ACTIVATION OF THE CARBONACEOUS MATERIAL FROM THE PYROLYSIS OF WASTE TIRES FOR WASTEWATER TREATMENT

This dissertation is submitted in fulfilment of the requirement for the Magister Technologiae:
Engineering: Chemical

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DECLARATION BY CANDIDATE

I Lucky Malise, declare that, to the best of my knowledge, my dissertation is the result of my original work except otherwise stated. It has not been submitted in candidature for any degree in any university or institution. Due references in literature were stated and acknowledged wherever other sources were involved according to the standard referencing practices.

Lucky Malise 31st July 2017

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ABSTRACT

The generation of waste tires is one of the most serious environmental problems in the modern world due to the increased use of auto mobiles all over the world. Currently there is a problem with the disposal of waste tires generated since there are strict regulations concerning their disposal through landfill sites. Therefore, there is a need to find ways of disposing these waste tires which pose serious health and environmental problem. The pyrolysis of the waste tires has been recognised as the most promising method to dispose the waste tires because it can reduce the weight of the waste tires to 10% of its original weight and produce products such as pyrolysis oil, pyrolysis char, and pyrolysis char. These products can be further processed to produce value added products. The char produced from the pyrolysis of waste tires can be further activated to produce activated carbon.

This study is based on the chemical activation of waste tire pyrolysis char to produce activated carbon for the removal of lead ions from aqueous solution. This was done by impregnating the waste tire pyrolysis char with Potassium hydroxide and activating it inside a tube furnace under inert conditions to produce waste tire activated carbon. Adsorbent characterisation techniques (SEM, FTIR, TGA, XRF, XRD, BET, and Proximate analysis) were performed on the waste tire pyrolysis char and the activated carbon produced to make a comparison between the two samples. The results showed that the waste tire activated carbon produced has better physical and chemical properties compared to the raw waste tire pyrolysis char.

Adsorption results revealed that waste tire activated carbon achieves higher removal percentages of lead ions from aqueous solution compared to waste tire pyrolysis char. The results also showed the effect of various process variables on the adsorption process. Adsorption isotherms, kinetics, and thermodynamics were also studied. The adsorption of lead ions agreed with the Freundlich isotherm model for both the waste tire pyrolysis char and waste tire activated carbon. In terms of adsorption kinetics, the experimental data provided best fits for the pseudo-first order kinetic model for both the waste tire pyrolysis char and the waste tire activated carbon. The adsorption thermodynamics study revealed that the process is an exothermic process and spontaneous in nature.

Response surface methodology was used to determine the combined effect of process variables on the adsorption of lead ions onto waste tire activated carbon and to optimise the process using numerical optimisation. The optimum conditions were found to be adsorbent dosage = 1g/100ml, pH = 7, contact time = 115.2 min, initial meta concentration = 100 mg/l, and temperature = 25°C to achieve a maximum adsorption capacity of 93.176 mg/l.

Keywords: *Waste tire activated carbon, Chemical activation, adsorption capacity, response surface methodology, numerical optimization.*

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SYMBOLS AND ABBREVIATIONS

Symbols

C_e – Concentration of the metal ions left in solution after equilibrium

C_i – Initial concentration of the metal ions

C_s – Concentration of

K_L – Langmuir isotherm constant

R_L – Langmuir isotherm model separation factor

K_f – Freundlich isotherm constant

$\frac{1}{n}$ – Empirical parameter related to the adsorption intensity of the adsorption process

ε – Polanyi potential

β – Activity coefficient which is related to the mean adsorption energy

E – Mean energy of the adsorption process

q_e – Concentration of the metal ions adsorbed at equilibrium

q_s – Maximum adsorption capacity for D-R isotherm model

q_m – Maximum adsorption capacity

k_1 – Pseudo first order kinetic model rate constant

k_2 – Pseudo second order kinetic model rate constant

k_i – Intraparticle diffusion rate constant

q_t - Concentration of the metal ions adsorbed at time t

ΔH° - Change in enthalpy

ΔG°- Gibbs free energy change

ΔS° - Change in entropy

K_D - Distribution coefficient

Abbreviations

BET – Brunauer – Emmett – Teller

CCD – Central Composite Design

FTIR – Fourier transform infrared spectroscopy

SEM – Scanning Electron Microscope

TGA – Thermogravimetric analysis

XRF – X-ray Fluorescene analysis

XRD – X-Ray Diffraction analysis

RSM – Response Surface Methodology

D-R – Dubinin- Radushkevich

Chapter 1 . INTRODUCTION

1.1 BACKGROUND

The increase in the demand for auto mobiles has resulted in the increased generation of waste tires worldwide which is a major concern since there are environmental problems associated with the disposal of waste tires. Waste tires are not biodegradable and as a result it is very difficult to dispose them via landfill sites since they cannot degrade, and they occupy large volumes of landfill sites. Another method of disposing waste tires is open dumping the waste tires which is not favourable because the waste tires occupy huge spaces which pose major health and environmental threats. Several methods and techniques have been investigated to safely dispose the waste tires in an environmentally safe manner for waste management, these methods include pyrolysis, rethreading, energy recovery, and recycling (Sienkiewicz et al., 2012).

Tires are composed of several components including carbon black, zinc oxide, sulphur and a mixture of rubber materials such as styrene–butadiene rubber, natural rubber, and polybutadiene (Murillo et al., 2006). The tires are also said to have a high fixed carbon and volatile mater content together with high heating values which are higher than those of coal and biomass which make them useful in several industrial applications in the fuel industries (González et al., 2006; Oyedun et al., 2012). Pyrolysis of waste tires is said to have considerable potential in the management of waste tires due to the continued improvement of the technologies used for the pyrolysis process (Sienkiewicz et al., 2012). Pyrolysis is a process involving the thermal treatment of a material at high temperatures in an oxygen free zone/medium. In waste tire pyrolysis waste tires are thermally treated at high temperatures in the absence of air/oxygen in order to give pyrolysis char, pyrolytic oil, and pyrolysis gases.

The char obtained from the pyrolysis of waste tires can be activated in order to produce activated carbon. There are two known activation processes namely the physical and the chemical activation process. The physical activation of the pyrolysis char involves the thermal treatment of the char inside a reactor with the heat supplied by superheated steam at temperatures above 800 °C for 2 to 3 hours or carbon dioxide at temperatures above 900°C for more than three hours (Antoniou et al., 2014). For the physical activation step, it has been reported that physical activation of the pyrolysis char using superheated steam results in the production of activated carbon having narrow micropores, large BET surface areas and also large micro pore volumes in comparison with the one activated using carbon dioxide (San Miguel et al., 2003).

Chemical activation step is another method of activation which is usually done to enhance the adsorption characteristics of the pyrolysis char product obtained after the pyrolysis of waste tires. In chemical activation, the pyrolysis char is impregnated with a chemical reagent which acts as an activating agent for the material (Antoniou et al., 2014). There is a number of chemicals which have been used as activation agents for the enhancement of the pyrolysis char to become a good activated carbon and these chemical reagents include nitric acid, hydrogen peroxide, phosphoric acid, zinc chloride, ammonium persulfate, potassium hydroxide, etc. (Pradhan and Sandle, 1999; Antoniou et al., 2014; Saleh et al., 2013). Chemical activation using these chemical reagents leads to the formation of surface oxygen complexes on the activated carbon. These surface oxygen complexes are important because they are accountable for the properties of the activated carbon such as its surface and physico – chemical properties (Pradhan and Sandle, 1999).

The presence of heavy metals in ground waters and drinking water poses major health and environmental threats to human life and the ecosystem. Typical heavy metals which are found to cause health and environmental problems to human life and the ecosystem include cadmium, zinc, copper, nickel, lead, mercury, arsenic, selenium, antimony, and chromium (Saleh and Gupta, 2014). The major processes which lead to the production of wastewater containing these heavy metals have been reported to include metal purification, electroplating, and metal smelting (Issabayeva et al., 2010). It is therefore very important that industrial effluents are treated before being discarded to the environment. The conventional methods used for the removal of heavy metals from wastewater include chemical precipitation, solvent extraction, membrane separation, ion exchange, adsorption, reverse osmosis, and filtration (Wang et al., 2011).

Among all the above-mentioned techniques for the treatment of waste water adsorption is said to be the most promising due to its high metal removal efficiency, easy handling, availability of different adsorbents, and cost effectiveness (Ho et al., 2002a). In an adsorption process the metal ions diffuse into the pores of the adsorbent where they bond with the surface of the adsorbent by physical or chemical forces. In instances where the bonding takes place by physical forces the adsorption process is said to be physisorption and in instances whereby the bonding takes place due to chemical forces between the adsorbate and the adsorbent the adsorption process is said to be chemisorption. The adsorbents used for adsorption processes commercially include activated carbon, zeolites, clays, polymers, resins, and silica gel.

Activated carbons are regarded to be potential adsorbents for heavy metals removal from wastewater because of their large surface area, micro porous structure and chemical nature which enables them to achieve high adsorption capacities (Ozcimen and Mericboyu, 2008). Commercial activated carbons include of coal activated carbon, wood activated carbon, and coconut shells activated carbon. The production of activated carbon from some material which are attractive as low-cost precursors for activated carbons have been studied and some of these materials include palm shell, chestnut shell and grape seed and sewage sludge (Issabayeva et al., 2010; Wang et al., 2011; Özçimen and Ersoy-Meriçboyu, 2009). All these materials were reported to be capable of removing heavy metals from aqueous solution to a certain extent.

The use of activated carbon derived from char obtained through pyrolysis of waste tires has also been reported to have good characteristics for use as an adsorbent. It has been reported that activated carbon derived from the waste tire pyrolysis char is efficient for the adsorption of lead and nickel ions and this was shown by the equilibrium data which best fits the Langmuir isotherm model and the pseudo second order kinetic model (Saleh et al., 2013).

Process parameters such as temperature, contact time, adsorbent dosage, initial metal concentration, and pH of the solution were reported to have certain effects on the adsorption process(Parlayıcı and Pehlivan, 2017; Gupta et al., 2011; Khani et al., 2016). In order to determine the effect of these process variables and to determine their optimum points there are two experimental design methods which can be applied namely the one factor at a time and the response surface methodology experimental design methods. One factor at a time experimental design is an experimental design in which the effect of one variable on the response variable is studied while all the other variables affecting the response are kept constant. Response surface methodology is a method of experimental design used when the response of interest is influenced by several variables and it is necessary to determine the effect of such process variables on the response of interest (Sahu et al., 2009). Several authors have found the use of these experimental design methods useful in the study of adsorption processes and also in optimising the process variables affecting the adsorption process (Sahu et al., 2009; Kalavathy et al., 2009; Saleh et al., 2013).

Factors such as adsorption isotherms, kinetics, and thermodynamics also play a very important role in understanding the adsorption process. Adsorption isotherms provide the relationship between the amount of metal ions adsorbed onto the activated carbon at equilibrium and the concentration of the metal ions in solution at equilibrium at a given temperature (Patnukao et al., 2008a). Adsorption kinetics provide the relationship between the adsorption capacity and the contact time for the adsorption process and they also enable us to understand how the rate of reaction varies as the adsorption process takes place(Gupta and Bhattacharyya, 2011). Adsorption thermodynamics are used to determine the spontaneous nature of the process.

In this study, the carbonaceous material obtained from the pyrolysis of waste tires was activated by chemical means to improve its removal efficiency of lead ions in water. The adsorption characterisation techniques such as Scanning Electron Microscope (SEM), proximate analysis, X-ray fluorescence (XRF), X-ray Diffraction (XRD), Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and Brunauer–Emmett–Teller (BET) surface area analysis was studied to gain an understanding of the activated carbon derived from waste tires and to compare the characteristics of the waste tire pyrolysis char and the waste tire activated carbon. The effect of adsorption process variables (temperature, adsorbent dosage, contact time, pH, and initial metal concentration) was studied and the process variables were optimised using a one factor at a time and a response surface methodology experimental design. The experimental data was fitted into the adsorption kinetics and isotherms models to determine the rate limiting step for the adsorption process and to study the adsorption equilibrium conditions of the process. The adsorption thermodynamics were studied to determine the spontaneous nature of the adsorption process.

1.2 PROBLEM STATEMENT

Rubber tires are used in the automobile industry. However, once these tires become worn out they cause land pollution and become difficult to dispose. On the other hand, the presence of heavy metals such as lead Pb^{2+} in wastewaters also pose major health and environmental threats to the ecosystem since these metal ions are toxic and can harm human and animal life when exposed to at concentrations above acceptable limits. This project focuses on the use of activated carbon derived from waste tires as an adsorbent for the removal of lead ions from aqueous solution. And thus, providing an alternative for a low-cost adsorbent for Pb^{2+} removal and simultaneously addressing land pollution effects of waste tires.

1.3 OBJECTIVES

1.3.1 Main Objective:

The main objective of this project is to determine the beneficiation of activated carbon derived from waste tires as an adsorbent for the removal of lead ions from aqueous solution.

1.3.2 Specific Objectives

a. To characterise the adsorptive properties of the waste tire derived activated carbon and the waste tire pyrolysis char using X-ray fluorescence (XRF), X-ray Diffraction (XRD), Thermogravimetric analysis (TGA), Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) analysis, Proximate analysis, and compare the characteristics between the waste tire activated carbon and waste tire pyrolysis char;
b. To compare the adsorption performance of waste tire pyrolysis char and waste tire activated carbon for the removal of lead ions from aqueous solution;
c. To determine the effect of process variables (adsorbent dosage, pH of the solution, initial metal concentration, contact time, and temperature) on the adsorption of lead ions onto waste tire activated carbon;
d. To optimise process variables (adsorbent dosage, pH value of the solution, initial metal concentration, contact time, and temperature) using one factor at a time and response surface methodology experimental designs method;
e. To determine which adsorption isotherm (Langmuir, Freundlich, and Dubinin-Radushkevich) and kinetics (Lagergren’s pseudo-first order, Ho’s pseudo-second order, and Intraparticle diffusion) model does the experimental data best fit and to determine the important thermodynamic parameters for the adsorption process.

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Chapter 2

LITERATURE REVIEW

2.1 THERMAL TREATMENT OF WASTE TIRE RUBBER

Recently a lot of research work has focused on the energy utilization of waste tires through thermal treatment processes due to their high heating value which are higher than those of coal (González et al., 2006; Choi et al., 2014; Galvagno et al., 2002; Karatas et al., 2012). Such thermal treatment processes also have the advantage of reducing the waste tire volume by 90 % which is useful in terms of the disposal of waste tires through landfill sites because they will occupy less volumes of the landfill space (Sharma et al., 2000). The thermal degradation of solid waste can be achieved through thermal processes like direct combustion, gasification, and pyrolysis.

2.1.1 Direct combustion

The direct combustion of waste tires has been the most promising commercial alternative method to landfilling waste tires due to the development of high technology for this process. Direct combustion of waste tires is aimed at burning the waste tires completely in the presence of air to recover energy from the waste tires in the form of heat. The advantages of direct combustion of waste tires are that it results in maximum heat recovery and it operates at reduced power requirement costs for production (Oriaku et al., 2013). However, this process is said to be uneconomical and not environmental friendly since it leads to the emission of hazardous gases such as SO_x, NO_x, and other light hydrocarbons which can result in air pollution and health problems to human life and the ecosystem (Choi et al., 2014). In addition, the direct combustion process has high operation costs, no materiel recovery, and there is a need to clean the flue gas produced from the process (Oriaku et al., 2013). Due to these disadvantages of direct combustion of waste tires a lot of research work has focussed on other thermal processes apart from direct combustion for the treatment of waste tires rubber.

2.1.2 Gasification

Another thermal process which can be applied for the thermal treatment of waste tires is gasification. Gasification is a process used to convert carbonaceous materials into gas products syngas (hydrogen gas and carbon monoxide), carbon dioxide and a solid product (char) in an oxygen free zone. The use of oxidizing agents such as carbon dioxide, steam, or air is also applied at controlled amounts during the gasification process in order to enhance the efficiency of the process and also the characteristics of the products obtained (Karatas et al., 2012; Janajreh and Raza,). The use of gasification as a thermal process for the recovery of high value products from waste tires has received great interest from researchers because the gas product (syngas) obtained from the gasifier has high calorific values and as a result serves as good potential as a gas fuel and the solid char can be further activated to produce a highly porous activated carbon.

A study was carried out in a rotary kiln reactor for the gasification of granulated waste tires. In this study, it was reported that both the gas and solid char yield were 67.5 % and 32.5 % respectively. The high heating value of the syngas produced was found to be 10.8 MJ/Nm^3 and this was adequate to sustain the gasification process. The char produced from the gasification process had low BET surface area of 34.46 m^2/g but however through steam activation the surface area could increase to 914 m^2/g producing a high surface area activated carbon (Molino et al., 2013). It was also found in another study carried out in a fluidized bed reactor for the gasification of waste tire that the production of syngas increases with increasing gasification temperature from 400℃ to 650℃ and that the yield of the char decreases with increasing temperature. The surface area of the char was low but through activation steam activated carbon having high surface areas between 500 – 1300 m^2/g were obtained (Xiao et al., 2008).

2.1.3 Pyrolysis

Pyrolysis refers to the thermal decomposition of materials at high temperatures under inert conditions. It is a reversible process and it alters changes in the chemical composition of the material pyrolyzed. Pyrolysis has also been extensively studied for the recovery of energy and valuable products from waste tires. Over the years pyrolysis has been receiving attention as a potential alternative for the thermal treatment of waste tires due to its environmentally friendly nature compared to direct combustion and as a result it is being looked at as a potential alternative for the direct combustion of waste tires (Sienkiewicz et al., 2012).

Figure *1* shows pyrolysis of waste tires which involves the thermal treatment of waste tires at elevated temperatures in the absence of oxygen in order to produce pyrolysis oil, gas, and char. The gaseous product obtained from the process is usually made up of hydrogen, light hydro carbons, and carbon oxides. The liquid fraction is usually made up of tar, water, and oils and lastly the solid product is usually a char which contains high percentages of fixed carbon, and low percentages of ash and sulphur content (Galvagno et al., 2002; Choi et al., 2014; Antoniou et al., 2014). The gaseous product is said to have a high calorific value and as a result it is usually used as a fuel to supplement the energy requirements for the process while the liquid product can be further processed in order to produce a liquid fuel which can be used as a fuel in boilers, combustion boilers and also as feedstock in petroleum refinery (Aydın and İlkılıç, 2012; Antoniou et al., 2014). The solid residue/char obtained from the pyrolysis of waste tires can be used as carbon black or as activated carbon in both liquid phase and gas phase adsorption processes after further modification.

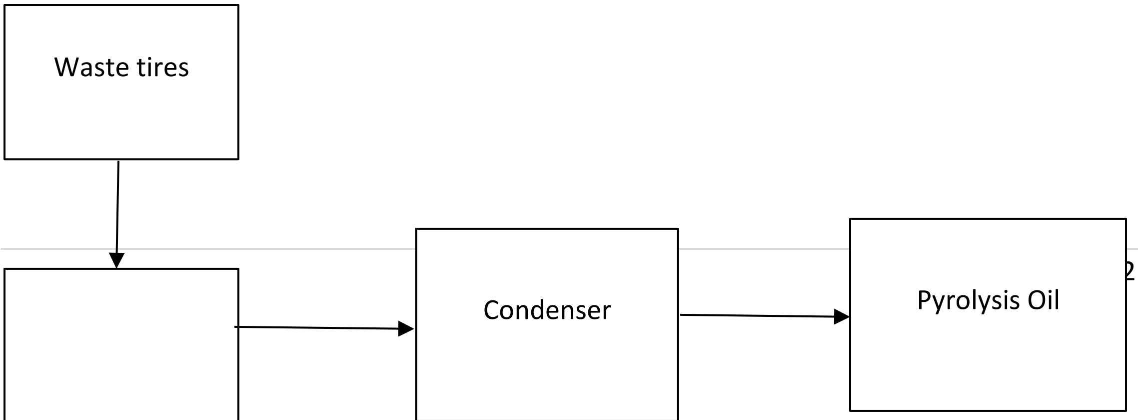

Figure 1: Schematic flow of the waste tire pyrolysis process

2.1.3.1 Factors affecting the pyrolysis process

Pyrolysis is a thermal process and as a result there are some factors which affect the process in terms of the yield and composition of the products obtained from the process. Process factors such as the temperature, residence time, heating rate, and the type of reactor used have a huge effect on the process (Mui et al., 2004; Murillo et al., 2006; Antoniou et al., 2014; San Miguel et al., 2003). Below the different process parameters are discussed further with special interest they have on the production of pyrolysis char.

2.1.3.1.1. Effect of pyrolysis temperature

The temperature of a pyrolysis process is the most important parameter affecting the yield and composition of the products obtained from the pyrolysis process. The process of pyrolysis is said to take place at temperatures ranging from 400℃ – 950℃ depending on the type of product desired. It has been reported that lower pyrolysis temperatures results in low yields of pyrolysis oil and gas while the yield of the pyrolysis char is higher (Zhang et al., 2008). The reason behind this trend has been said to be due to the incomplete thermal cracking of the waste tires at lower pyrolysis temperatures. As the temperature increase the yield of the pyrolysis char tends to decrease while the yield of the pyrolysis oil and gas increase. The increase in the yield of pyrolysis oil with an increase in the temperature is attributed to an increase in the thermal cracking of the waste tires at higher temperatures (Galvagno et al., 2002; Choi et al., 2014; Mui et al., 2004). As the temperature increases further the pyrolysis oil yield does however decrease and the gas yield increase. This is due to some light hydrocarbons vaporizing to gases at higher temperatures (Fernández et al., 2012).

2.1.3.1.2. Effect of pyrolysis residence time

There is negligible effect of final pyrolysis time on the yield of pyrolysis char. It has been reported that the yield of pyrolysis char remains constant for final pyrolysis time ranging from 1 – 4 hours but there is an observed decrease in the carbon content of the char resulting from the continued degradation after the volatile matter has been released (Mui et al., 2010b). The decrease in the carbon content consequently results in the increase in the sulphur and ash content of the char. It has also been reported that the internal surface area and pore volume of the char increase with increasing final pyrolysis time. This is said to be due to the release of volatile matter from the char leading to developed pores and larger surface areas. In another study, it was observed that lower pyrolysis residence times of 30 min to 1 hour had a significant impact on the pyrolysis char recovery but as the residence time increased beyond 1 hour there were no significant changes on the yield of the char (Danmaliki and Saleh, 2016).

