.05	0.09	0.37	2.04	0.96	0.18
SD	1.05	0.69	0.00	0.02	0.06	0.03	0.25	0.17	0.05
%RSD	1.55	2.42	0.00	39.73	72.66	9.51	12.30	17.94	29.72

Appendix G: EDX microanalysis of GLB

Electron-Dispersive/Wavelength-Dispersive (EDX/WDS) X-ray Microanalysis results for sodium hydroxide - activated carbons from *Vitis vinifera* leaf litter

GLB	Elemental composition (%)										
	C	O	N	Na	Mg	Al	Si	P	Cl	Ca	Cu
Spectrum 1	63.759	28.611	0.000	0.272	0.372	0.611	2.003	0.047	0.041	4.125	0.159
Spectrum 2	64.718	27.961	0.000	0.259	0.346	0.570	1.442	0.055	0.033	4.392	0.225
Spectrum 3	68.449	25.784	0.000	0.384	0.332	0.563	1.492	0.000	0.077	2.738	0.180
Mean	65.64	27.45	0.00	0.30	0.35	0.58	1.65	0.03	0.05	3.75	0.19
SD	2.48	1.48	0.00	0.07	0.02	0.03	0.31	0.03	0.02	0.89	0.03
%RSD	3.77	5.39		22.59	5.83	4.42	18.87	87.26	47.18	23.67	17.85