2.1.3.1.3. Effect of heating rate

The heating rate of the waste tires during the pyrolysis process influences the yield and the characteristics of the char produced from the process. In one study, the yield of pyrolysis char was reported to decrease in percentages when the heating rate was increased from 1 K/min to 20 K/min. It was further reported that higher heating rates results in chars having lower BET surface areas and pore volumes (Mui et al., 2010a). Several researchers have reported similar observations for the pyrolysis of another materials such as pistachio-nut shells (Lua et al., 2004). It has been reported that lower heating rates have a slight effect on the waste tire pyrolysis product yields but at higher heating rates the gas yield fraction of the products gradually increases due to the secondary cracking reactions of volatiles (Antoniou and Zabaniotou, 2015).

2.1.3.1.4. Effect of particle size

The particle size of the raw waste tires to for pyrolysis has been reported to have a considerable impact on the product yields of the pyrolysis products. It has been reported that larger particle sizes result in pyrolysis products having little variations in terms of their yields but smaller particle sizes lead to greater reaction areas due to their larger surface areas and thus leading to the release of volatile matter from the waste tires during the pyrolysis process (Antoniou and Zabaniotou, 2015). A smaller particle size was also reported to lead to lower yields of gas fractions at the expense of the pyrolysis char.

2.2 ACTIVATED CARBON

Activated carbon can be defined as a highly porous carbonaceous material which has enhanced adsorptive properties and as a result can be used as an adsorbent in adsorption processes. Because of its good adsorptive characteristics activated carbon can be used as an adsorbent for the separation of gaseous mixtures, decolourisation of waste water, removal of heavy metals from waste water, recovery of solvents, and removal of air pollutants (Yagsi, 2004). The characteristics of activated carbon (Figure 2) which determine its suitability for use as an adsorbent include its high internal surface area, pore volume and size distribution, particle size, surface functional groups of the activated carbon, and the nature of the material used a precursor. As a result, it is very important to understand how these factors influence the performance of an activated carbon as an adsorbent. Below the characteristics of activated carbon are discussed further.

Figure 2: Structure of activated carbon (Stoeckli, 1990)

2.2.1 Characterization of activated carbon

For a carbonaceous material to find use as an activated carbon it has to have certain characteristics which will make it suitable for use as activated carbon. Such characteristics include the surface properties of the material (internal surface area, pore volume, and pore size distribution), chemical nature of the char, and the surface chemistry of the char. These characteristics are very important to study in order to determine whether a carbonaceous material will be suitable to be used as an adsorbent or not. Below different activation processes are studied and the effect they have on the characteristics of the activated carbon are discussed.

2.2.1.1 Surface area

A good activated carbon is characterised by its internal surface area. The larger the surface area of an activated carbon, the larger the adsorption capacity of the activated carbon. As a result, the internal surface area of activated carbon is regarded as its most important characteristic. The internal surface area is usually determined through a method known as the Brunauer-Emmett-Teller (BET) method. The BET method for determining the internal surface area of activated carbon involves the adsorption of nitrogen gas at 77 K. The amount of gas adsorbed at a given temperature in turn allows for the determination of the BET surface area. A lot of research has been done on the enhancement of the BET surface area of activated carbon adsorbents and as a result a lot of work has been reported regarding the topic. Below is a table showing the BET surface area of waste tire activated carbon prepared by different researchers through different methods for the enhancement of the adsorptive characteristics of the activated carbon. Table 1 shows the surface area obtained by various researchers in their previous studies.

Table 1: surface area obtained from previous studies

BET surface area (m^2/g)	Raw material	Method of activation	Reference
1070	Waste tire rubber	steam activation	San Miguel et al., 2003
621	Waste tire rubber	Chemical activation (KOH)	Al-Rahbi and Williams, 2016
402	End of life tires	Chemical activation (KOH)	Antoniou and Zabaniotou, 2015
242-720	granulated scrap tires	Chemical (KOH) &Physical activation (CO_2)	Lopez et al., 2016
1317	Waste tire rubber	Physical activation (Steam)	Gonzalez et al., 2006

2.2.1.2 Pore size distribution

The pore sizes in activated carbon and the distribution of these pores throughout the surface of the activated carbon is also regarded as another important characteristic of activated carbon. The pores found in activated carbon can be categorised into three classes depending on their sizes. The first class is known as the micropores and they are characterised by pore sizes having a width below 2nm, the second class is known as mesopores and they are characterised by pore sizes having a width ranging from 2 – 50 nm and lastly the last class is known as the macropores and they are characterised by pores sizes having widths higher than 50 nm. For the application of activated carbon in separation processes its performance depends on these pore sizes together with their distribution throughout the surface of the activated carbon. For example, when adsorbing very small adsorbates micropores are more suitable than mesopores and macropores due to their small widths, and when adsorbing molecules which are larger mesopores are suitable since these molecules cannot be adsorbed by micropores. The macropores on the other hand are important in adsorption since they provide channels for the adsorbates to the interior surface of the activated carbon and thus finding their way to the mesopores and micropores (Achaw, 2012). For this reason, it is very important to understand the pore sizes present in the activated carbon and also know the distribution of these pores. A lot of research has been done on the characteristics of activated carbon with specific interest on the pore size and distribution in activated carbon. Pelekani and Snoeyiek, (1999) studied the role of pore size distribution and pore volume of activated carbon and mentioned that these properties are important because they determine the accessibility of the pore volume for the adsorption of a given molecule.

2.2.1.3 Surface functional groups

The surface chemistry of activated carbon has also been regarded as an important characteristic of activated carbon. Several studies have been done to understand the effect of surface oxygen groups on the adsorption capacity of activated carbon for the adsorption of different adsorbates. The surface chemistry of activated carbon is an important characteristic of activated carbon because it is accountable for the properties of activated carbon such as its surface and physico – chemical properties (Pradhan and Sandle, 1999). The surface functional groups present in the surface of activated carbon are necessary to be studied because they provide an insight about whether the activated carbon is acidic or basic and hydrophilic or hydrophobic. This is important because it helps to identify in which application the activated carbon would be best suited according to their chemical characteristics (Brennan et al., 2001). For heavy metal removal, the surface functional groups which are important are said to be the oxygen containing groups since the cations can bind onto them easier (Bohli and Ouederni, 2015). The oxygen containing functional groups which are regarded to be important include the carboxylic acids, phenols, lactones, quinones, and hydroquinones (Bansal and Goyal, 2005). The presence of these oxygen containing functional groups on the surface of the activated carbon is strongly dependent on the chemical nature of the activated carbon precursor, the activation process used and the kind of chemical reagents the precursor is exposed to during the modification process (Bohli and Ouederni, 2015). Studies have revealed that activated carbon prepared from waste tires contains oxygen containing functional groups like hydroxyl, carboxyl, carbonyl, and phenols (Hofman and Pietrzak, 2011; Gupta et al., 2013a; Jin et al., 2014). The presence of these functional groups was reported to enhance the adsorption capacity of the waste tire activated carbon for the adsorption of heavy metals like chromium(III), lead, copper, and As (V) and also gases like NO_2.

2.2.2 Activation

The activation of a carbonaceous material can be applied in order to enhance its adsorptive characteristics and hence make it suitable for use an alternative for low cost activated carbon. Generally, there are two types of methods for activating carbonaceous materials, namely, physical and chemical activation. Although the physical and chemical activation methods are the used methods for the preparation of commercial activated carbon adsorbents, other researchers have studied the preparation of activated carbon using a combination of both the physical and chemical activation methods for the preparation of activated carbon. Below the different activation methods are discussed further.

2.2.2.1 Physical activation

Physical activation of carbonaceous materials is the conventional method of producing activated carbon. The physical activation method involves two steps of activating carbonaceous materials. The first step involves a low temperature pyrolysis of the raw material in a nitrogen or helium atmosphere aimed at producing a pyrolysis char and the second step involves partial gasification of the resulting pyrolysis char using oxidizing agents such as steam or carbon dioxide to activate the pyrolysis char and hence produce an activated carbon with a high internal surface area and large pores. The characteristics of the activated carbon produced is highly dependent on the type and grade of oxidizing agent used during the activation process and on the process parameters influencing the activation process. Such process parameters include temperature, activation time, particle size, flow rate of the oxidizing agent, and the heating rate. Several studies have been done on the production of activated carbon through physical activation (Teng and Wang, 2000; San

Miguel et al., 2003; González et al., 2006; Pastor-Villegas and Duran-Valle, 2002). Below is a discussion of how these process parameters affect the production of the activated carbon.

2.2.2.1.1. Factors affecting the physical activation process

2.2.2.1.1.1. Oxidising agent

As it has been stated before that the type and grade of oxidising agents used for the physical activation of pyrolysis char is very critical for the production of high grade activated carbon. The type of oxidizing agents which are usually used commercially for the physical activation of carbonaceous materials include steam, carbon dioxide, air, or their mixture (Zhang et al., 2004; San Miguel et al., 2003; Tay et al., 2009). It has been reported that using steam as an activating agent for the production of activated carbon results in the production of porous activated carbon having large BET surface area and large micropore volumes when compared to carbon dioxide (González et al., 2006). It has also been reported that steam is a better activating agent since it is more reactive than carbon dioxide (San Miguel et al., 2003).

2.2.2.1.1.2. Activation residence time

The amount of time the pyrolysis char is in contact with the activating agent during physical activation plays a vital role in the preparation of activated carbon. For instance, like activation temperature, the activation time has an effect on the physical structure of the activated carbon produced, adsorption capacity and also the yield of the activated carbon. Bae et al. (2014) studied the effect of activation time on the characteristics of high surface area activated carbon produced from walnut shells and jujube seeds and in their findings, they reported that an increase in the activation time (1 – 2 hours) resulted in an increase in iodine adsorption but further declined as the activation period increased (3 – 4 hours) during activation temperatures ranging from 600 – 700℃. It was also observed that at higher activation temperatures (800- 900℃) iodine adsorption decreased with increasing activation time from 1 – 4 hours. In another study, an increase in activation time was reported to result in activated carbon having higher BET surface areas and larger micropore and mesopore volumes (Chang et al., 2000). It is also important to note that activation time influences the burn off of carbon during the activation period. It has been reported that longer activation periods lead to higher percentages of burn off and this develops the porous structure of activated carbon produced, but it does however also lead to a decrease in the yield of activated carbon produced (González et al., 2006). Table 2 shows the ccomparison of physically activated carbon from waste tires with other activated carbon precursors

Table 2: Comparison of physically activated carbon from waste tires with other activated carbon precursors.

Precursor	Oxidising agent	BET surface area (m^2/g)	Micropore Volume (cm^3/g)	Total pore Volume (cm^3/g)	Comments	Reference
Pistachio shell	Carbon dioxide	778	0.222	0.466	Lower heating rates favoured the formation of high BET surface area values	Lua et al., 2004
Waste tire	Steam	1317	0.47	1.72	Pores formed were predominantly mesopores due to high carbonisation temperatures	Gonzalez et al., 2006
Macadamia nut shell	Steam Carbon dioxide	844 487	0.3911 0.2392	0.4852 0.2522	Comparison of steam and CO_2 activation shows that activated carbon prepared by steam gives better surface characteristics	Aworn et al., 2008
Corn hull		1010	0.4348	0.8341		

Oak	Carbon dioxide	845	0.3212	0.6011	Activated carbon prepared from different precursors has different surface characteristics, which suggest that the type and nature of the precursor used has an impact on the type of activated carbon produced.	Zhang et al., 2004
Corn stover		712	0.2849	0.5494		
Waste tire	Steam	1177	0.54	1.76	Acid treatment of pyrolysis char prior to activation with steam enhances the surface characteristics of the activated carbon produced	Ariyadejwanich et al., 2003
		755	0.22	0.9		

2.2.2.2 Chemical activation

Chemical activation is another method of activating carbonaceous materials in an attempt to improve its adsorptive characteristics by developing the micropores, increasing the internal surface area and also improving its surface chemistry. Chemical activation involves chemical impregnation of carbonaceous materials followed by carbonization of the chemically impregnated sample in order to produce a final product of activated carbon having great adsorption characteristics. One of the advantages of chemical activation include carbonization of carbonaceous materials at lower temperatures and shorter carbonization periods which can result in reduced operation costs compared to physical activation (Ho et al., 2002a; Issabayeva et al., 2010; Pradhan and Sandle, 1999). There has been some research work done on the preparation of activated carbon by chemical activation and it can be noted that factors such as the type of chemical reagent used for impregnation used, chemical impregnation ratio, carbonisation temperature and time play a very important role in the preparation of high adsorption capacity activated carbon (Pradhan and Sandle, 1999).

2.2.2.2.1 Factors affecting chemical activation

2.2.2.2.1.1 Chemical reagent used for activation

The type of chemical reagent used for the impregnation of carbonaceous materials during chemical activation is a very important factor in the preparation of commercial grade activated carbon. Generally chemical reagents used for chemical activation are usually dehydrating agents such as transition metal salts like zinc chloride, alkali earth metal and alkaline salts like sodium hydroxide and potassium hydroxide, and also acids like phosphoric acid, sulphuric acid, and nitric acid. The presence of these dehydrating agents during the chemical activation process has an influence on the pyrolytic decomposition of carbonaceous materials resulting in the inhibition of tar formation which in turn results in high carbon yield (Viswanathan et al., 2006). These dehydrating agents also lead to the development of pores on the surface of the activated carbon material (Kula et al., 2008).

Kilic et al. (2012) studied the preparation of activated carbon from Euphorbia rigida using ZnCl, H_3PO_4, K_2CO_3, and NaOH. In their study, they found that the type of dehydrating agent used for activation plays a major role in the preparation of activated carbon having high surface area.

Surface areas obtained were 2613 m^2/g, 1115 m^2/g, 790 m^2/g, and 396 m^2/g for K_2CO_3, ZnCl, H_3PO_4, and NaOH respectively. The surface areas obtained for K_2CO_3 and ZnCl were said to be comparable with those of commercial activated carbons. One study focussed on the activation of waste tire char by chemical activation using alkali metals KOH, K_2CO_3, NaOH, and Na_2CO_3. In this study, it was reported that chemical activation by KOH resulted in activated carbon having larger surface area and micropore volume (Al-Rahbi and Williams, 2016; Acosta et al., 2016).

2.2.2.2.1.2 Effect of chemical impregnation ratio

The impregnation ratio of the carbonaceous material during chemical activation is defined as the ratio of the chemical reagent used for impregnation in grams to weight of the carbonaceous material in grams. It has been reported that the chemical impregnation ratio during chemical activation of waste tire char has a significant impact on the surface properties of the activated carbon produced (Al-Rahbi and Williams, 2016; Acosta et al., 2016). It was reported that for impregnation with KOH the BET surface area and adsorption capacity of the activated carbon produced increases with an in increase with the impregnation ratio from 1:1 – 3:1 g/g (Al-Rahbi and Williams, 2016). This was said to be a result of more Potassium salts forming complexes on the surface of the carbon at higher impregnation ratios leading to them acting as gasification sites before carbonisation resulting in improved adsorption properties after carbonisation. Similar trends have also been reported with impregnation using other chemical reagents such as Potassium silicate, Potassium Carbonate, Sodium hydroxide, Nitric acid, and Phosphoric acid (Kong et al., 2014; Acosta et al., 2016; Pradhan and Sandle, 1999).

2.2.2.2.1.3 Effect of carbonisation temperature

One advantage of chemical activation has been reported to be the fact that activation can be carried out at lower temperatures compared to physical activation (Issabayeva et al., 2010). A study was carried out to determine the effect of activation temperature on the BET surface area and micropore volume of activated carbon produced from waste tire char by KOH activation. In this study, it was reported that increasing the activation temperature from 700℃ – 900℃ led a significant increase in the BET surface area of the activated carbon produced and that the micropore volume of the activated carbon produced at 900℃ was 5 times greater than the one activated at 700℃ (Al-Rahbi and Williams, 2016).

2.2.3 Application of activated carbon

Activated carbon prepared from waste tires has been studied extensively for the adsorption of different adsorbates. Examples include the low temperature control of NO_X (Al-Rahbi and Williams, 2016), adsorption of SO_2 from fuel pollutants (Nieto-Márquez et al., 2016), adsorption of textile dyes (San Miguel et al., 2003; Teng and Wang, 2000; Gupta et al., 2014; Mui et al., 2010b; Saleh and Danmaliki, 2016), adsorption of heavy metals (Molino et al., 2013; Al-Rahbi and Williams, 2016; Gupta and Ali, 2004; Li et al., 2010; Li et al., 2015), adsorption of pesticides (Gupta et al., 2011). Table 3 shows the ccomparison of chemically activated carbon from waste tires with other activated carbon precursors.

Table 3: Comparison of chemically activated carbon from waste tires with other activated carbon precursors

Precursor	chemical reagent used	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Comments	References
Waste tire char	KOH	814	0.169	1.163	Activated carbon produced was highly mesoporous	Acosta et al., 2016
Cassava peel	KOH	1605	0.513	0.691	BET surface area and pore volumes increased with increasing impregnation ratio	Sudaryanto et al., 2006
Pistachio shell	K2CO3	1800	0.73	0.82	BET surface area and pore volumes increase with increasing temperature	Hayashi et al., 2002
Rice husk	ZnCl	750	0.38	0.39	Study was done at low retention times (30 - 60 min)	Kalderis et al., 2008
Fox nut shell	ZnCl	2869	1.68	1.96	BET surface area and pore volume increased with	Kumar and Jena. 2015

increasing impregnation ratio from 0.5 - 2 g/g at an activation temperature of 600℃

2.2.3.1 Factors affecting the adsorption process

Several factors have been reported to affect the process of adsorption of heavy metals using waste tire derived activated carbon. For liquid adsorption processes the factors which have a critical impact on the adsorption capacity have been listed as the pH value of the solution, the adsorbent dosage of the activated carbon, the initial metal concentration of the solution to be adsorbed, and the contact time of the adsorption process. Several studies have reported on the effect of these process parameters on adsorption processes using waste tires activated carbon as an adsorbent. Below these parameters are discussed on how they affect the adsorption of heavy metals from waste water.

2.2.3.1.1 Effect of pH value of the solution on the adsorption capacity

The pH value of the solution is regarded as the most important parameter affecting the adsorption capacity of an adsorbent for the removal of heavy metals. It has been reported that for the adsorption of lead and copper the adsorption capacity of waste tire activated increases with an increase in pH from 2 – 7 and decreases as the pH continues to increase (Al-Rahbi and Williams, 2016). This was said to be a result of the solution having a lot of hydrogen protons at low pH values competing with the metal ions for adsorption sites on the surface of the activated carbon but as the pH value increases there are less hydrogen protons present competing for adsorption sites which leads to higher adsorption capacities. As the pH goes beyond a value of 6 the metals in solution begin to hydrolyse and precipitate in solution which leads to a decrease in the adsorption capacity of the activated carbon. Similar observations have been made in the adsorption of lead and nickel ions from aqueous solution using waste tire activated carbon. It has been reported that the enhanced adsorption capacity of the activated carbon for lead and nickel ions at a pH value of 7 is due to the negative surface charge of the activated carbon being able to attract the positively charged metal ions at this pH value (Gupta et al., 2012).

2.2.3.1.2 Effect of adsorbent dosage on the adsorption capacity

The adsorbent dosage during an adsorption process is a very important parameter to study since it affects the process efficiency and effectiveness. The removal efficiency of lead (II) ions has been reported to increase with an increase in adsorbent dosage until an optimum point of adsorbent dosage is reached in which equilibrium is reached and an increase in the adsorbent dosage does not result in any further significant increase in the removal of lead ions. Although this trend is observed in the adsorption of lead ions from different activated carbon materials, the optimum adsorbent dosage for the removal of lead ions from an aqueous solution does however depend on the nature of the precursor used for the preparation of activated carbon. Several authors have studied the effect of adsorbent dosage on the adsorption of lead from solution using different activated carbon materials and reported different optimum adsorbent dosages due to the difference in the activated carbon materials (Naiya et al., 2009; Gupta and Ali, 2004; Rafatullah et al., 2009; Anwar et al., 2010). Saleh et al., 2013 studied the adsorption of lead ions onto activated carbon prepared from waste tires with thermal and oxidation process. In their study, they reported that the removal of lead ions from aqueous solution increased from 15 – 85 % when adsorbent dosage was varied from 0.1 – 0.5 g/l.

2.2.3.1.3 Effect of temperature on the adsorption capacity

The temperature during an adsorption process is one of the parameters which affects the adsorption process and studying its effect on the adsorption capacity of an adsorbent is very important since it can give an indication of the nature of adsorption process taking place. It is said that an adsorption process is exothermic in nature if the percentage removal of the adsorbate decreases with increasing temperature and endothermic when it increases with increasing temperature (Sekar et al., 2004a; Alinnor, 2007). Alinnor (2007) reported that a decrease in the removal percentage of heavy metals with an increase in temperature may be explained to be as a result of an increase in the average kinetic energy of metal ions, leading to insufficient attractive forces between the binding sites of activated carbon and the heavy metal ions.

2.2.3.1.4 Effect of contact time on the adsorption capacity

The contact time of an adsorption process is said to have considerable effect on the uptake of lead ions onto activated carbon. Ahmad et al, (2009) reported that the uptake of lead and copper ions onto activated carbon derived from Meranti tree sawdust increased with an increase in the contact time of the process. They also reported that the rate of the metal uptake onto the surface of activated carbon is higher at lower contact times which is due to the availability of many binding sites on the surface of the adsorbent during the initial stage of the adsorption process. As the surface binding sites become exhausted with time the rate of the metal ions uptake decreases and is then controlled by the rate of transport from the external surface binding sites to the internal binding sites of the activated carbon particles. Several other researchers made similar observations in their studies (Imamoglu and Tekir, 2008; Sekar et al., 2004a; Saleh et al., 2013)

2.2.3.1.5 Effect of initial metal concentration

The initial metal concentration is one of the factors which has an effect on the adsorption of lead ions onto activated carbon. The initial metal concentration is said to have a major impact on the rate of the adsorption process. Shukla et al, (2002) has reported that the rate of adsorption is high at low initial metal concentrations and equilibrium in these cases is achieved very fast while at higher initial metal concentrations equilibrium is not reached fast. It has also been reported that at a given adsorbent dosage the percentage removal of lead ions increases with a decrease in the initial metal concentrations while the actual amount of lead ions adsorbed increase with an increase in the initial metal concentration. The increase in the percentage removal of lead ions with a decrease in the initial metal concentration is said to be due to the fact that the ratio of the adsorbent surface-active sites to the metal ions to be removed is higher at low initial metal concentrations than at high initial metal concentrations which will result to higher percentages being achieved at lower initial metal concentrations (Amarasinghe and Williams, 2007).

2.2.3.1.6 Effect of particle size on the adsorption capacity

The particle size of an activated carbon material used is very important in adsorption studies since it is strongly related to the surface area of the activated carbon. Shukla et al, (2002) reported that a decrease in the particle size of activated carbon would result in an increase in the surface area of the activated carbon which will result to higher availability of adsorption sites on the surface of the pores. Feng et al, (2004) studied the effect of particle size of activated carbon on the removal of lead ions and found that the amount of lead ions adsorbed increased from around 5 – 10 mg/g when the particle size of the activated carbon was reduced from less than 175 µm to particle sizes just above 43µm.

2.2.3.1.7 Effect of agitation speed on the adsorption capacity

The speed of agitation during an adsorption process has a significant influence on the distribution of the solute in the solution and also in the formation of the external boundary film and as a result it is considered one of the important parameters which affects the adsorption process (Wang et al., 2010; Crini et al., 2007).

2.2.4 Response Surface Methodology

Response surface methodology (RSM) is a method of experimental design which makes use of a collection of mathematical and statistical techniques to improve processes by developing processes and optimizing products (Danmaliki et al., 2017). RSM is also important because it can determine how process variables affect the response of interest and as such it is possible to determine the relationship between the response and the response variable through developed empirical models (Danmaliki et al., 2017; Mohamed et al., 2016). RSM makes use of Design of experiments which is ensures careful planning of tests experiments to determine the effect of process variables on the response variable and hence to optimize the process. There are two types of design of experiments which are commonly used in RSM and they include central composite design and Box Behken design(Van Thuan et al., 2017; Tan et al., 2008a; Thajeel, 2013). All these designs of experiments are important in the optimization of a process through the planning and conducting of experiments and to fit the response variable to the model(Thajeel, 2013; Danmaliki et al., 2017). In this study, the central composite design is the selected design of experiment. Central composite design is the most commonly used design of experiment. Central composite designs are first order designs 2^n, with 2n axial points, and nc replicable number of the center points(Thajeel, 2013). The number of experiments in central composite design can be calculated using Equation 1.

$$N = 2^n + 2n + nc \tag{1}$$

N is the number of experiments for the design, n is the number of independent variables, and nc is the replicable number of the center points. Central composite design leads to a reduced number of experiments compared to full factorial design.

2.2.5 Adsorption isotherms

Adsorption isotherms are very important in adsorption studies. They provide information relating to the relationship between the amount of metal ions adsorbed onto the activated carbon at equilibrium and the concentration of the metal ions in solution at equilibrium at a given temperature (Patnukao et al., 2008a). The adsorption isotherms are also instrumental in determining the adsorption capacity of the adsorbent. There are a lot of isotherm models which can be used to provide the adsorption equilibrium relationship at equilibrium and these include the Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R), and the Brunaur-Emmer-Teller (BET) method isotherm models. The two mostly studied isotherm models are the Langmuir and the Freundlich isotherm models.

2.2.5.1 Langmuir Isotherm model

The Langmuir isotherm model assumes monolayer coverage of the adsorbate onto the surface of the adsorbent and that adsorption takes place at certain specific homogeneous sites on the surface of the adsorbent (Sari et al., 2007a). The Langmuir isotherm model can be represented by equation 2.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

Linearizing Equation 2 results in the linear form of the Langmuir isotherm model equation (3) below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right)\frac{1}{C_e} \tag{3}$$

Where q_e & C_e are the concentration of the metal ions adsorbed at equilibrium (mg/g) and the concentration of the metal ions left in solution after equilibrium has been reached (mg/L). q_m is the maximum monolayer adsorption coverage capacity (mg/g). The maximum monolayer adsorption capacity is said to be dependent on factors such as the availability and accessibility of binding sites on the surface of the adsorbent, the chemical state of the binding sites, and also the affinity between the adsorbent binding sites and the heavy metal ions (Febrianto et al., 2009; Eslami et al., 2014). K_L is the Langmuir isotherm constant which is related to the free energy of the adsorption process (L/mg). The relationship between the value of K_L and the temperature of an adsorption process is very important since it can be used as an indicator to determine whether the adsorption process is exothermic or endothermic in nature. An increase in the value of K_L with an increase in temperature is said to describe an endothermic process resulting in chemisorption while a decrease in the value of K_L with an increase in temperature is said to describe an exothermic process leading to physio-sorption (Febrianto et al., 2009).

2.2.5.2 Freundlich isotherm model

The Freundlich isotherm model is an empirical isotherm model. The Freundlich isotherm model is used to describe adsorption processes in which adsorption of the adsorbate takes place on the heterogeneous surface of the adsorbent and is not restricted to monolayer coverage of the adsorbate on the surface of the adsorbent (Dada et al., 2012a; Sari et al., 2007a). The Freundlich isotherm model can be represented by equation 4.

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

Linearizing Equation (4) gives the linear form for the Freundlich isotherm equation:

$$\ln q_e = lnK_f + \frac{1}{n} lnC_e \tag{5}$$

Where q_e & C_e are the concentration of the metal ions adsorbed at equilibrium (mg/g) and the concentration of the metal ions left in solution after equilibrium has been reached (mg/L) respectively K_f is the Freundlich isotherm constant which is related to the adsorption capacity and $1/_n$ is an empirical parameter which is related to the intensity of the adsorption process and also indicates the effect of concentration on the adsorption capacity (Kumar and Kirthika, 2009). Table 4 shows a summary and comparison of the different isotherm models used.

2.2.5.3 Dubinin-Radushkevich (D-R) isotherm model

The Dubinin-Redushkevish (D-R) isotherm model is also an empirical isotherm model used to describe the adsorption of subcritical vapours onto the micropores following a pore filling mechanism (Foo and Hameed, 2010). It is normally used to determine whether the adsorption process is physical or chemical in nature. To describe the D-R isotherm model Equation 6 is used:

$$Inq_e = Inq_m - B\varepsilon^2 \qquad (6)$$

Where q_e and q_m are the amount of metal ions adsorbed at equilibrium (mol/L) and the monolayer adsorption capacity (mol/g) respectively, B is the activity coefficient related to the mean energy of adsorption (mol^2/J^2), Ɛ is the Polanyi potential and Eis the mean energy of the adsorption process (kJ/mol). Equation 7 and 8 are used to determine the Polanyi potential and the mean energy of adsorption respectively.

$$\varepsilon = RTIn\left(1 + \frac{1}{1/_{C_e}}\right) \qquad (7)$$

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (8)$$

Table 4: A summary and comparison of the different isotherm models used (Febrianto et al., 2009)

Isotherm	Functional form	Advantages	Disadvantages
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	Its expression is simple and also it contains surface heterogeneity parameter	Does not have saturation limit, no Henry's law, not structured, and also it is not applicable over a wide range of concentration
Langmuir	$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e}$	It has Henry's law and it is applicable over a wide range of concentration since it has finite saturation limit	It is based on the assumption that only monolayer coverage is possible on the surface of the adsorbent
Tempkin	$q_e = \frac{RT}{b} \ln (aC_e)$	Contains a simple expression	Like Freundlich it does Henry's law limit and saturation limit, and it is also not applicable over a wide range of concentration
Dublinin-Rdushkevich (D-R)	$q_e = q_{max} e^{(-(\frac{RTln({}^{C_e}/_{C_s})^2)}{\beta E_o}}$	Temperature dependent	It violates thermodynamic principle at zero loading or very low concentrations

Brunauer, Emmett and Teller (BET)	$q_e = q_{max}\frac{BC_e}{(C_e - C_s)\left[1 + (B - 1)({}^{C_e}/_{C_s})\right]}$	Multilayer adsorption	It is only valid at moderate concentrations

2.2.6 Adsorption kinetics

While the adsorption equilibrium studies are important in studying the efficiency of adsorption processes it is also important to understand the mechanism of the adsorption process in a system. Adsorption kinetic models are important because they can be used to understand the mechanism of the adsorption process and also for the determination of the rate controlling steps for the adsorption process and all this is very critical in the design of an adsorption system (Qiu et al., 2009a; Namdeti and Pulipati, 2014; Ho, 2006; Momčilović et al., 2011b). Adsorption kinetics can be explained as the solute removal rate controlling the residence time of the adsorbate in the solid-solution interface (Qiu et al., 2009a; Febrianto et al., 2009).

To describe the adsorption kinetics of the process there are kinetic models which can be applied for this purpose. These kinetic models include the pseudo first order and second order kinetic model (Qiu et al., 2009a; Ho, 2006). The pseudo first order and second order kinetic models are the most frequently used kinetic models to fit the experimental data in order to determine the rate limiting step (Momčilović et al., 2011b; Febrianto et al., 2009; Sekar et al., 2004a).

2.2.6.1 Pseudo first order kinetic model

The pseudo first order kinetic model is regarded as the earliest model related to the adsorption rate based on the adsorption capacity. The pseudo first order kinetic rate equation can be expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{9}$$

By integration of Equation (9) using boundary conditions $t = 0$, $q = 0$ and $t = t$, $q = q$ then the linear form of the equation becomes:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{10}$$

Where q_e & q_t are the concentrations of the metal ions adsorbed at equilibrium at time t (mg/g) respectively. k_1 is the rate constant of the reaction (min^{-1}). The rate constant can be obtained as the slope from the plot of $ln(q_e - q_t)$ vs t (Namdeti and Pulipati, 2014).

K_1 is used to describe how fast equilibrium can be reached during the adsorption process.

The pseudo first order kinetic model assumes that adsorption occurs only on localised sites on the surface of the adsorbent.

2.2.6.2 Pseudo second order kinetic model

The pseudo second order kinetic model based on the adsorption capacity of the solid phase surface can be expressed as shown in Equation 11.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{11}$$

Then integrating Equation 11 with the boundary conditions t = 0, q= 0, and t = t, q = q_t gives the linear form of the second order kinetic model as given in Equation 12.

$$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) t + \left(\frac{1}{q_e}\right) \tag{12}$$

Where q_e & q_t are the concentrations of the metal ions (mg/g) adsorbed at equilibrium and at time t (min). There has been a lot of work on the adsorption kinetics of lead ions onto activated carbon and some work has reported that the experimental data fitted best the pseudo second order kinetic model more than the first order kinetic model (Aroua et al., 2008; Momčilović et al., 2011b; Febrianto et al., 2009; Namdeti and Pulipati, 2014).

2.2.7 Adsorption Thermodynamics

Thermodynamic considerations in an adsorption process are very important to conclude whether the process is spontaneous in nature or not. The important thermodynamic parameters which are usually evaluated include the change in enthalpy(ΔH), change in entropy (ΔS), and the gibbs free energy change (ΔG). ΔG is used to determine the spontaneity of an adsorption reaction and usually the reaction is considered spontaneous if at a given temperature the value of the ΔG is negative (Saha and Chowdhury, 2011). The Gibbs free energy change for an adsorption process can be obtained with the aid of Equation 13.

$$\Delta G = -RTInK_D \tag{13}$$

Where ΔG is the Gibbs free energy change (KJ/mol), R is the universal gas constant (8.314 J/mol.K), K_D is the distribution coefficient or equilibrium constant which is dependent on temperature, and T is the temperature (K).

Other thermodynamic parameters such as the enthalpy change ΔH and the entropy change ΔS are also important and should be considered. The ΔH is very important in determining whether the adsorption process is exothermic or endothermic in nature. A negative value for ΔH suggests that the process is exothermic and spontaneous at low temperatures while a positive value for ΔH suggests that the process is endothermic and the process is spontaneous at high temperatures (Ho, 2006; Namdeti and Pulipati, 2014; Ho and Ofomaja, 2006). It has been said that the value of the ΔH can also be used to describe whether the type of adsorption process taking place is physisorption, chemisorption, or ion exchange adsorption (Anirudhan and Radhakrishnan, 2008; Saha and Chowdhury, 2011; Inglezakis and Zorpas, 2012). The different ΔH for the several types of adsorption processes are shown in table 5. The value of the ΔS of the adsorption process is very important to determine if the process involves a dissociative mechanism or not (Saha and Chowdhury, 2011). A positive value for ΔS is said to describe a dissociative mechanism, increasing randomness at the solid-liquid interface during an adsorption process and it also reflects the affinity of the adsorbent for the metal ion adsorbed(Ho, 2006; Ho and Ofomaja, 2006; Saha and Chowdhury, 2011).

To determine the values of the ΔH & ΔS an equation relating the ΔG to ΔH & ΔS is applied as shown in Equation 14.

$$\Delta G = \Delta H - T\Delta S \tag{14}$$

Where ΔH is the enthalpy change (KJ/mol) and ΔS is the entropy change$(KJ/mol.K)$. Substituting Equation 13 into Equation 14 gives Equation 15 which can be used to obtain the values of ΔH & ΔS through a plot.

$$InK_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{15}$$

Several authors have studied the adsorption thermodynamics of lead ions onto activated carbon material. Namdeti and Pulipati, (2014) reported that the adsorption of lead ions onto activated carbon derived from Ficus Hispida leave powder gave ΔG, ΔH, and ΔS to be -1.84266 KJ/mol, 113.09 KJ/mol, and 0.37 KJ/mol. k respectively. From this they concluded that the process is spontaneous in nature due to the negative ΔG value, endothermic due to the positive ΔH value and feasible since the value of ΔS was positive. On another study Uslu and Tanyol, (2006) determined the thermodynamic parameters to be -21.20 KJ/mol, -18.69 KJ/mol, and 8.4 KJ/mol. K for the values of $\Delta G, \Delta H,$ and ΔS respectively. In this study, it was reported that the process is spontaneous and exothermic in nature at the studied temperature of 298 K due to the negative values obtained for the ΔG and ΔH. And it was said that there is some increased randomness at the solid-solution interface during the adsorption process. Table 5 gives the comparison of the properties of the different types of adsorption.

Table 5: Comparison of the properties of the different types of adsorption

Property	Chemisorption	Physisorption	Ion Exchange adsorption	Reference
Type of interaction	Chemical reaction (covalent bonding)	Weak Van de Waals forces	Electrostatic or ion dipole interactions	Silveira et al., 2003
Heat of adsorption	> 80 KJ/mol	< 80 KJ/mol	8- 40 KJ/mol	Inglezakis and Zorpas, 2012
Coverage	monolayer coverage	multilayer coverage		
Nature	Irreversible	reversible	reversible	Silveira et al., 2003

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Chapter 3

EQUILIBRIUM, KINETICS, AND THERMODYNAMICS OF CHEMICAL ACTIVATED CARBON DERIVED FROM WASTE TIRE PYROLYSIS CHAR

Abstract

Waste tire activated carbon was prepared from waste tire pyrolysis char by chemical activation using KOH and adsorption studies were carried out by varying process variables (pH, adsorbent dosage, contact time, initial metal concentration, and temperature). Characterization techniques such as SEM, proximate analysis, XRF, XRD, and BET surface area were used to determine the characteristics of the activated carbon produced and compare them with the waste tire char. The adsorption results revealed that waste tire activated carbon was more efficient than the waste tire pyrolysis char. The results further showed the effect of process variables on the removal of lead ions and optimum operating conditions for these variables were obtained for the waste tire activated carbon at (pH of the solution = 7, adsorbent dosage = 0.25 g/100ml, initial metal concentration = 400mg/l, contact time = 120 min, and temperature = 25°C). Adsorption isotherm studies showed that the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char followed the Freundlich isotherm model. Adsorption kinetics study revealed that the experimental data best fitted the pseudo-first order kinetic model. Adsorption thermodynamics parameters $\Delta H°$, $\Delta G°$, and $\Delta S°$ were calculated and showed that the process is exothermic in nature.

Keywords: Waste tire activated carbon, Adsorption, Adsorption isotherms, Adsorption kinetics, Adsorption thermodynamics

3.1. INTRODUCTION

Heavy metals pollution in water has remained a critical concern throughout the world for many years, more especially in developing countries due to industrial activities (Ali et al., 2016; Bagbi et al., 2016). The major concern with heavy metals is that they are very toxic and again non-biodegradable which makes them a health hazard to humans and animal life (Mousavi et al., 2010). The most dangerous heavy metals to human health include Cu, Zn, Cd, Fe, Hg, Mn, and Pb ions. Amongst all these heavy metals, Pb^{2+} ions are one of the most hazardous posing serious health threats due to its presence in most waste water streams. Pb^{2+} is mostly introduced into the environment through industries such as battery manufacturing companies, mining companies, pigments and paints manufacturers, and explosives manufacturing companies (Dil et al., 2017; Verma et al., 2016; Momčilović et al., 2011a). According to the World Health Organization (WHO), the tolerance limit for Pb^{2+} ions concentration in drinking water should not exceed 0.05 mg/l (Momčilović et al., 2011a). Exposure to Pb^{2+} at concentrations above the acceptable limit can lead to severe health problems to humans and this effects include kidney problems, fertility problems, brain and liver damage, and problems in the nervous system(Ayanda et al., 2016; Verma et al., 2016; Asuquo et al., 2017a). Due to these effects, there is a need to come with measures to ensure that the presence of Pb^{2+} in waste water is reduced before being discharged to the environment.

Several techniques have been applied to remove Pb^{2+} ions from waste water and these techniques include methods such as metal precipitation, ion exchange, membrane filtration, reverse osmosis, and adsorption (Wang et al., 2016; Cataldo et al., 2016). Amongst all these processes, adsorption of Pb^{2+} using activated carbon is gaining a lot of recognition due to its high efficiency, easy operation, low costs, and energy efficiency (Verma et al., 2016). Commercial activated carbon is the most used adsorbent for the adsorption of heavy metals since it is very porous, has high surface area (500 – 5000 m^2/g), and has high adsorption capacities for Pb^{2+} which enables it to be suitable for the removal of Pb^{2+} (Asuquo et al., 2017a). The major concern about commercial activated carbon is that it is very expensive and for this reason it's use is limited. This has led to a growing demand to produce low cost activated carbon for the removal of Pb^{2+} ions from waste water. Efforts have been made to produce activated carbon from agricultural wastes, solid wastes, and by-products form other processes. For example, lignocellulosic wastes (Nayak et al., 2017), tamarind wood (Sahu et al., 2016), banana peels (Van Thuan et al., 2016), and coconut shells (Caccin et al., 2016).

Waste tires are creating a great environmental problem throughout the world since the rate at which they are being produced continues to increase rapidly every year and it is becoming difficult to dispose them in an environmentally friendly manner. The strict regulations restricting the disposal of waste tires into landfill sites means that there is a need for other alternative environmentally safe ways of disposing waste tires. Pyrolysis of the waste tires has been regarded as the most promising method for the utilization of the waste tires since the process can reduce the weight of the waste tires by up to 90 % of its original weight and it results in the production of by products such as waste tire pyrolysis oil, pyrolysis char, and pyrolysis gas (Acosta et al., 2016; Al-Rahbi and Williams, 2016; Galvagno et al., 2002; González et al., 2006).

The waste tire pyrolysis char can further be processed by activation to produce activated carbon with good adsorption properties. The activation methods include chemical and physical activation. Chemical activation involves the use of chemical reagents to produce activated carbon with superior adsorption properties and physical activation involves the use of oxidizing agents such as carbon dioxide and superheated steam to produce activated carbon with good adsorption properties(González et al., 2006; Antoniou et al., 2014; Pradhan and Sandle, 1999). This study aims at producing activated carbon by means of chemical activation using Potassium Hydroxide (KOH) as an activating agent and for the removal of lead ions from aqueous solution. Different characterization techniques are applied to determine the physical and chemical properties of activated carbon produced. Adsorption experiments are performed to determine the effect of process variables on the percentage Pb^{2+} removal from aqueous solution. Lastly adsorption isotherms, kinetics, and thermodynamics are being used to understand the adsorption equilibrium, rate limiting step, and the process thermodynamics of the adsorption process.

3.2. MATERIALS AND METHODS

3.2.1 Materials

Waste tire pyrolysis char obtained in powder form from a local supplier was used as the activated carbon precursor for this study. Chemical reagents used include KOH for the activation of the waste tire pyrolysis char, NaOH and HCl for the control of the pH of the solution during the adsorption process, and $Pb(NO)_3$ for the preparation of Pb^{2+} synthetic solution. The instrument used to analyse the samples after the adsorption experiments is an Atomic absorption spectrometer.

3.2.2 Adsorbent preparation

100g of the sample was firstly washed with distilled water to wash away the impurities present in the sample. The washed sample was then placed in a drying oven for 24 hours at 100°C to dry. The sample was then sieved to a particle size less than 100µm. After sieving, the sample was impregnated with a 500ml aqueous solution of KOH at an impregnation ratio of 2:1 (weight of

KOH: weight of char) and the mixture was stirred at 80°C for 24 hours to complete the impregnation process. The slurry produced from the impregnation process was dried in a drying oven at 100°C for 24 hours to remove moisture. The dry sample was then taken for activation in a tube furnace in the presence of nitrogen. The activation process took place in a tube furnace at 600°C for 1 hour under nitrogen atmosphere. After the activation process the furnace was left to cool in the presence of nitrogen gas until room temperature was reached and the sample was then removed from the furnace and washed with 1M solution of HCl to remove ash and sulphur content. The sample was then dried overnight and then stored until further use.

3.2.3 Adsorbent characterization

Several characterization techniques were used to characterize the samples used on this study to determine the adsorption characteristics of the waste tire char and activated carbon from waste tire char. A Phillips XL 30S Scanning Electron Microscope (SEM) was used to study the morphology of the samples. The process included scattering the samples on an adhesive carbon plate and sputter-coating it with a thin layer of gold before analysis. Proximate analysis was used to determine the moisture content, volatile matter, and ash content. In proximate analysis mass loss was determined by mass loss at 150 °C, the volatile matter was determined on the dried sample under nitrogen at 450 °C, the ash content determined as the mass loss at 650 °C and lastly the fixed carbon was calculated by subtracting the sum of the above from 100. XRF analysis was performed to determine the elemental analysis of the sample. Nitrogen adsorption was used to determine the BET surface area. The samples were degassed at 250 °C under vacuum. To determine the micropores the t-plot was used up to 20A°. XRD analysis was performed to determine the phase analysis of the samples. The black loading preparation method was used to prepare the samples for XRD analysis. The analysis was done using a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert High score plus software. Lastly the relative phase amounts (weight %) were estimated using the Reitveld method.

3.2.4 Adsorbent experiments

The adsorption experiments were carried out to determine the effect of process variables (pH, temperature, adsorbent dosage, initial metal concentration, and contact time) on the percentage removal of Pb^{2+} from aqueous solution using waste tire char and activated carbon. The experiments were carried out in sealed Erlenmeyer flasks and stirred in a shaking incubator operating at 200rpm. After the adsorption process the samples were filtered using 125µm filter papers. The filtrates were then diluted for analysis and analysed using an atomic absorption spectrometer to determine the concentration of lead ions present in solution after adsorption process. The percentage removal of Pb^{2+} from aqueous solution using waste tire char and activated carbon was determined using Equation 16.

$$\%\, removal\ of\ Pb^{2+} = \frac{C_i - C_o}{C_i} \times 100 \qquad (16)$$

Where C_i is the initial concentration of the Pb^{2+} initially present in solution before the adsorption process and C_o is the concentration of Pb^{2+} after the adsorption process.

3.3. RESULTS AND DISCUSSIONS

3.3.1 Adsorbent characterization

3.3.1.1 Scanning Electron Microscopy (SEM)

Shown in ***Figure*** 3 are the SEM images depicting the surface morphology of the waste tire pyrolysis char and the waste tire activated carbon. Figure 3 (a) shows that the morphology of the raw waste tire char consists of large particles which are not porous on the surface of the char as compared to Figure 3 (b) where chemical activation produced waste tire activated carbon with a well-developed surface morphology containing a surface with finer porous particles.

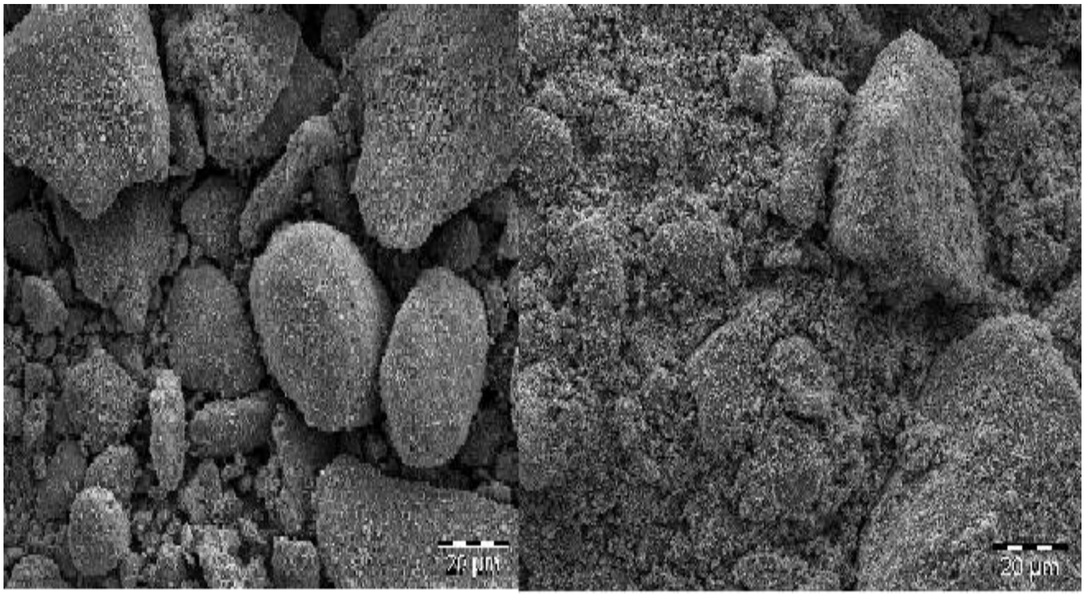

Figure 3: Scan electron micrograms of (a) raw waste tire pyrolysis char and (b) activated carbon derived from waste tire pyrolysis char under $20\mu m$ magnification.

3.3.1.2 Proximate analysis

Table 6 shows the results obtained from the proximate analysis. It is seen that there is a slight increase in the moisture content and fixed carbon content for the waste tire activated carbon while there is a slight decrease in the volatile and ash content after chemical activation with KOH at 600 °C. The increase in the moisture content of the waste tire activated carbon has been reported in a previous study and can be attributed to an increase in the surface area of the activated carbon after the activation of the waste tire pyrolysis char and the improved adsorption properties of the produced activated carbon (Nieto-Márquez et al., 2016). The decrease in the volatile matter and increase in the fixed carbon content can be linked to the effect of KOH during the activation process. As the volatile matter was decreased, the fixed carbon content was increased. There was also a slight decrease in the ash content of the activated carbon due to washing the activated carbon with HCl after activation.

Table 6: Proximate analysis of the raw waste tire pyrolysis char and the waste tire activated carbon

Proximate analysis		
Test description (%)	Raw waste tire pyrolysis char	Waste tire activated carbon
Moisture	3	3.4
Volatiles	1.1	0.8
Ash content	15.3	12.0
Fixed carbon	80.6	83.8

3.3.1.3 X- ray fluorescence (XRF) results

Table 7 shows the results obtained from the XRF analysis of the waste tire char and waste tire activated carbon. The results show a comparison between the metals present in the waste tire pyrolysis char and the waste tire activated carbon produced. From Table ***7***, there is a decrease in the amounts of the metals which were originally present in the char. The decrease in the amounts of the metals can be linked to the leaching effect of HCl towards the metals during the washing process after chemical activation. The increase in the amount of Potassium (K) was due to the introduction of KOH in the activation stage. (López et al., 2013) reported similar results using acid demineralization of the char before activation. It was also observed that the inorganic matter decreases drastically after the acid demineralization of the tire pyrolysis char.

Table 7:XRF results showing the inorganic components found in the waste tire pyrolysis char and the waste tire activated carbon:

XRF Results				
Metal	Waste tire char (mg/kg)	Waste tire char (%)	Waste tire activated carbon (mg/kg)	Waste tire activated carbon (%)
K	76	1.24	516	9.82
Ca	306	5.00	215	4.09
Ti	17	0.28	15	0.29
Cr	3.1	0.05	2.06	0.04
Mn	4.5	0.07	4.1	0.08
Fe	711	11.62	631	12.00
Co	287	4.69	239	4.55
Ni	31	0.51	< 0	0

Cu	305	4.99	261	4.91
Zn	4377	71.55	3374	64.18
Total	6117.6	100	5257.16	100

3.3.1.4 Brunauer–Emmett–Teller (BET) surface area

The surface area of activated carbon is one of the most important physical property for the adsorption of heavy metals. The BET surface area results as shown in **Table 8:** BET results for the waste tire char and waste tire activated carbonTable 8 show that the surface area of the pyrolysis char and the waste tire activated carbon were $51\ m^2/g$ & $71\ m^2/g$ respectively and the micropore volumes were $0.004\ cm^3/g$ and $0.007\ cm^3/g$ respectively. The results show an improvement in the BET surface area of the waste tire activated carbon and this can be attributed to the activation process which was applied for the improvement of the activated carbon. Other studies have reported similar results of BET surface areas for waste tire activated carbon and reported that the activated carbon could perform well in the adsorption of heavy metals such as Pb^{2+} (Nieto-Márquez et al., 2016; Jamradloedluk and Lertsatitthanakorn, 2014).

Table 8: BET results for the waste tire char and waste tire activated carbonTable 8:BET results for the waste tire char and waste tire activated carbon.

BET results		
	Waste tire char	Waste tire activated carbon
BET surface area (m^2/g)	51	71
Micropore volume (cm^3/g)	0.004	0.007

3.3.1.5 X- ray diffraction (XRD) analysis

The XRD patterns of the samples show that the waste tire pyrolysis char had smaller diffraction peaks and no sharp peaks present and the char was more. However, as the activation temperature increased to 400°C and 600°C there is an observed increase in the presence of sharp peaks at $2\theta = 36°$ which is attributed to Sphalerite and Wurtzite crystal phases. The pattern of the activated carbon at activation temperature of 600°C (Figure 4) shows that the waste tire activated carbon is composed of both a crystalline and amorphous structure. A similar study to produce activated carbon from waste tires made similar observations and that the activate carbon produced has both amorphous and crystalline structure(Gupta et al., 2013b; Undri et al., 2013).

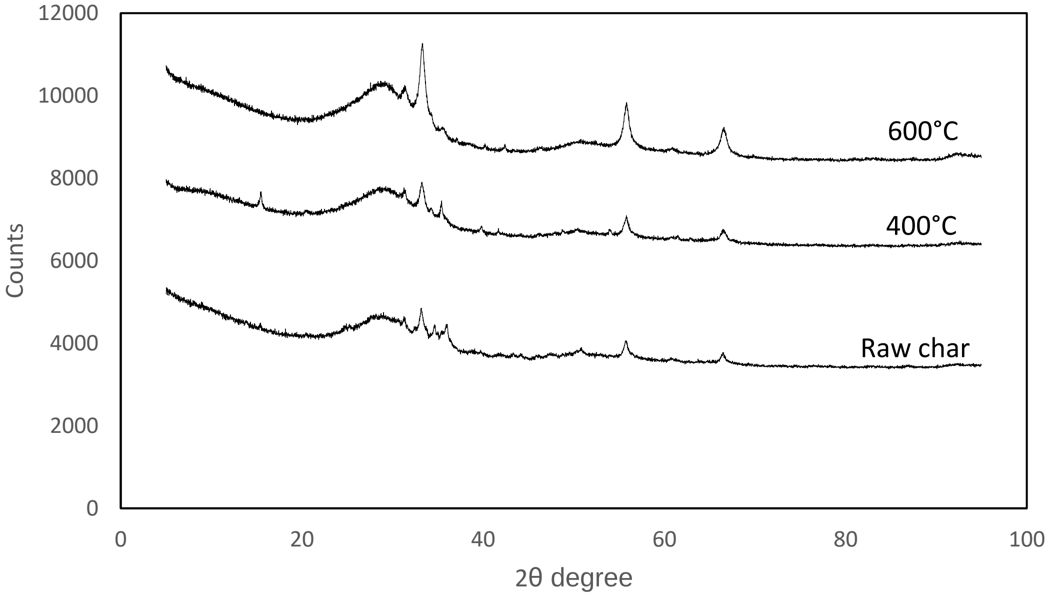

Figure 4: XRD results showing a comparison between waste tire pyrolysis char and waste tire activated carbons activated at different activation temperatures.

3.3.2.1 Effect of contact time on the % removal of $Pb^{2+}$from aqueous solution using waste tire activated carbon and char

The effect of contact time on the percentage removal of lead ions is shown in Figure 5. The percentage removal of lead ions increases with an increase in the contact time for both the waste tire activated carbon and the waste tire pyrolysis char. The notable observation here is that the waste tire pyrolysis char reaches equilibrium at 100 min which is faster than the waste tire activated carbon which achieved equilibrium at 120 min. It is also seen that the percentage removal of lead ions by waste tire activated carbon is higher than that of the waste tire pyrolysis char. For the waste tire activated carbon, between a contact time of 40 min to a contact time of 100 min the rate of increase in the percentage removal of lead ions was higher than the rate of increase in the percentage removal of lead ions from 100 min to 120 min, this is because adsorption takes place rapidly in the early stages of the adsorption process due to the availability of adsorption sites on the surface of the activated carbon but as the contact time increased from 100 min to 120 min the rate at which the percentage removal of lead ions increased reduced because the activated carbon had limited adsorption sites. From 120 min to 140 min the activated carbon was saturated and could not allow more adsorption of the lead ions. As a result, a contact time of 120 min was selected as the optimum contact time for this study using waste tire activated carbon and 100 min using waste tire char.

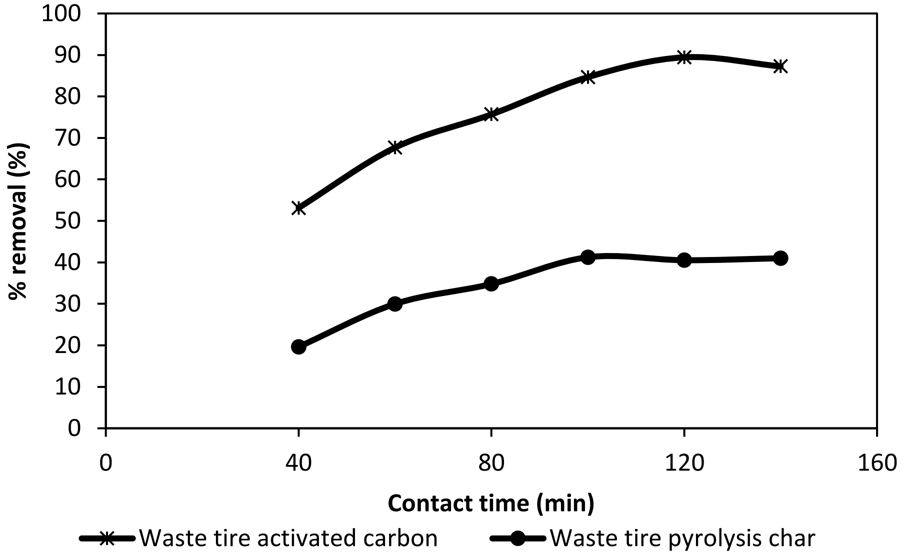

Figure 5: Effect of contact time on the % removal of lead ions from aqueous solution (Adsorbent dosage = 0.2 g/100 ml, pH = 6, Initial metal concentration = 100 mg/l, Temperature = 25˚C)

3.3.2.2 Effect of pH on the % removal of Pb^{2+} from aqueous solution using waste tire activated carbon and char

The pH value of the solution in an adsorption process is very important because it plays a role in the ionization of the functional groups responsible for adsorption which are present on the surface of the activated carbon and the charge of the metal ions adsorbed(Okoli et al., 2017). Figure **6** shows the effect of pH on the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char from aqueous solution. It is visible that waste tire activated carbon achieved higher percentage removal of lead ions than waste tire char and this shows that the chemical activation of the waste tire char produced waste tire activated carbon and this played a significant role in enhancing the adsorption properties. Figure 6 also shows us as that as the pH value of the solution increases, the percentage removal of lead also increases until the highest removal is achieved at pH 7 from which then the percentage removal starts to decrease again. The low removal percentages of lead ions at low pH values takes place due to the presence of hydrogen atoms in solution at low pH values which compete with the lead ions for adsorption sites on the surface of the waste tire activated carbon which causes the low percentage removal of lead ions. As the pH value of the solution is increased, there is an observed increase in the percentage removal of lead ions until the highest removal is achieved at pH 7. This behaviour is due to a decrease in the hydrogen atoms competing with the lead ions for adsorption sites as the pH of the solution is increased. As the pH of the solution moves from pH 7 to pH 8 the removal percentage of lead decreased. This is because as the pH of the solution increases beyond a neutral pH the lead ions present in solution start to hydrolyse and as a result they cannot be removed from solution which decreases the percentage removal of lead ions. A pH value of 7 is found to be relevant for the adsorption of lead ions because it results in the highest percentage removal of lead ions from the aqueous solution. Many studies have observed similar trends with respect to the effect of pH on the adsorption of lead ions from aqueous solution and they have explained this type of effect to be due to the ionization of the surface functional groups and again on the charge of the metal ions to be adsorbed (Asuquo et al., 2017b; Kucherova et al., 2017; Okoli et al., 2017).

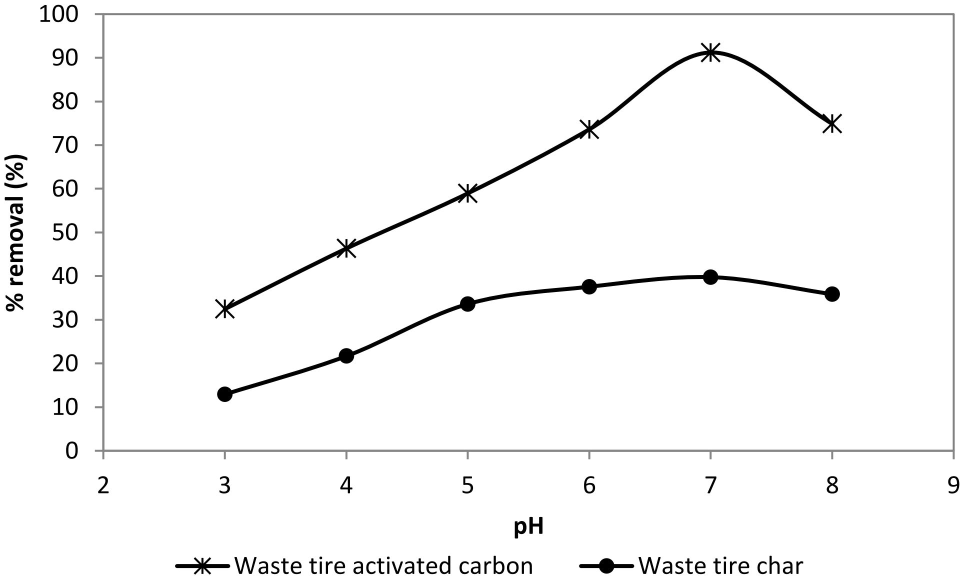

Figure 6: Effect of pH on the % removal of lead ions from aqueous solution (Adsorbent dosage = 0.2 g/100 ml, initial metal concentration = 100 mg/l, contact time = 100 min, Temperature = 25°C)

3.3.2.3 Effect of adsorbent dosage on the % removal of Pb^{2+} from aqueous solution using waste tire activated carbon and char

The dosage of activated carbon is one of the process variables which affect the adsorption process at a greater extent. Figure 7 shows the effect of adsorbent dosage on the percentage removal of lead ions from aqueous solution. From figure 4, it is seen that the percentage removal of lead ions increases gradually with an increase in the adsorbent dosage from 0.1 g/100ml to 0.25g/100ml and thereafter the removal percentage remains unchanged with an increase in the adsorbent dosage from 0.25g/100ml to 0.35g/100ml for both the waste tire activated carbon and waste tire pyrolysis char. The increase in the percentage removal of lead ions as the adsorbent dosage is increased from 0.1g/100ml to 0.25g/100ml takes place due to the availability of adsorption sites on the surface of the activated carbon leading to more lead ions being adsorbed onto the adsorption sites of the adsorbent. However, increasing the adsorbent dosage from an adsorbent dosage beyond 0.25g/100ml does not result in any further increase in the percentage removal of lead ions from aqueous solution. This behaviour is takes place because at an adsorbent dosage of 0.25g/100ml to 0.35g/100ml equilibrium between the adsorption sites on the surface of the adsorbent and the lead ions in solution has been reached and at this point the rate of adsorption is equal to the rate of desorption from the adsorption sites of the adsorbent which results in a constant percentage removal of lead ions. A study reported that this behaviour takes place due to the formation of aggregates of the adsorbent at higher adsorbent dosages which decreases the effective surface area for adsorption(Rao et al., 2016a). Other studies on the adsorption of lead ions using activated carbon have reported this similar behaviour and explained this behaviour to be due to the saturation of the adsorbent adsorption sites at higher adsorbent dosages (Abbaszadeh et al., 2016) and also due to a decrease in the active surface area for adsorption (Tang et al., 2017). For this study, an adsorbent dosage of 0.25g/100ml was the optimum adsorbent dosage since it yielded the highest percentage removal of lead ions using a lower adsorbent dosage.

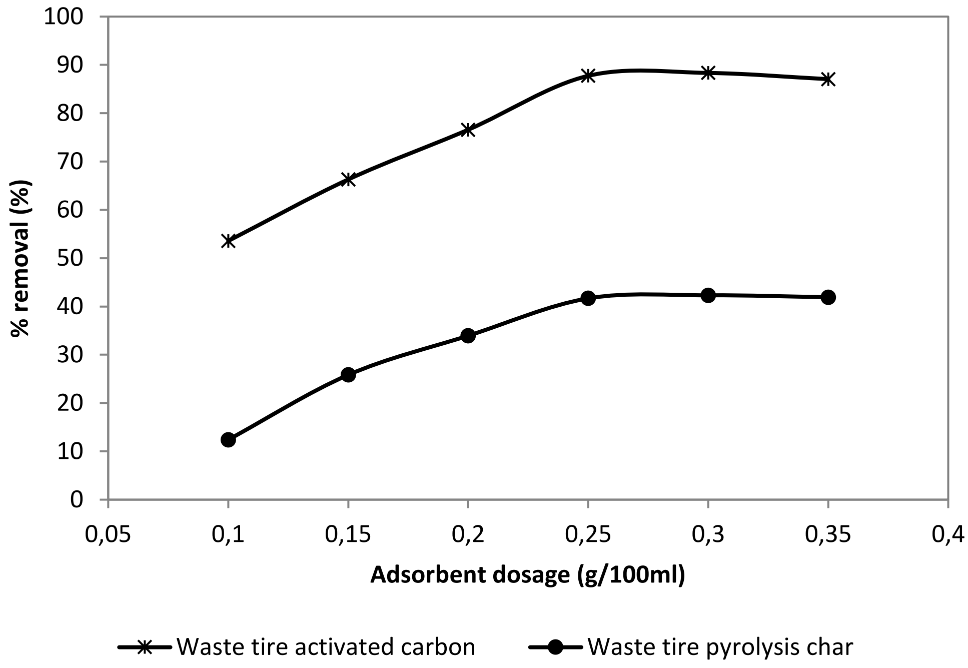

Figure 7: Effect of adsorbent dosage on the lead ions % removal (pH = 6, Initial metal concentration = 100 mg/l, Contact time = 100 min, temperature = 25˚C)

3.3.2.4 Effect of initial metal concentration on the % removal of Pb^{2+} from aqueous solution using waste tire activated carbon and char

The effect of initial metal concentration on the adsorption capacity of the waste tire activated carbon and waste tire pyrolysis char for lead ions is depicted in Figure 8. From Figure 8 waste tire activated carbon achieved higher adsorption capacities for lead ions compared to waste tire pyrolysis char and this is due to the activation of the pyrolysis char to produce the waste tire activated carbon. For the waste tire activated carbon, as the initial metal concentration increased the adsorption capacity of the waste tire activated carbon increased until an initial metal concentration of 400mg/l where it started to fall gradually thereafter. The increase in the adsorption capacity resulting from an increase in the initial metal concentration is due to the increased concentration gradient between the bulk lead ions in solution and the availability of adsorption sites on the surface of the waste tire activated carbon(Tan et al., 2016). This behaviour suggests that increasing the initial metal concentration ensures that more lead ions are adsorbed onto the adsorption sites of activated carbon due to increased mass transfer between the lead ions in solution and the adsorbent facilitated by a greater concentration gradient between the lead ions and the available adsorption sites on the surface of the waste tire activated carbon(Saeed et al., 2009). Therefore, in this study an initial metal concentration of 400mg/l is considered as the optimum initial metal concentration since the adsorption capacity achieved at this initial metal concentration was the highest at 85 mg/g. The optimum initial metal concentration for the adsorption of lead ions onto waste tire char is 200 mg/l which yielded an adsorption capacity of 27 mg/g.

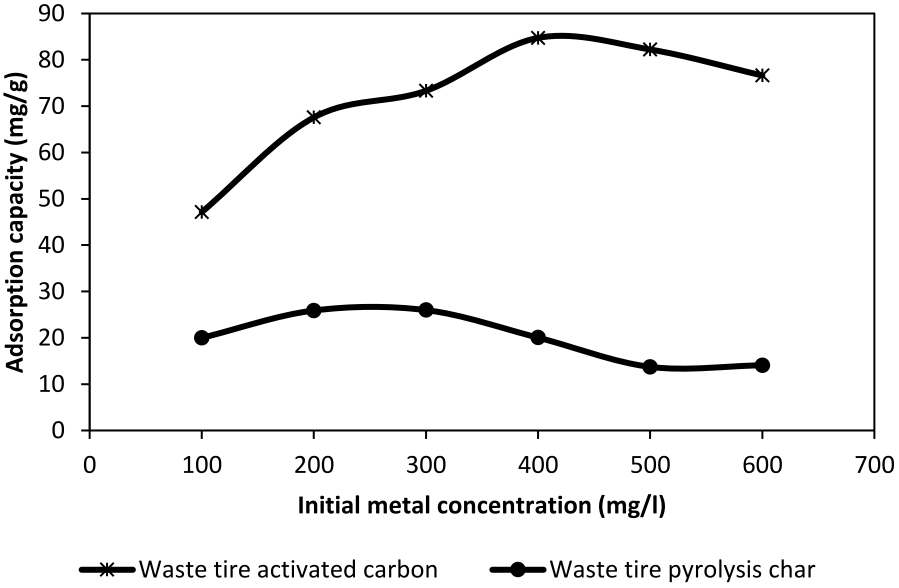

Figure 8: Effect of initial metal concentration on the % removal of lead ions from aqueous solution (Adsorbent dosage = 0.2g/100ml, pH = 6, contact time = 100 min, Temperature = 25˚C)

3.3.2.5 Effect of temperature on the % removal of Pb^{2+} from aqueous solution using waste tire activated carbon and char

Figure 9 shows the effect of temperature on the percentage removal of lead ions. It is evident that this process is temperature dependent. As the temperature is increased from 25°C to 50°C there is a decrease in the percentage removal of lead ions 92% to 40% by waste tire activated carbon and 37 % to 11 % for the waste tire pyrolysis char. From this behaviour, it can be said that the adsorption of lead ions onto waste tire activated carbon is an exothermic process. The decrease in the percentage removal of lead ions with an increase in temperature takes place because as the temperature increases the attractive forces between the adsorption sites on the surface of the activated carbon and the lead ions in solution weakens which causes a decrease in the removal of lead ions as the temperature is increased (Eloussaief and Benzina, 2010). It has also been reported that a decrease in the percentage removal of lead ions with an increase in temperature is due to the tendency of the lead ions to desorb from the surface of the activated carbon into solution(Sari et al., 2007b). A similar study on the adsorption of lead onto rubber tire activated carbon also reported that an increase in temperature caused a decrease in the removal of lead ions from aqueous solution and in this study the process was said to be an exothermic process(Rao et al., 2016a).

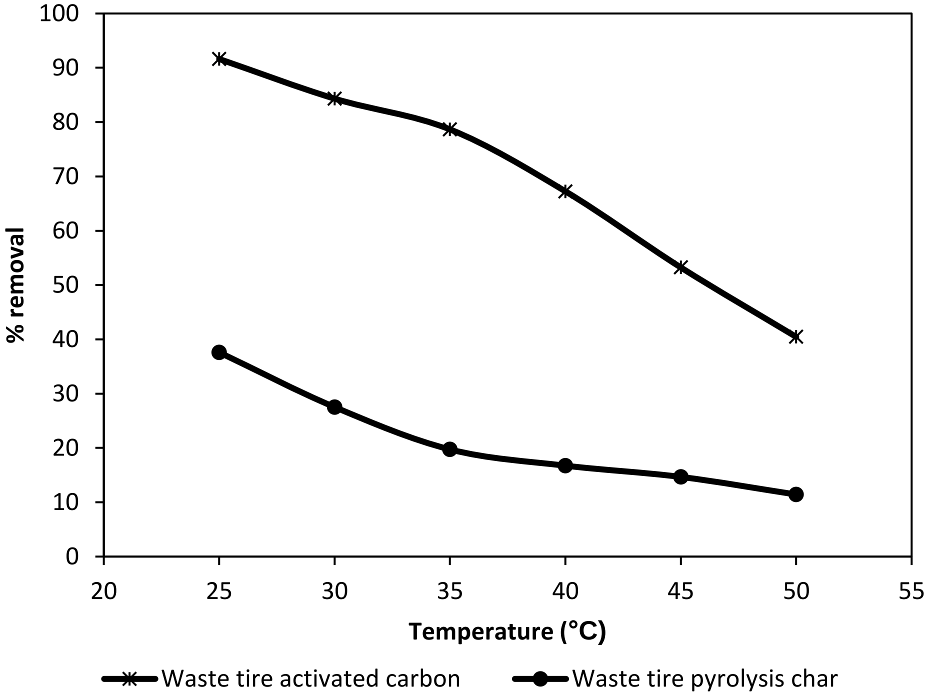

Figure 9: Effect of temperature on the % removal of lead ions from aqueous solution (pH = 6, adsorbent dosage = 0.2g/100ml, initial metal concentration = 100mg/l).

3.3.2 Adsorption isotherms

Adsorption isotherms are very important in adsorption studies because they provide the necessary information relating the relationship between the amount of metal ions adsorbed onto the adsorbent at equilibrium and the concentration of the metal ions in solution at equilibrium at a given temperature (Patnukao et al., 2008b). They are also important in determining the adsorption capacity of the adsorbent. In this study three adsorption isotherm models were used to describe the experimental data more accurately and they include included the Langmuir, Freundlich, and Dubinin-Redushkevich isotherm models.

The Langmuir isotherm model assumes monolayer coverage of the adsorbent onto the surface of the adsorbent and that adsorption only takes place at certain specific homogeneous sites on the surface of the adsorbent(Sari et al., 2007b). The Langmuir isotherm model can be represented by:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right)\frac{1}{C_e} \tag{17}$$

Where q_e and C_e are the concentration of the lead ions adsorbed at equilibrium (mg/g) and the concentration of the lead ions left in solution after equilibrium has been reached (mg/l). q_m is the maximum monolayer adsorption capacity (mg/g) and K_L is the Langmuir isotherm constant related to the free energy of the adsorption process (L/mg). For Langmuir isotherm model, it is important to determine a dimensionless equilibrium parameter known as the separation factor (R_L) which determines whether Langmuir isotherm model is favourable or not for the adsorption of lead ions onto waste tire activated carbon and waste tire char. R_L is given by Equation 18.

$$R_L = \frac{1}{1 + K_L q_m} \tag{18}$$

A value of $R_L > 1$ implies that the model is unfavourable, $0 < R < 1$ the model is favourable, $R = 1$ the model is linear, and $R = 0$ the model is irreversible (Tan et al., 2007; Foo and Hameed, 2010)

The Freundlich isotherm model is an empirical isotherm model used to describe adsorption processes in which adsorption takes place on the heterogeneous surface of the adsorbent and adsorption is not limited to monolayer coverage of the adsorbate on the surface of the adsorbent (Dada et al., 2012b). The Freundlich isotherm model can be represented by Equation 19.

$$\ln q_e = lnK_f + \frac{1}{n} lnC_e \quad (19)$$

Where q_e and C_e are the concentrations of the lead ions adsorbed at equilibrium (mg/g) and the concentration of the lead ions left in solution at equilibrium (mg/l). K_f is the Freundlich isotherm constant related adsorption capacity and 1/n is an empirical parameter related to the intensity of the adsorption process. A value of 1/n less than 1 implies that the adsorption process is favourable and a value of 1/n greater than 1 implies that the adsorption process is not favourable.

The Dubinin-Redushkevich isotherm model assumes that the characteristic of an adsorption curve is related to the porous structure of the adsorbent. This type of isotherm model is usually used to determine whether the adsorption process is chemical or physical in nature. Equation 20 is used to describe the Dubinin-Redushkevich isotherm model:

$$Inq_e = Inq_m - B\varepsilon^2 \quad (20)$$

Where q_e is the amount of lead ions adsorbed onto the surface of the waste tire activated carbon (mol/L), q_m is the monolayer adsorption capacity (mol/g), B is the activity coefficient which is related to the mean adsorption energy (mol^2/J^2), Ɛ is the Polanyi potential, and lastly E is the mean energy of the adsorption process (kJ/mol). Equations 21 and 22 are used to calculate the Polanyi potential and the mean energy of the adsorption process respectively.

$$\varepsilon = RTIn\left(1 + \frac{1}{1/C_e}\right) \quad (21)$$

$$E = \frac{1}{\sqrt{-2\beta}} \quad (22)$$

Table 9: Langmuir, Freundlich, and Dubinin-Redushkevich isotherm constants for the adsorption of lead ions onto waste tire activated carbon.

	Adsorption Isotherm models									
	Langmuir				Freundlich			D-R model		
	q_m (mg/g)	K_L (L/mg)	R^2	R_L	K_F	1/n	R^2	q_s(mol/g)	E(kJ/mol)	R^2
Waste tire char	25.71	0.126	0.7123	0.073	8.051	0.2675	0.7634	21,83	78.57	0.7395
Waste tire activated carbon	65.36	0.066	0.7137	0.13	10.048	0.4243	0.8163	48.73	55	0.7135

The equilibrium data was fitted into the different adsorption isotherm models to determine which model had the best fit. Figure 10, Figure 11 and Figure 12 show the Langmuir, Freundlch, and Dubinin-Redushkevich isotherm plots for the adsorption of lead ions onto both the waste tire pyrolysis char and waste tire activated carbon respectively. Table 9 shows the isotherm constants obtained for the three adsorption models and from the Table Freundlich isotherm model showed best fit for the experimental data achieving correlation coefficients 0.8163 and 0.7634 for the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char respectively. This implies that the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char is not restricted to monolayer coverage of the adsorbent onto the surface of the adsorbate and that the interaction between the adsorbents and the lead ions allows for the formation of multilayers. The values of K_f and 1/n were calculated from the slope and intercept of figure 8. The values of 1/n were found to be 0.4243 and 0.2675 for the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char respectively and this indicates that the adsorption process was favourable under the studied conditions (Tan et al., 2007). The correlation coefficients achieved for Langmuir isotherm model were 0.7137 and 0.7123 for the waste tire activated carbon and waste tire pyrolysis char respectively and both these values were lower than those achieved under the Freundlich isotherm model. The maximum Langmuir adsorption capacity (q_m) and energy of adsorption (K_L) were calculated from Figure 10 as 65.36 mg/g and 25.71 mg/g and 0.066 L/mg and 0.126 L/mg for the waste tire activated carbon and waste tire pyrolysis char respectively. The increase in the monolayer maximum Langmuir adsorption capacity from 25.71 mg/g (waste tire pyrolysis char) to 65.36 mg/g (waste tire activated carbon) shows that the activation process plays a significant role in improving the adsorptive properties of the waste tire char which results in increased adsorption capacity. The Langmuir separation factor was calculated to be 0.13 and 0.073 for the waste tire activated carbon and the waste tire pyrolysis char respectively and this shows that the model was favourable for the adsorption of lead ions onto waste tire char and activated carbon. The experimental data was also fitted to the Dubinin-Redushkevich isotherm model. The correlation coefficient obtained for the Dubinin-Redushkevich isotherm model was 0.7135 and 0.7395 for the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char respectively. The Dubinin-Redushkevich isotherm model is important in determining the adsorption mechanism by distinguishing whether the process follows chemical or physical adsorption through the determination of the mean free energy E (kJ/mol). The D-R isotherm model constants are tabulated in *Table 9*. The values of q_s were calculated to be 48.73 mol/g and 21.83 mol/g from Figure 12 respectively for the waste tire activated carbon and char. The values of the mean free energy of adsorption were calculated to be 55kJ/mol and 78.57 kJ/mol for the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char respectively and this suggests that the adsorption process taking place is physical adsorption since the mean energies of adsorption is in the range 16 kJ/mo l<E< 80 kJ/mol (Ho et al., 2002b).

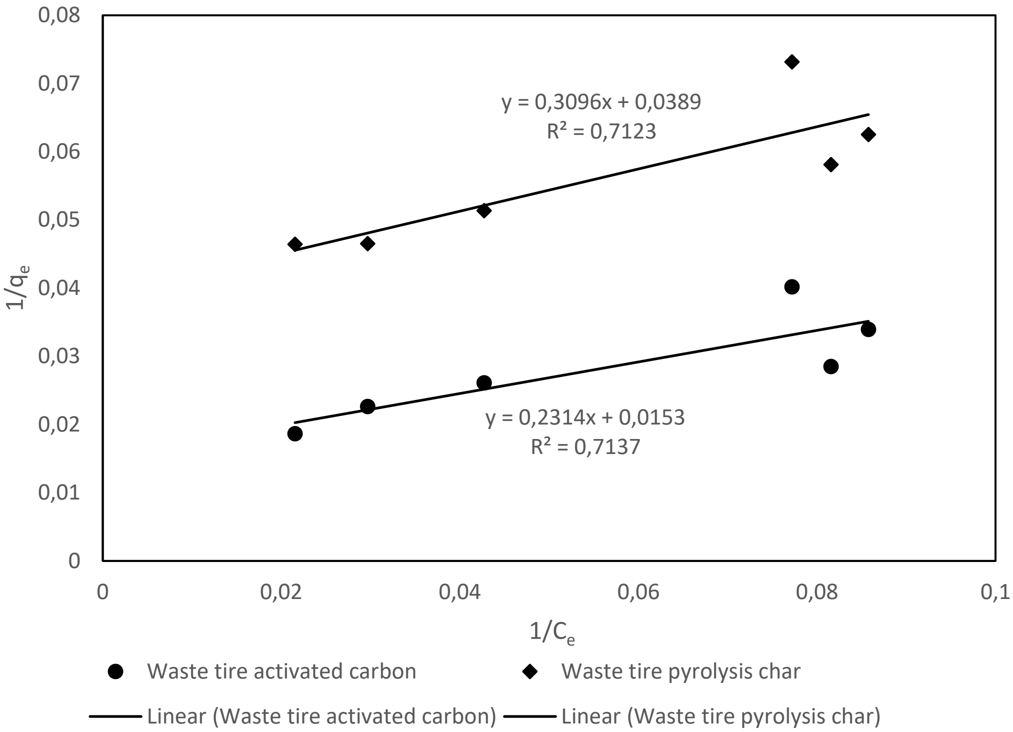

Figure 10: Langmuir adsorption isotherm plot for the adsorption of lead ions onto waste tire activated carbon.

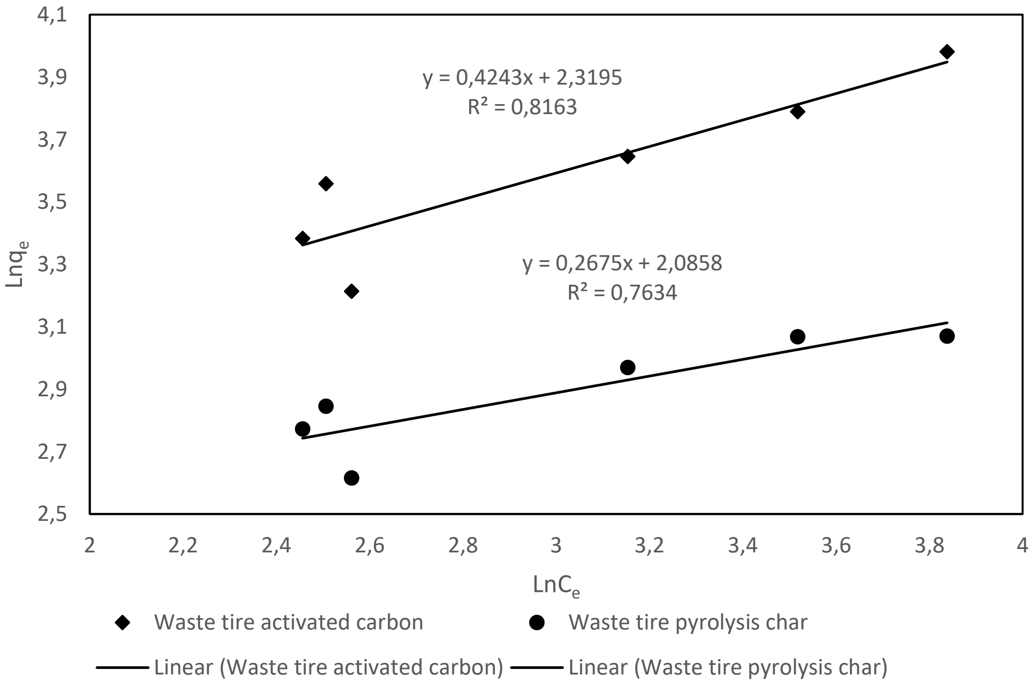

Figure 11: Freundlich adsorption isotherm plot for the adsorption of lead ions onto waste tire activated carbon.

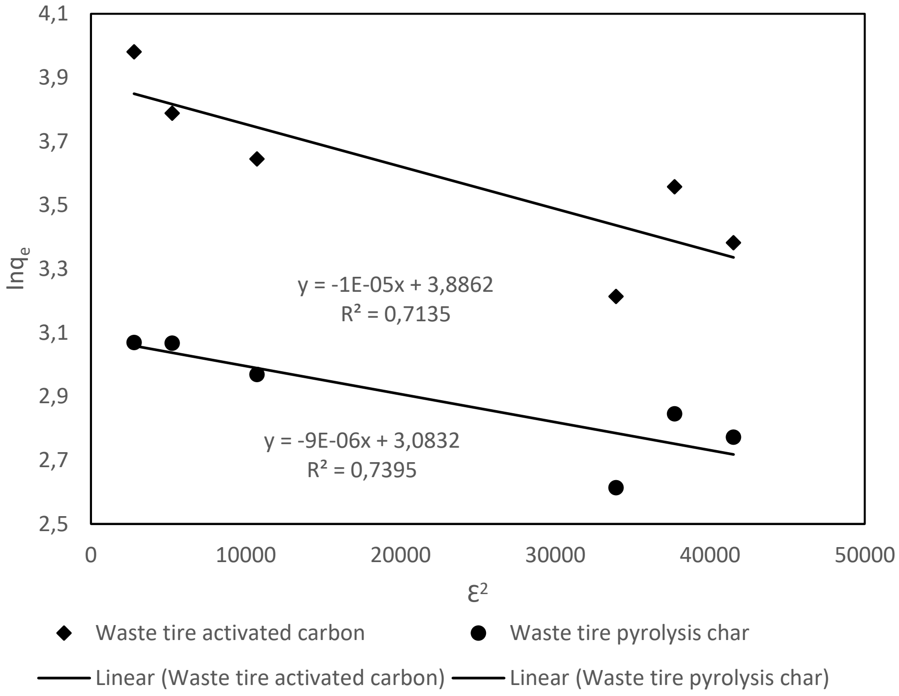

Figure 12: Dubinin-Radushkevich isotherm plot for the adsorption of lead ions onto waste tire activated carbon.

3.3.3 Adsorption kinetics

Table 10: Adsorption kinetics constant for the adsorption of lead ions onto waste tire activated carbon.

	Adsorption kinetics						
	Pseudo-first order kinetic		Pseudo-second order		Intraparticle diffusion		
	K_1 (min^{-1})	R^2	K_2 (g/mg.min)	R^2	K_i (mg/g.min$^{1/2}$)	C	R^2

Waste tire activated carbon	0.0353	0.9935	3.35E-4	0.9655	4.7705	0.7127	0.9447
Waste tire pyrolysis char	0.0544	0.9968	0.003	0.9934	1.6227	5.1511	0.7978

Adsorption kinetics were applied in this study because they play a very critical role in determining the rate controlling step for the adsorption process which is very vital to understand for the design of an adsorption process (Yuh-Shan, 2004). Adsorption kinetics are important in the determination of the residence time required for the completion of the adsorption process (Qiu et al., 2009b). The adsorption kinetics models which were applied on this study include the Lagergren’s pseudo-first order, Ho’s pseudo-second order, and intraparticle diffusion kinetic models.

Lagergren’s pseudo-first order kinetic model (Figure 13) is considered as one of the earliest kinetic models used to describe the adsorption of solids in solid-liquid systems (Yuh-Shan, 2004). The pseudo-first order kinetic model is expressed by Equation 23.

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{23}$$

Where q_e and q_t are the concentrations of the metal ions adsorbed at equilibrium and time t (mg/g) respectively. K_1 is the pseudo-first order rate constant of the reaction (min^{-1}). Table 10 shows the pseudo-first order kinetic model constants for the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char. The plots in Figure 13 was used to determine the values of k_1. From Table 10 it is visible that pseudo-first order kinetic model obtained the highest correlation coefficients for the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char as $R^2 = 0.9935$ and $R^2 = 0.9968$ respectively which suggests that the adsorption of lead ions onto waste tire activated carbon is best described by the pseudo-first order kinetic model. The rate constants obtained were 0.0353 min^{-1} and 0.0544 min^{-1} for the waste tire activated carbon and waste tire pyrolysis char respectively.

Ho’s pseudo-second order kinetic model Figure 14) suggests that the rate limiting step is controlled by chemical adsorption which involves violent forces comprised of the sharing of electrons or the exchange of electrons between the adsorbent and the adsorbate (Yuh-Shan, 2004). The model also follows the Langmuir adsorption isotherm model concerning the monolayer coverage of the adsorbate onto the surface of the adsorbent (Qiu et al., 2009b; Ünlü and Ersoz, 2006). Ho's pseudo-second order kinetic model is described by Equation 24.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{24}$$

Where q_t and q_e are the concentration of the lead ions adsorbed after time t (min) and at equilibrium respectively and k_2 is the pseudo-second order reaction rate constant. The value of k_2 was calculated from the plot of t/q_t as 3.35E-4 (g/mg.min) and 0.003 (g/mg.min) for the adsorption of lead ions onto waste tire activated carbon and char respectively. The correlation coefficients obtained for the pseudo-second order kinetic model were lower than those obtained under pseudo-first order kinetic model which suggests that the process is not controlled by chemical adsorption. These findings are in excellent agreement with the results obtained from the D-R isotherm model.

Intraparticle diffusion kinetic model which was proposed by Weber and Morris has been widely applied to study the rate limiting step in the adsorption of heavy metals as shown in Figure 15. Equation 25 is used to describe the intraparticle diffusion kinetic model.

$$q_t = k_i t^{1/2} + C \tag{25}$$

Where q_t (mg/g) is the concentration of lead ions adsorbed after time t (min) has been reached, k_i is the intraparticle diffusion rate constant and C is the intercept. A plot of q_t vs $t^{1/2}$ must be a straight line passing through the origin with k_i being the slope of the plot for intraparticle diffusion to be the sole rate limiting step. It is not always the case that a plot of q_t vs $t^{1/2}$ passes through the origin and this suggests that intraparticle diffusion is not the sole rate limiting step but the adsorption kinetics may be controlled by film diffusion in the initial stage of the reaction followed by intraparticle diffusion later during the reaction. The correlation coefficients obtained for intraparticle diffusion kinetic model were 0.9447 for the adsorption of lead ions onto waste tire activated carbon and 0.7978 for the adsorption of lead ions onto waste tire pyrolysis char which were lower than both the pseudo-first order and second order kinetic models. Since the plot of q_t vs $t^{1/2}$ does not pass through the origin, this implies that intraparticle diffusion is not the sole rate limiting step but it might be accompanied by film diffusion (Bulut and Aydın, 2006).

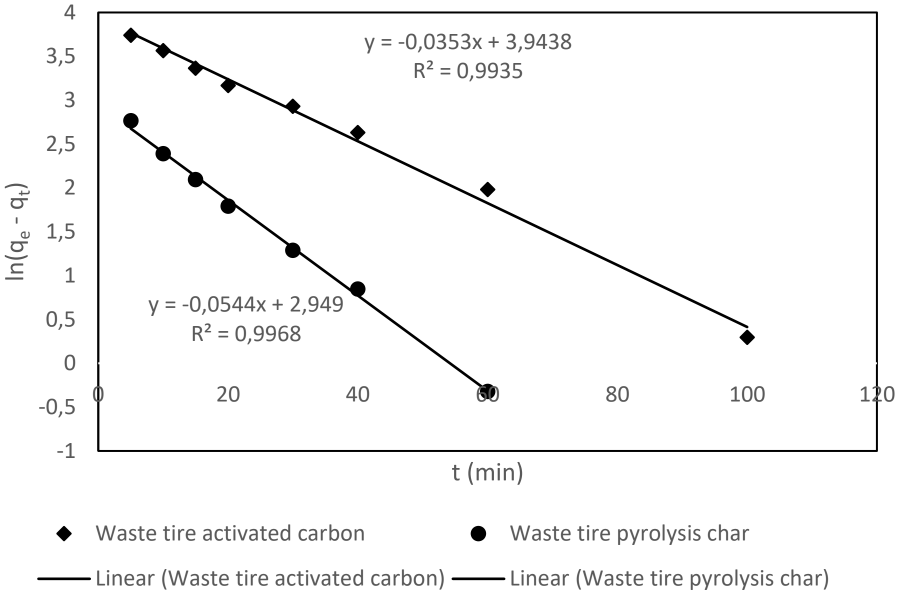

Figure 13: Lagergren's pseudo-first order kinetic model plot for the adsorption of lead ions onto waste tire activated carbon.

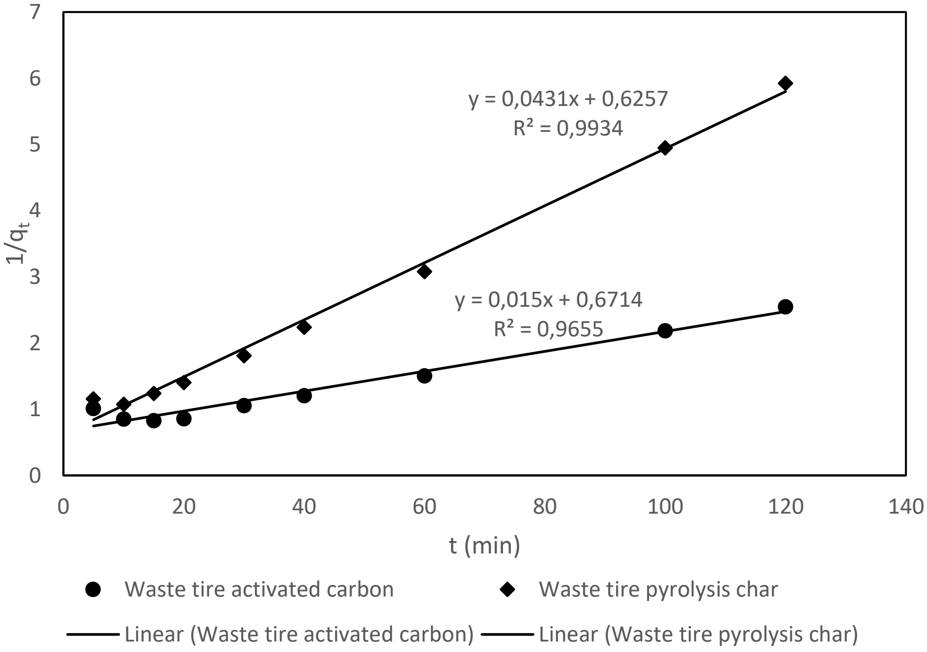

Figure 14: Ho’s pseudo-second order kinetic model plot for the adsorption of lead ions onto waste tire activated carbon.

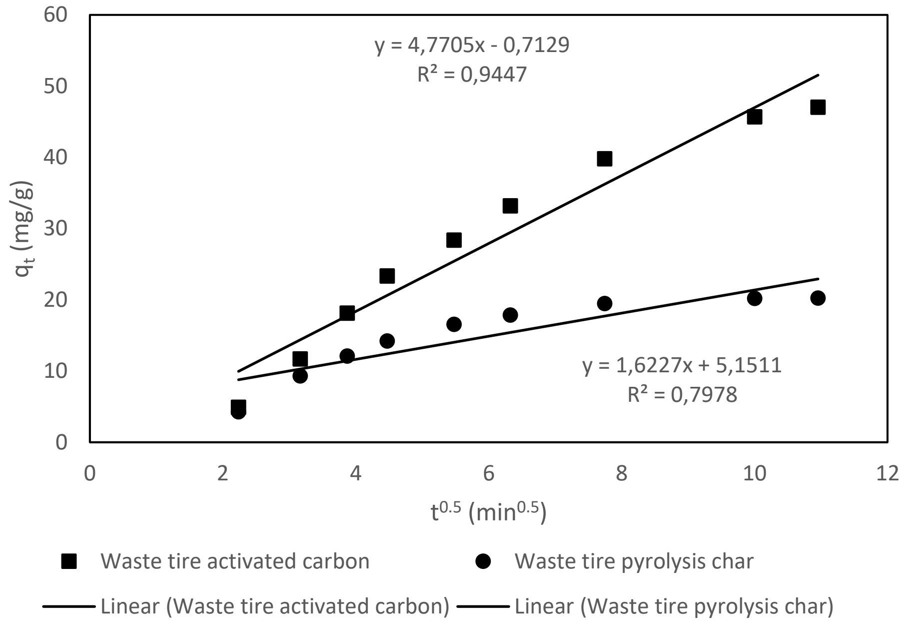

Figure 15: Weber and Morris intraparticle diffusion kinetic model for the adsorption of lead ions onto waste tire activated carbon and char.

3.3.4 Adsorption thermodynamics

Table 11:Thermodynamic parameters for the adsorption of lead ions onto waste tire activated carbon.

Adsorption thermodynamics parameters			
Temperature (K)	ΔG° (kJ/mol.K)	ΔH° (kJ/mol.K)	ΔS° (kJ/mol.K)
298	-2.606	-52.419	0.167
308	-0.875		
318	0.546		
328	2.5		

Table 12: Thermodynamic parameters for the adsorption of lead ions onto waste tire pyrolysis char.

Adsorption thermodynamics parameters			
Temperature (K)	ΔG° (kJ/mol.K)	ΔH° (kJ/mol.K)	ΔS° (kJ/mol.K)
298	2.971	-40.77	0.148
308	5.368		
318	6.487		
328	7.473		

Adsorption thermodynamics were evaluated in this study to determine whether the adsorption of lead ions onto waste tire activated carbon and waste tire pyrolysis char is a spontaneous process in nature or not. Thermodynamic parameters such as the enthalpy change (ΔH°), Gibbs free energy change (ΔG°), and entropy change (ΔS°) were determined. Equation 26, Equation 27 and Equation 28 were used to determine the values of these adsorption thermodynamics parameters.

$$\Delta G = -RTlnK_D \tag{26}$$

$$InK_D = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{27}$$

$$K_D = \frac{q_e}{C_e} \tag{28}$$

Where ΔG is the Gibbs free energy change (kJ/mol), R is the universal gas constant (8.314 J/mol.k), T is the absolute temperature of the solution (K), K_D is the distribution coefficient or equilibrium constant which is dependent on temperature, ΔH° is enthalpy change (kJ/mol.K), ΔS° in entropy of the process (kJ/mol.K). The plot of InK_D vs 1/T was used to obtain the values of the thermodynamic parameters ΔH° and ΔS°. The values of ΔH° and ΔS° were calculated to be -52.419 kJ/mol.K and -0.167 kJ/mol.K respectively for the adsorption of lead ions onto waste tire activated carbon as shown in Table 11. The negative value of ΔH° shows that the adsorption process is exothermic in nature (Saleh et al., 2017; Özcan et al., 2005). The negative value of ΔS° indicates that there is somewhat decreased randomness at the solid solution interface during the adsorption process (Sekar et al., 2004b; Saleh et al., 2017). The value of ΔG° was calculated by using equation (11) and it was found to be -2.606 kJ/mol.K at a temperature of 298 K. The increase in the value of ΔG° as the temperature increases further confirms the exothermic nature of the process (Özcan et al., 2005). From the adsorption of lead ions onto waste tire pyrolysis char, values of adsorption thermodynamic parameters ΔH°, ΔS°, and ΔG° at 298 K are tabulated in Table 12 and were calculated to be -40.77 kJ/mol.K, 0.148 kJ/mol.K and 2.971 kJ/mol.K respectively.

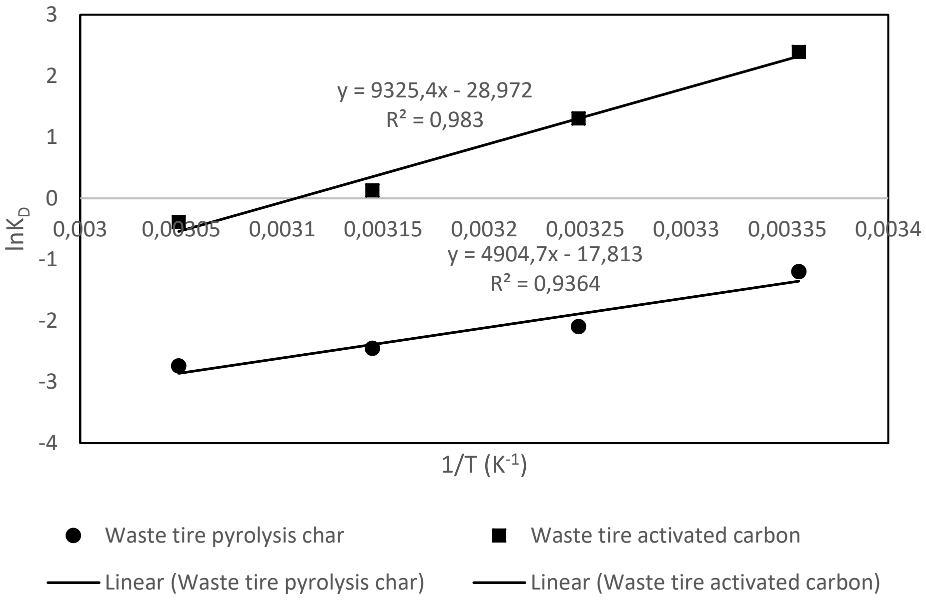

Figure 16: Plot of $\mathrm{InK_D}$ vs 1/T for the estimation of adsorption thermodynamic parameters for the adsorption of lead ions onto waste tire activated carbon.

CONCLUSION

Activated carbon was prepared by chemical activation with KOH from waste tire char. Adsorbent characterisation was performed to determine the characteristics of the activated carbon produced form the waste tire char. SEM micrographs show that chemically activating the waste tire char with KOH improved the surface morphology of the activated carbon by enhancing the pores present on the surface of the activated carbon. The proximate analysis performed on the activated carbon showed a decrease in the volatile and ash content of the activated carbon produced compared to the waste tire char. XRF analysis further confirmed that activating the waste tire char with KOH produces an activated carbon with decreased amounts of inorganic matter. The BET surface area of the waste tire char and the waste tire activated carbon were also obtained and a slight increase in the BET surface area was observed from 51 m^2/g to 71m^2/g and the micro pore volume from 0.004 cm^3/g to 0.007cm^3/g. XRD analysis was performed for the waste tire char and waste tire activated carbon prepared from different activation temperatures and the patterns show that the char was predominantly amorphous but activation at 500°C and 600°C produced activated carbon which is composed of a crystalline and amorphous structure. The adsorption parameters (adsorbent dosage, pH, contact time, initial metal concentration, and temperature) were studied to determine how they affect the removal of lead ions from aqueous solution and their optimum operating conditions were determined from the experimental data obtained. Adsorption isotherm models (Langmuir, Freundlich, Dubinin- Redushkevich) were studied and the equilibrium data was best fitted by the Freundlich isotherm model implying that the adsorption of lead ions is not restricted to monolayer coverage of the adsorbate onto the surface of the adsorbent but instead multilayer coverage of the lead ions onto the activated carbon is possible. Adsorption kinetics were evaluated to determine the rate limiting step for the adsorption of lead ions onto waste tire activated carbon and pseudo-first order kinetic model gave the best fit. Lastly adsorption thermodynamics were studied to determine the nature and spontaneity of the process. Thermodynamic parameters obtained for the adsorption of lead ions onto waste tire activated carbon showed that the process is exothermic in nature and spontaneous at lower temperatures. The thermodynamic parameters also showed that there is decreased randomness at the solid/liquid interface during the adsorption of lead ions onto waste tire activated carbon.

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Chapter 4

PREPARATION OF CHEMICALLY ACTIVATED CARBON FROM WASTE TIRE CHAR FOR LEAD IONS ADSORPTION AND OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY

Abstract

The use of tires in automobiles is very important in the automobile industry. However, there is a serious environmental problem concerning the disposal of these rubber tires once they become worn out. The main aim of this study was to prepare activated carbon from waste tire pyrolysis char by impregnating KOH on pyrolytic char. Adsorption studies on lead onto chemically activated carbon was carried out using response surface methodology. The effect of process parameters such as temperature (°C), adsorbent dosage (g/1000ml), pH, contact time (minutes) and initial lead concentration (mg/l) on the adsorption capacity were investigated. It was found that the adsorption capacity increases with an increase in contact time, pH, temperature and decreases with an increase in lead concentration. Optimization of the process variables was done using a numerical optimization method. Fourier Transform Infrared Spectra (FTIR) analysis, XRay diffraction (XRD), Thermogravimetric analysis (TGA) and scanning electron microscope was used to characterize the pyrolytic carbon char before and after activation. The optimum points 1g/ 100 ml for adsorbent dosage, 7 for pH value of the solution, 115.2 min for contact time, 100 mg/l for initial metal concentration, and 25°C for temperature were obtained to achieve the highest adsorption capacity of 93.176 mg/g with a desirability of 0.994. Fourier Transform Infrared Spectra (FTIR) analysis and Thermogravimetric analysis (TGA) show the presence of oxygen containing functional groups on the surface of the activated carbon produced and that the weight loss taking place during the activation step is small.

Keywords: *Waste tire pyrolysis char, Chemical activation, Central Composite design (CCD), adsorption capacity, numerical optimization*

4.1 INTRODUCTION

With the continued increase in the utilization of auto mobiles, the generation of waste tires continues to increase rapidly every year throughout the world. The disposal of waste tyre poses a huge environmental havoc. It has been reported that around 10 million tires are generated as waste tires in South Africa every year and more than 5 million tons of waste tires are generated worldwide every year (Pilusa et al., 2014; Troca-Torrado et al., 2011; Ariyadejwanich et al., 2003).

Previously methods such as land filling, stock-pilling, and open dumping of waste tires have been used for the disposal of waste tires however some drawbacks have been reported regarding such methods. The disposal of waste tires through land fill sites causes environmental pollution since the waste tires are not biodegradable and they occupy huge spaces of landfill sites (Mui et al., 2004). Stock-pilling and open dumping the waste tires is said to be undesirable since waste tires pose fire hazards and can be a breeding ground for mosquitoes and vermin which can lead to health threats to humans (Betancur et al., 2009; Ko et al., 2004).

Recent research has focused on the utilization of waste tires through thermal processes such as direct combustion, gasification, and pyrolysis for not only the disposal of waste tires but also for the recovery of value added products from waste tires and energy recovery (Antoniou et al., 2014; Bae et al., 2014; Choi et al., 2014; Fernández et al., 2012; Karatas et al., 2012; Molino et al., 2013; Murillo et al., 2006). These thermal treatment processes are also said to have the advantage of reducing the volume of the waste tires by 90 % of its original volume after the thermal process which reduces the volume of waste tire that could have been disposed to landfill (Sharma et al., 1998).

Out of all these thermal processes, pyrolysis of waste tires has received great attention and continues to do so due to its environmentally friendly nature compared to thermal processes such as direct combustion and because of continued improvement in the pyrolysis technology process over the years (Sienkiewicz et al., 2012). In pyrolysis, the waste tires are subjected to thermal treatment inside a furnace at elevated temperatures under inert conditions. The products obtained from the pyrolysis of waste tires include pyrolytic oil, pyrolytic char, and pyrolysis gas which can all be upgraded into valuable products. The char obtained from the pyrolysis of waste tires is said to have a high carbon content and thus can be used as carbon black or it can serve as a raw material to produce activated carbon (San Miguel et al., 2003). Activated carbon from pyrolytic tire char can be obtained through an activation process. The activation process is necessary to ensure that the activated carbon produced contains improved adsorption characteristics for its application in adsorption processes.

There are two types of activation processes which can be applied in the preparation of activated carbon and these includes physical and chemical activation. Physical activation involves the use of oxidizing agents such as steam or CO_2 (Antoniou et al., 2014; Troca-Torrado et al., 2011). Chemical activation involves the impregnation of the carbon char with chemical agents such as KOH, ZnCl, H_3PO_4, HNO_3 and NaOH followed by carbonization to give a final product of activated carbon (Al-Rahbi and Williams, 2016).

Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques used for the improvement, optimization, and development of a process. (Montgomery, 2001). The main aim of RSM is to be able to determine the optimum operating conditions for a process. The method used to design experiments (RSM), is used as a tool to improve the efficiency of a process by optimizing an output variable which is influenced by several independent variables (Tan et al., 2008b). The input variables are varied during experimental test runs to evaluate how they affect the output variables and thus enables the possibility to identify the optimum operation conditions for the input variables (Garg et al., 2008).

In Response Surface Methodology, there are two types of design of experiments which are commonly used namely central composite designs and Box Behnken designs (Thajeel, 2013; Allen, 2006). Central composite design is commonly used to model a response variable with curvature by adding both center and axial points to a previously done factorial design. In this study, central composite design was used to determine the effect of 5 process parameters on the adsorption capacity of waste tire derived activated carbon for the adsorption of lead ions from aqueous solution and to also optimize the adsorption capacity of the lead ions onto activated carbon.

In this study activated carbon prepared from waste tire pyrolysis char was chemically impregnated with KOH to improve the adsorption characteristics of the activated carbon produced. The activated carbon produced was used as an adsorbent for the adsorption of lead ions from aqueous solution. Fourier Transform Infrared Spectra (FTIR) analysis, XRay diffraction (XRD), Thermogravimetric analysis (TGA) and scanning electron microscope (SEM) was used to characterize the pyrolytic carbon char before and after activation.

4.2 MATERIALS AND METHODS

4.2.1 Adsorbent preparation

Waste tire pyrolysis char was obtained from a local supplier. The char was obtained in powder form. Firstly, 150g of the char was washed with warm distilled water in order to remove impurities and then dried in a drying oven at 100℃ overnight to remove moisture. After drying, the sample was sieved to a particle size less than 100µm. 100g of the sample was then impregnated with an aqueous mixture of KOH at an impregnation ratio (weight of KOH: weight of char) of 2:1 inside a 500ml beaker and stirred for 24 hours at 80℃ to aid the impregnation process. After mixing, the slurry mixture of the char and KOH was dried inside a drying oven for 24 hours. The dried chemically impregnated was activated using a furnace under atmosphere nitrogen to ensure inert conditions for the activation process at 600℃ for 60 minutes. After the activation, the sample were washed with 1 M solution of HCl to remove the ash and sulphur content formed during the activation process. After washing with HCl, the activated carbon was rinsed with distilled water until the pH value reached pH 7 and then dried inside a drying oven at 100℃ for 24 hours.

4.2.2 Characterization of the adsorbent

Thermogravimetric analysis on pyrolysis char and activated carbon were performed using a Pyris 1 Perkin Elmer TGA instrument. The thermogravimetric analysis was done from 25-950 °C at 10 °C/minute.

Fourier Transform Infrared Radiation (FTIR) analysis was done to determine the functional groups present on the surface of the samples before activation and after the activation process. A Perkin Elmer spectrum (400 FT-IR/FT-NIR) was used and the samples were scanned and recorded in the range of 650 – 4000 cm^{-1} wave numbers.

A Scanning Electron Microscope (SEM) was used to study the morphology of the waste tire pyrolysis char and the waste tire activated carbon. The analysis was done using a Phillips XL 30S SEM. The process was done by scattering the samples on an adhesive carbon plate and sputter coating the sample with a thin layer of gold before analysis with SEM.

X-RAY Diffraction analysis was done on the waste tire pyrolysis char and the waste tire activated carbon to determine the phase analysis on the two samples. Sample preparation for the waste tire char and waste tire activated carbon was done using the black loading preparation method. A PANalytical Empyrean diffractometer with a PIXecl detector and fixed slits with Fe filtered Co-Kα radiation was used for the analysis. The phases were determined by using X'Pert High score plus software and the relative phase amounts (weight %) were estimated using the Reitveld method.

4.2.3 Batch adsorption procedure

Adsorption experiments were done using a shaking incubator operating at constant shaking rate of 200 rpm. After adsorption process, the samples were quickly filtered using 125 µm filters and then the filtrate samples were diluted and analyzed for lead concentration using an atomic absorption spectrometer. The adsorption capacity of lead ions onto activated carbon adsorption was calculated using Equation 29.

$$q_e = \frac{(C_i - C_e)V}{W} \tag{29}$$

Where q_e is the equilibrium adsorption capacity of the activated carbon, C_i is the initial metal concentration before the adsorption process $(\mathrm{mg/l})$, C_e is the concentration of metal ions left in solution after equilibrium has been reached $(\mathrm{mg/l})$, V is the volume of the solution used for the adsorption process (l), and W is the dry weight of the activated carbon used for the adsorption process (g).

4.2.4 Central composite design experimental design for the optimization of parameters

For the adsorption of lead ions onto waste tire derived activated carbon, the response surface methodology used was central composite design for five independent variables (adsorbent dosage, initial metal concentration, pH, contact time, and temperature) with the response variable being the adsorption capacity of the lead ions onto waste tire activated carbon as shown in Table 13. The design consisted of α = 1 and five factors. The number of experiments which were obtained from the design were 50 batch adsorption experiments with 32 factorial points, 10 axial points, and 8 center points. A design expert 6.0.6 software was used. Equation 30 below is used to calculate the number of experiments required for the central composite design.

$$N = 2^n + 2n + nc \tag{30}$$

Where N is the number of experiments required for the design, n is the number of factors or independent variables, and nc is the replicate number of the center points in each experiment.

A mathematical model that relates the adsorption capacity to the process parameters through a third polynomial Equation 31 was used.

$$Y = \beta_O + \sum_{j=1}^{4} \beta_j X_j + \sum_{i,j=1}^{4} \beta_{ij} X_i X_j + \sum_{j=1}^{4} \beta_{jj} X_j^2 + \sum_{k,i,j=1}^{4} \beta_{kij} X_k X_i X_j + \sum_{j=1}^{4} \beta_{jjj} X_j^3 \tag{31}$$

Where Y is the predicted adsorption capacity (mg/g), where b_o , b_j, b_{ij} , b_{jj} , b_{kij} and b_{jjj} represents the offset term, linear effect, first order interaction effect, squared effect, second order interaction effect and cubic effect respectively .

Table 13: Experimental range and levels of variables chosen for this study.

Variable	Coding	Units	Levels		
			-1	0	1
Adsorbent dosage	x_1	g/100ml	0.1	0.55	1
pH	x_2		2	4.5	7
Contact time	x_3	min	30	75	120
Initial metal concentration	x_4	mg/l	100	300	500
Temperature	x_5	c	25	40	55

4.2.5 Model fitting and statistical analysis

The Design expert software of version 6.0.6 was used for regression analysis, the evaluation of the statistical significance and the fitting of model to a third order polynomial equation.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Characterization of the adsorbent

4.3.1.1 Thermogravimetric analysis (TGA) and Differential thermogravimetric analysis (DTGA) -

Thermogravimetric analysis was used to determine the thermal decomposition of waste tire pyrolytic char and the activated carbon derived from chemical activation.

Figure 17 shows the TGA and DTGA plots for the two samples. For both the raw char and chemically impregnated char it is visible that the weight loses are experienced in the temperature range of 50 – 900°C with regions of 50 – 100 ˚C, 150 – 201 ˚C, and again at 450 – 500 ˚C appearing to be the most prominent regions where considerable weight loses are experienced. Similarly, previous studies have reported that the thermal decomposition of waste tires takes place in the temperature range of 200 – 500°C (Choi et al., 2014; Mui et al., 2010b). The weight loss experienced at 50 – 100 ˚C and 150 – 201 ˚C can be attributed to the release of moisture from the samples. The weight loss experienced in the temperature range of 400 – 500℃ can be attributed to the loss of volatile matter from the samples resulting from the incomplete pyrolysis of the waste tires.

At temperature above 500°C the weight loss experienced by the samples is low and takes place at a lower rate. It can be clearly seen that there is a difference in weight loss in the two samples. There is more weight loss experienced in the chemically treated char and this is because the KOH used in the impregnation of the char acts as a dehydrating agent which enables more volatile matter present in the char to be driven out and thus more pores are developed at the surface which can improve the adsorption process. Potassium hydroxide interacts with the carbons and catalyses' the dehydrogenation reaction producing a porous carbon. The mechanism at which the pore develop on the surface of activated char can be shown by the following redox reactions (Al-Rahbi and Williams, 2016).

$$6KOH + 2C \rightarrow 2K + 2K_2CO_3 + 3H_2 \qquad (32)$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \qquad (33)$$

$$K_2O + H_2 \rightarrow 2K + H_2O \qquad (34)$$

$$K_2O + C \rightarrow 2K + CO \qquad (35)$$

During the activation, potassium hydroxide decomposes to potassium oxide as shown in Equations 32 and 33 and the potassium oxide is reduced to form potassium as shown in Equation 33, 34 and 35. The intercalation of potassium open the carbon pores making them porous.

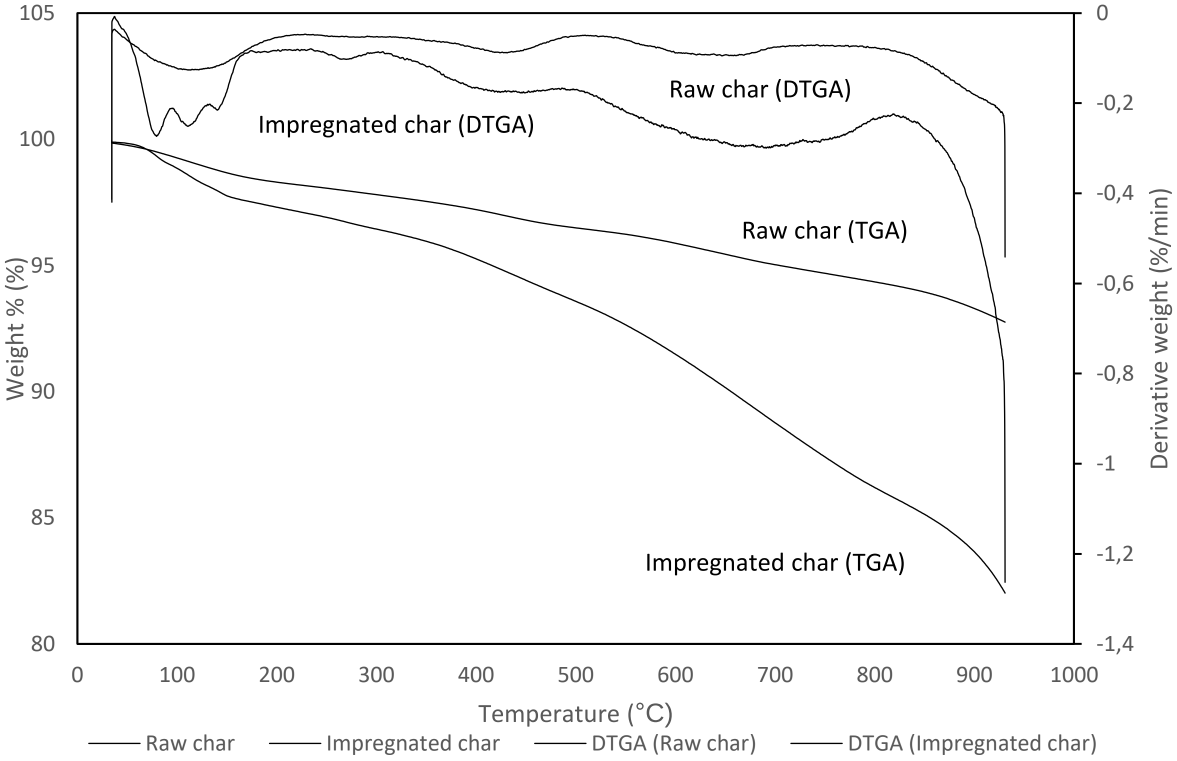


Figure 17: TGA and DTGA plots for the waste tire pyrolysis char and chemically impregnated waste tire pyrolysis char.

4.3.1.2 Fourier Transform Infrared Spectra(FTIR)

The presence of oxygen containing functional groups has been reported to enhance the adsorption capacity of the adsorbent for heavy metals adsorption (Salehin et al., 2016; Park et al., 2016; Pradhan and Sandle, 1999). Figure 18 shows the FTIR spectra obtained from analyzing raw waste tire pyrolysis char and activated carbon produced by chemical activation by impregnation of KOH onto pyrolytic waste tire char. As shown in the Figure 18, the raw waste tire pyrolysis char, the functional groups present include the presence of bands at 960, 1550, 1816, 2112, 1996, 2354, 2677, 3419, and 3798 cm^{-1} wavenumbers. The band at 960 cm^{-1} can be attributed to the $=C-H$ bend in the alkenes group. The band at 1550 cm^{-1} can be attributed to the $N-O$ asymmetric stretch in the nitro compounds. The band experienced at 2112 cm^{-1} can be attributed to the $-C\equiv C-$ stretch in the alkynes group. For activated carbon derived from pyrolytic char, the bands experienced include at 1000, 1348, 1740, 2110, and 2700 cm^{-1} wavenumbers. The band experienced at wavenumber 1000 cm^{-1} can be attributed to the strong $C-O$ stretch in the alcohols, carboxylic acids, esters, and ethers functional groups. The band experienced at 1348 cm^{-1} can be attributed to the $N-O$ symmetric stretch in the nitro compounds. The band experienced at 1740 cm^{-1} can be attributed to the strong $C=O$ stretch in the carbonyl and carboxylic acids groups. The band at 2110 cm^{-1} can be attributed to the $-C\equiv C-$ stretch in the alkynes group and lastly the band at 2700 cm^{-1} $H-C=O$ stretch in the aldehydes group and in the $O-H$ stretch in the carboxylic acids group (Seng-eiad and Jitkarnka, 2016). It has been reported that by chemically activating the waste tire char, prominent bands of oxygen containing functional groups were visible on the surface of the activated carbon produced which enhances the adsorption process (Gupta et al., 2012; Saleh and Gupta, 2014; Karmacharya et al., 2016; Aftab et al., 2016).

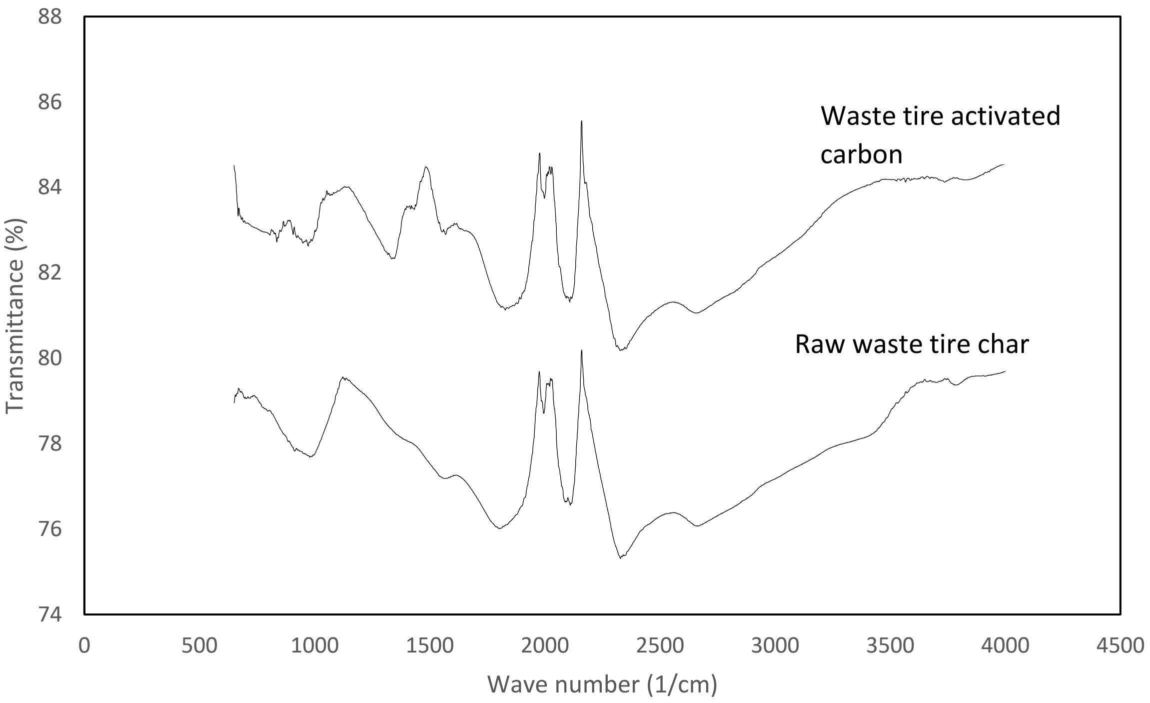
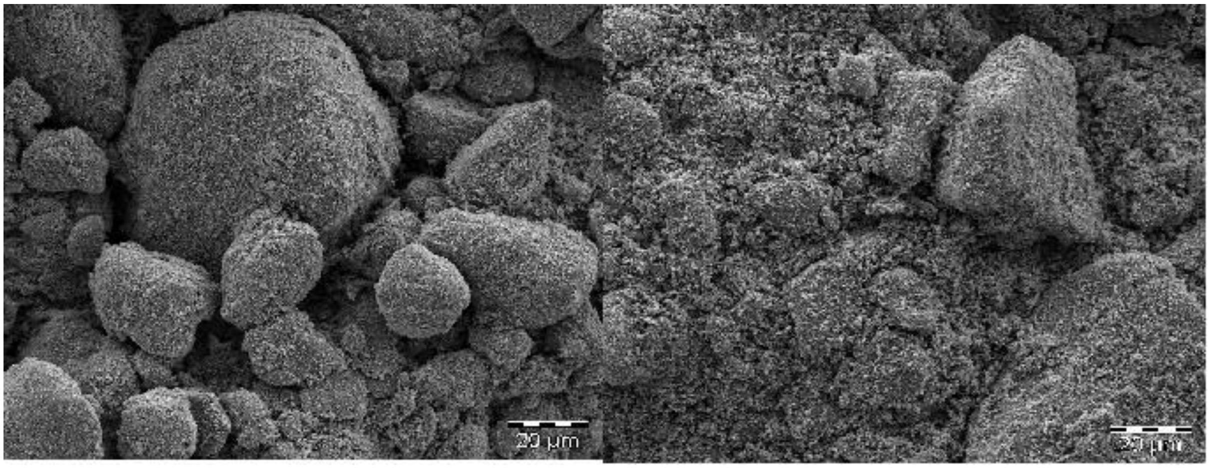


Figure 18: Fourier Transform Infrared Spectra of (a) chemically activated waste tire activated carbon and (b) raw waste tire pyrolysis char.

4.2.2.1 Scanning Electron Microscopy (SEM)

Scan Electron Microscope (SEM) images presented below in Figure 19 display the surface morphology of the waste tire pyrolysis char and waste tire activated carbon. The SEM image of the waste tire char shows that the morphology of the char consists of a surface which is dominated by large particles. On the other hand, the SEM image of the waste tire activated carbon shows that the morphology of the activated carbon consists of finer and porous particles on the surface of the waste tire activated carbon. This shows that chemical activation of the waste tire char produces waste tire activated carbon which has improved surface morphology.



(a) (b)

Figure 19: Scan electron micrographs of (a) waste tire pyrolysis char and (b) waste tire activated carbon

4.2.2.2 X- Ray Diffraction (XRD) patterns

X-Ray Diffraction analysis was performed on the waste tire pyrolysis char and waste tire activated carbon. Figure 20 below shows the XRD patterns of the waste tire char. The XRD patterns show that the char had smaller diffraction peaks which reveals its amorphous structure. The diffraction peaks of the waste tire activated carbon prepared at 600°C shows that the waste tire activated carbon consists of sharp peaks at $2θ= 36°$, 55°, and 67°. The sharp peak experienced at $2θ = 36°$ shows the presence of the Wurtzite and Sphalerite crystal phases. This reveals the crystalline nature of the activated carbon produced.

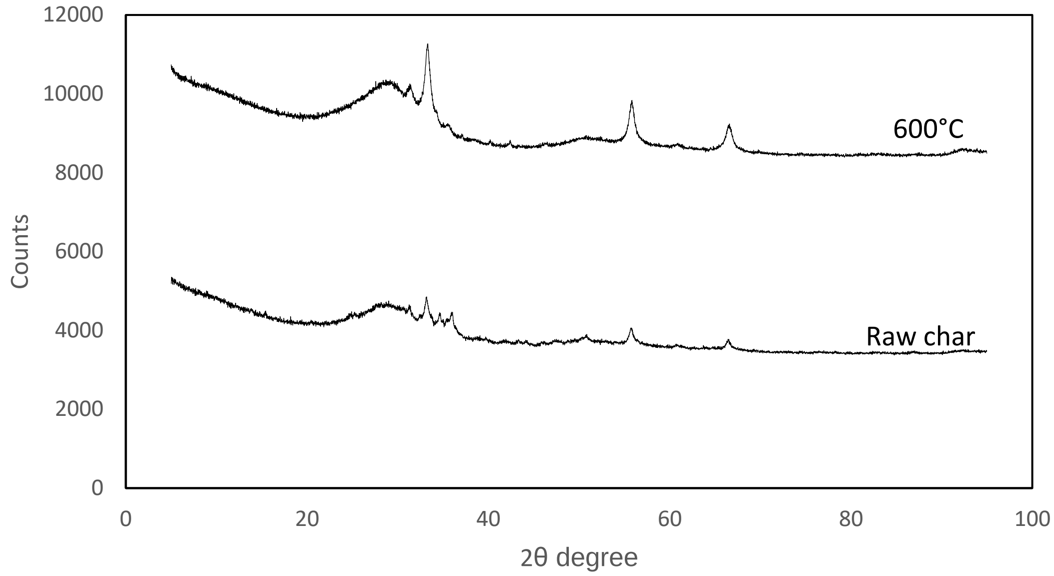


Figure 20: XRD patterns for waste tire pyrolysis char and waste tire activated carbon (600°C)

4.3.2 Development of regression model equation

Table 14 shows the experimental design matrix and the results obtained on the adsorption of lead ions onto waste tire derived from activated carbon.

Table 14: Experimental design matrix and results for the adsorption of lead ions onto waste tire derived activated carbon.

Run	Experimental variables					Response variable
	Adsorbent dosage x_1 (g/100ml)	pH x_2	Contact time x_3(min)	initial metal concentration x_4 (mg/l)	Temperature x_5 (℃)	Adsorption capacity y (mg/g)
1	0.1	2	30	100	25	45.8
2	1	2	30	100	25	33
3	0.1	7	30	100	25	60.7
4	1	7	30	100	25	78
5	0.1	2	120	100	25	50.7
6	1	2	120	100	25	57.4

7	0.1	7	120	100	25	70.6
8	1	7	120	100	25	94.1
9	0.1	2	30	500	25	6.8
10	1	2	30	500	25	3.2
11	0.1	7	30	500	25	11.3
12	1	7	30	500	25	20.3
13	0.1	2	120	500	25	7.8
14	1	2	120	500	25	8.3
15	0.1	7	120	500	25	7.9
16	1	7	120	500	25	40.1
17	0.1	2	30	100	55	40.4
18	1	2	30	100	55	46.8
19	0.1	7	30	100	55	56.8
20	1	7	30	100	55	50.7
21	0.1	2	120	100	55	50.3
22	1	2	120	100	55	58.6
23	0.1	7	120	100	55	56.9
24	1	7	120	100	55	77.8
25	0.1	2	30	500	55	4.5
26	1	2	30	500	55	5
27	0.1	7	30	500	55	10.9
28	1	7	30	500	55	9
29	0.1	2	120	500	55	5.8
30	1	2	120	500	55	4.2
31	0.1	7	120	500	55	6.5
32	1	7	120	500	55	11
33	0.1	4.5	75	300	40	12.1
34	1	4.5	75	300	40	38.7
35	0.55	2	75	300	40	19.3
36	0.55	7	75	300	40	30.8
37	0.55	4.5	30	300	40	15.6

38	0.55	4.5	120	300	40	35.5
39	0.55	4.5	75	100	40	60.3
40	0.55	4.5	75	500	40	15.8
41	0.55	4.5	75	300	25	36.4
42	0.55	4.5	75	300	55	20.1
43	0.55	4.5	75	300	40	25.7
44	0.55	4.5	75	300	40	30.1
45	0.55	4.5	75	300	40	24.7
46	0.55	4.5	75	300	40	32.8
47	0.55	4.5	75	300	40	26.4
48	0.55	4.5	75	300	40	24.7
49	0.55	4.5	75	300	40	20
50	0.55	4.5	75	300	40	24

Table 14 shows the experimental design matrix results obtained for the response which was the adsorption capacity. Central composite design was the type of response surface methodology used to determine the relationship between the dependent process parameters namely; adsorbent dosage, pH, contact time, initial metal concentration, and temperature and the adsorption capacity as an independent variable. From Table 14 the adsorption capacity obtained when varying these process variables ranges from 3.2 to 94.1 mg/g depending on the process conditions. This shows that the process parameters have significant effect on the adsorption capacity. Furthermore, the experimental results obtained from the experimental results were fitted with the second order polynomial equation is shown in Equation 36.

$$\begin{aligned} Y = {} & 26.49138 + 3.835294x_1 + 7.220588x_2 + 4.255882x_3 - 23.8382x_4 - 3.44412x_5 \\ & - 1.53276{x_1}^2 - 1.88276{x_3}^2 + 11.11724{x_4}^2 + 1.317241{x_5}^2 + 2.96875x_1x_2 \\ & + 2.69375x_1x_3 - 0.76875x_1x_4 - 1.30625x_1x_5 + 0.3x_2x_3 - 2.85x_2x_4 \\ & - 3.3125x_2x_5 - 2.6125x_3x_4 - 0.9625x_3x_5 + 0.1x_4x_5 \end{aligned} \tag{36}$$

The positive sign in front of the terms specifies a synergistic effect, while the negative sign indicates an antagonistic effect. The coefficient correlation (R^2) can be used to evaluate the quality of the model. The R^2 for Equation 33 is 0.9625. This suggests that 96.3 % of the total deviation in the adsorption capacity responses is clarified by the model.

Figure 21 shows a plot of the experimental against the predicted values of adsorption capacity plotted against a unit slope. The results indicate that the regression model was very accurate in predicting the experimental data.

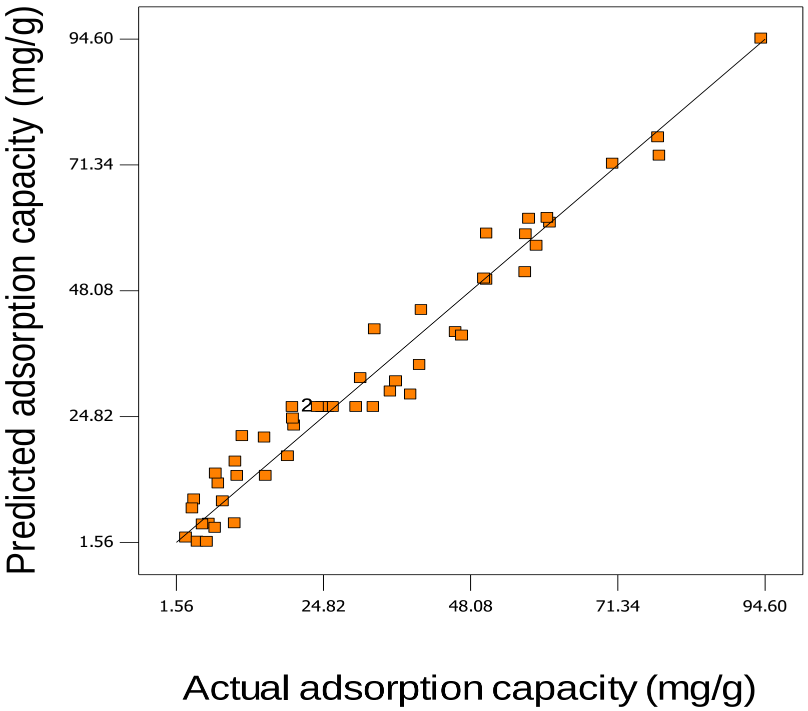


Figure 21: Predicted versus the experimental values of the adsorption capacity.

4.3.3 Model adequacy check

The analysis of variance (ANOVA) was used to verify the acceptability of the model in *Table 15*. The cubic model was verified at a 95 % confidence level and was found to be significant since the computed value (37.23) was higher than theoretical $F_{0.05\ (20,29)}$ (3.96). This shows that the regression model is accurate in predicting the adsorption capacity. From Table 15, it was observed that generally the initial metal concentration (x_4) had the most noticeable effect due to the large value of its sum squares; it was followed by the pH (x_2), contact time (x_3), adsorbent dosage (x_1)

and temperature (x_1) in respective order. All the process variable had a significant effect on the adsorption capacity based on a 95 % confidence level.

The quadratic terms x_4, had enormous influence on the adsorption capacity compared to the variables x_2, x_1, x_3 and x_5 variable has a minor influence on the adsorption capacity in respective order. The cubic terms do not affect the adsorption capacity. The interaction amongst the variable (x_1 x_2) has a significant impact on the adsorption capacity compared to the interaction term (x_1 x_2), (x_1 x_5), (x_1 x_4) and (x_2 x_3) which were non-significant based on 95% confidence level in descending order this can be seen from Table 15.

Table 15: Analysis of variance table for the adsorption capacity of waste tire derived activated carbon in the removal of lead ions from aqueous solution.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	24846.91	20	1242.346	37.23857	< 0.0001	significant
x_1	500.1224	1	500.1224	14.99087	0.0006	
x_2	1772.654	1	1772.654	53.13426	< 0.0001	
x_3	615.8262	1	615.8262	18.45902	0.0002	
x_4	19320.89	1	19320.89	579.1321	< 0.0001	
x_5	403.3062	1	403.3062	12.08886	0.0016	
x_1^2	5.810757	1	5.810757	0.174174	0.6795	
x_2^2	8.767473	1	8.767473	0.2628	0.6121	
x_3^2	4.729093	1	4.729093	0.141752	0.7093	
x_4^2	305.6886	1	305.6886	9.162832	0.0051	
x_5^2	4.291567	1	4.291567	0.128637	0.7224	
x_1x_2	282.0313	1	282.0313	8.453718	0.0069	
x_1x_3	232.2013	1	232.2013	6.960094	0.0133	
x_1x_4	18.91125	1	18.91125	0.566853	0.4576	
x_1x_5	54.60125	1	54.60125	1.63664	0.2109	
x_2x_3	2.88	1	2.88	0.086326	0.7710	
x_2x_4	259.92	1	259.92	7.790946	0.0092	

x_2x_5	351.125	1	351.125	10.52476	0.0030
x_3x_4	218.405	1	218.405	6.546559	0.0160
x_3x_5	29.645	1	29.645	0.888591	0.3536
x_4x_5	0.32	1	0.32	0.009592	0.9227
Residual	967.4922	29	33.3618		

4.3.4 Individual influence on process variables on the adsorption capacity

To illustrate how the individual process variables influenced the adsorption capacity a perturbation plot is given as Figure 22. The perturbation plot is like a one factor at a time experimentation where the influence of one factor on the adsorption capacity is studied while other process variables are kept constant. The plot shows the effects of all process variables at a particular point in the design space (Ramakrishna and Susmita, 2012). The initial metal concentration showed a greater influence on the adsorption capacity than any other process variable followed by the pH value of the solution, adsorbent dosage, contact time and temperature.

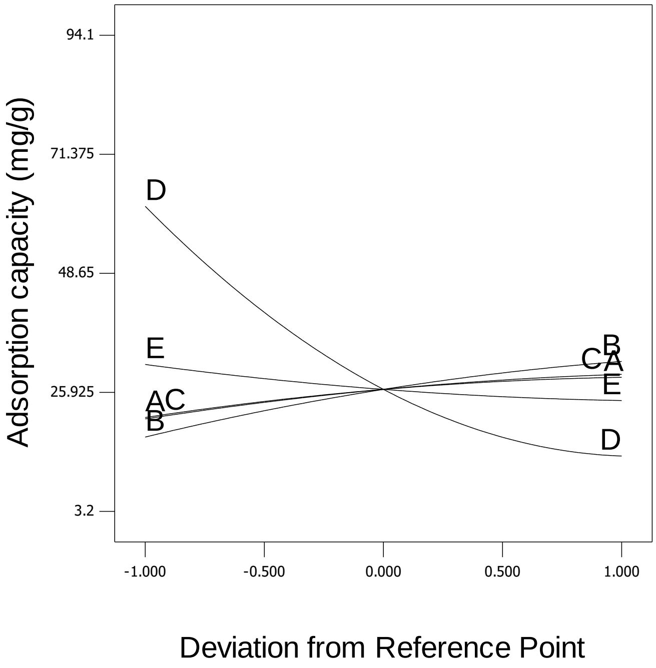


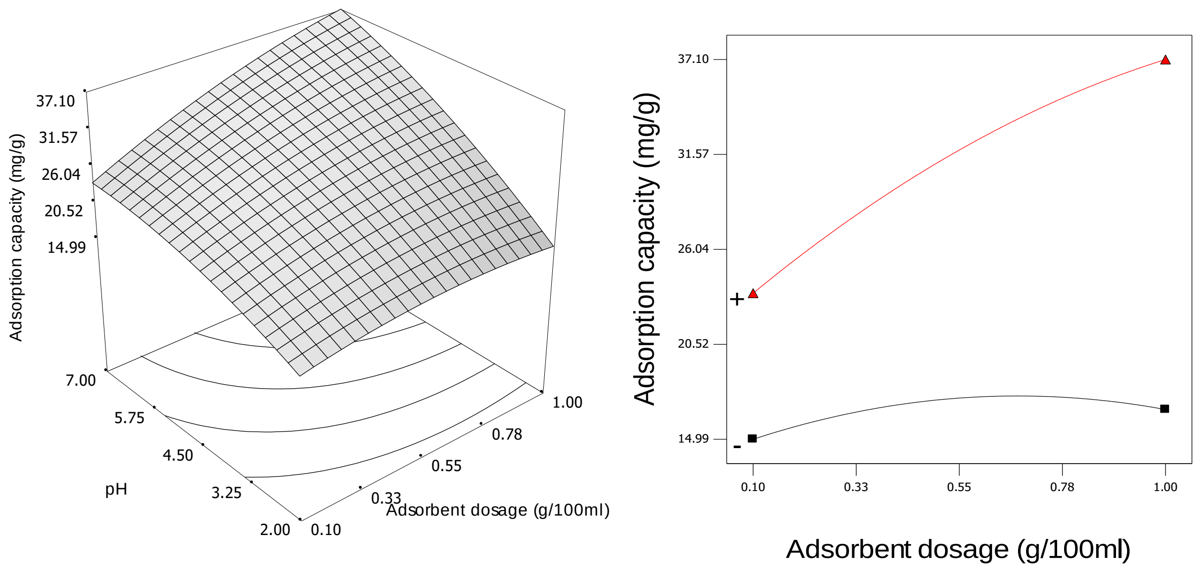
Figure 22: Perturbation plot showing how individual process variables (A – adsorbent dosage, B – pH value of the solution, C – contact time, D – Initial metal concentration, E – temperature) influence the adsorption capacity.

4.3.5 Effect of process variables on the adsorption of lead onto activated carbon derived from waste tire char

4.3.5.1 Effect of adsorbent dosage and pH on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 23 displays the variations in adsorption capacity with the changes in the adsorbent dosage (x_1) and pH (x_2). The contact time (x_3), initial metal concentration (x_4) and temperature (x_5) were kept constant at 75 minutes, 300ppm and 40°C respectively.

From Figure 23, it can be seen that as the pH of the solution increases there is an increase in the adsorption capacity of the activated carbon. This is because at low pH values the lead ions compete with hydrogen atoms for the adsorption sites on the surface of the activated carbon leading to low adsorption capacities. But however, as the pH value increases the presence of hydrogen atoms in solution decrease and provide less competition for lead ions on the adsorption sites of the activated carbon and this leads to increased adsorption capacities. (Saleh et al., 2013; Rao et al., 2016b). From the Figure 23, it is observed that pH value of 7 leads to high adsorption capacities for the activated carbon compared to at pH levels of 2. At high pH as the adsorption dosage is increased the adsorption capacity increases at a greater extend. At low pH of 2 as the adsorbent dosage is increased there is a slight increase in the adsorption capacity and adsorption capacity decreases at higher adsorbent dosage. This is due to completion of leads ions and hydrogen atoms for the adsorption sites on the surface at low pH (Rao et al., 2016b).



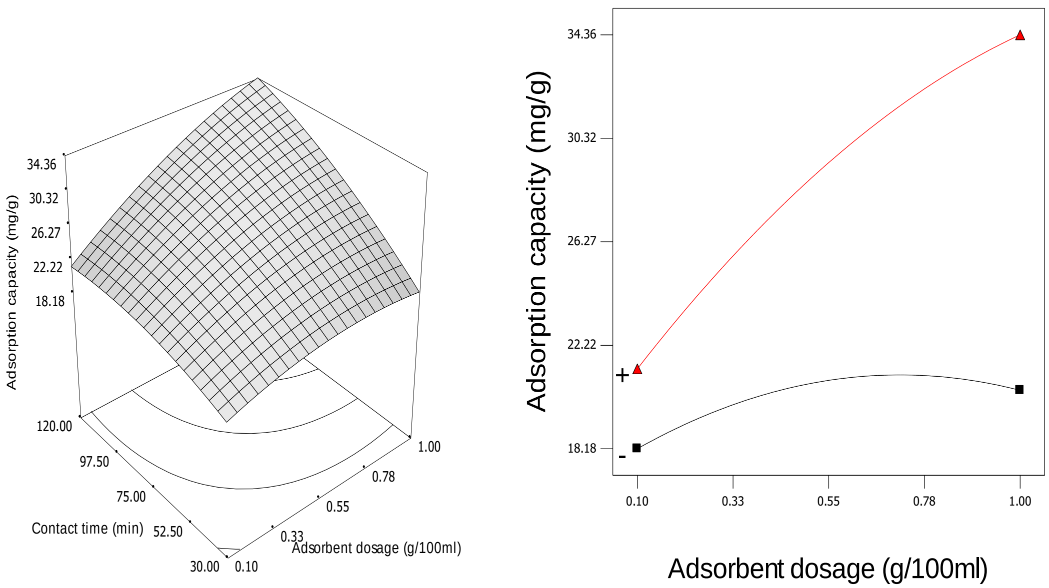
(a) (b)

Figure 23: The effect of pH and adsorbent dosage on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where pH is held at + 7 and – 2.

4.3.5.2 Effect of adsorbent dosage and contact time on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 24 depicts the variations in adsorption capacity with the changes in the adsorbent dosage (x_1) and contact (x_3). The pH (x_2), initial metal concentration (x_4) and temperature (x_5) were kept constant at 4.5, 300ppm and 40°C respectively.

Figure 24 shows the effect of contact time and adsorbent dosage on the adsorption capacity of waste tire derived activated carbon for the removal of lead ions. From the Figure 24 it is evident that an increase in both the adsorbent dosage and contact time results in the increase in the adsorption capacity of the waste tire derived activated carbon. The increase in the adsorption capacity with an increase in the adsorbent dosage is due to an increase in the adsorption sites available for the adsorption of lead ions as the adsorbent dosage is increased. Similarly, an increase in the adsorption capacity as the contact time is increased is due to the increased amount of time for the adsorbent to be in contact with the lead ions which results in adsorption and hence higher adsorption capacities at higher contact times. Similar results were reported by Rao et al, 2016 and Gupta et al., 2012, in their work they found out that the adsorption capacity of waste tire activated carbon was affected by the contact time. Gupta et al., 2012 reported that a contact time of 120 min yields the optimum adsorption capacity for waste tire activated carbon for lead ions. This is excellent agreement with results obtained from this work. At high contact time (120 min) as the adsorption dosage is increased the adsorption capacity increases at a greater extent. At lower contact time (30 min) as the adsorbent dosage is increased there is a slight increase in the adsorption capacity and adsorption capacity decreases at adsorbent dosage of 1.45g/l, this is because there is less time for the adsorbent to be in contact with the lead ions.



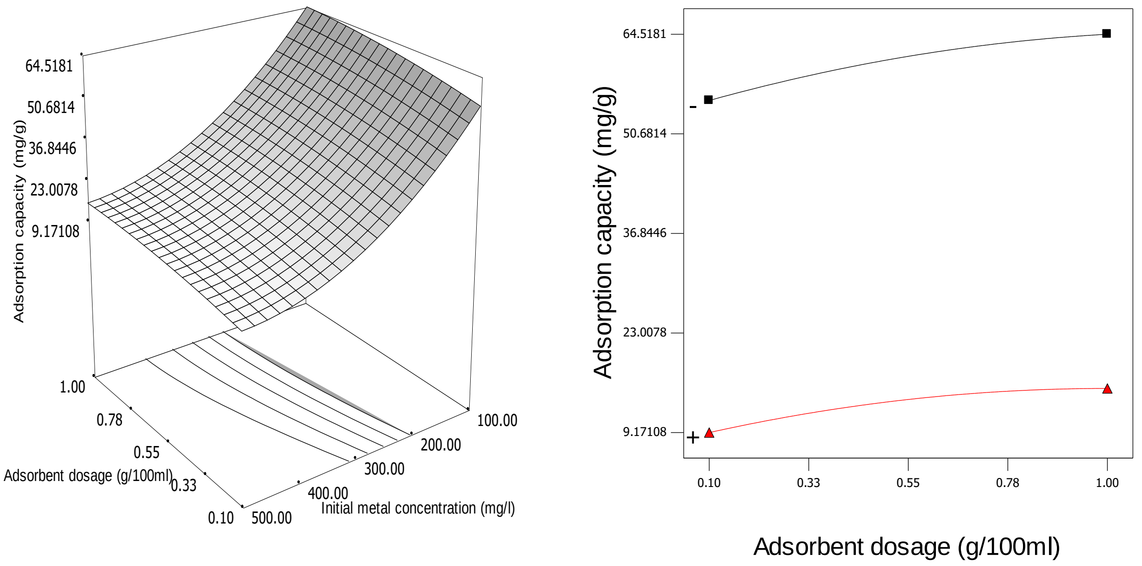
(a) (b)

Figure 24: The effect of contact time and adsorbent dosage on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where contact time is held at + 120 minutes and – 30 minutes.

4.3.5.3 Effect of adsorbent dosage and initial metal concentration on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 25 depicts the variations in adsorption capacity with the changes in the adsorbent dosage (x_1) and initial metal concentration (x_4). The pH (x_2), contact time (x_3) and temperature (x_5) were kept constant at 4.5, 75 minutes and 40°C respectively.

As shown in Figure 25 there is a slight increase in the adsorption capacity as the adsorbent dosage increases. On the other hand, as the initial metal concentration increases there is a decrease in the amount of adsorption capacity achieved. This can be explained as follows at low initial metal concentration there is low competition for the adsorption sites on the surface of the activated carbon, this means there will be more adsorption taking place hence a higher adsorption capacity is expected at low initial metal concentration. However, at high initial metal concentration there is more competition for the adsorption active site and eventually the adsorption site of the activated carbon derived from waste tire pyrolytic char becomes saturated and hence there will be a reduction in the adsorption capacity. This is in excellent agreement with the results obtained by Rao et al., 2016. As the adsorption dosage is increased, there is a slight increase in the adsorption capacities at both low and high metal initial concentration.



(a)

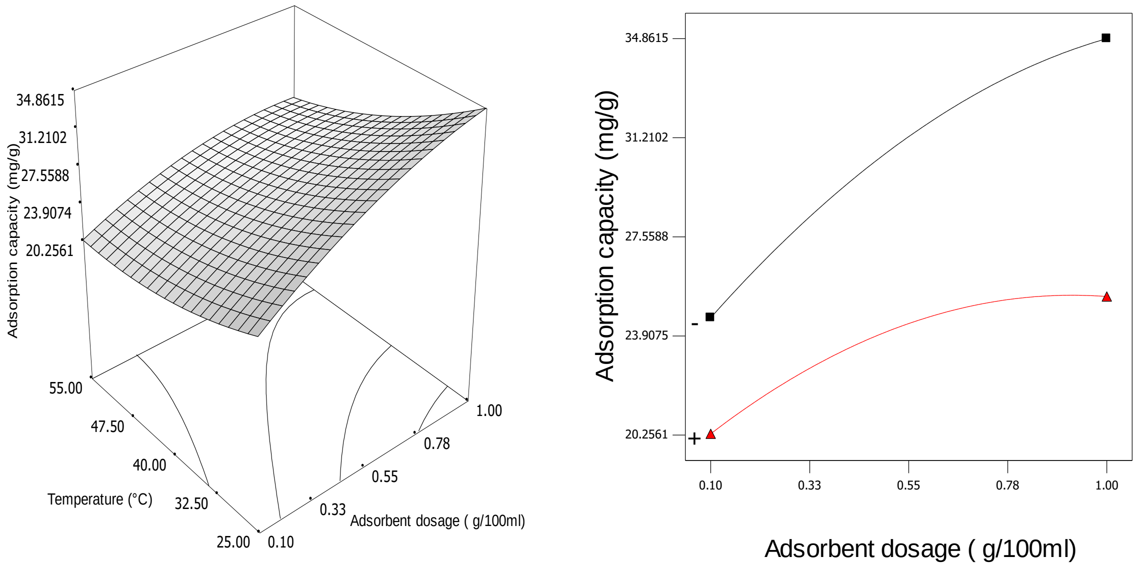
(b)

Figure 25: The effect of adsorbent dosage and initial metal concentration on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where pH is held at + 500 mg/l and – 100 mg/l.

4.3.5.4 Effect of adsorbent dosage and temperature on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 26 shows the variations in adsorption capacity with the changes in the adsorbent dosage (x_1) and temperature (x_5). The pH (x_2), contact time (x_3), initial metal concentration (x_4) were kept constant at 4.5, 75 minutes and at 300ppm respectively.

As shown in Figure 26 adsorption capacity increases with an increase in the adsorbent dosage but decreases with a decrease in the temperature. A decrease in the adsorption capacity at a higher temperature suggests that the process follows an exothermic nature (Saleh et al., 2014). Similar results were obtained by Rao et al., 2016) on their work on the adsorption of lead ions onto waste tire derived activated carbon and activated carbon from biomass. Another possible explanation these results is that the adsorption sites on the surface of the activated carbon are more activate at lower temperatures than at elevated temperatures where the adsorptive forces between the activated carbon and lead ions are weaker. Another study reported that this behavior is a result of lead ions escaping from the solid phase at higher temperatures (Guyo et al., 2015). As the adsorbent dosage is increased at low temperature (25℃), the adsorbent capacity increases and at high temperature (55℃), the adsorbent increases silently and increment stop at an adsorbent dosage of 5.5gl.



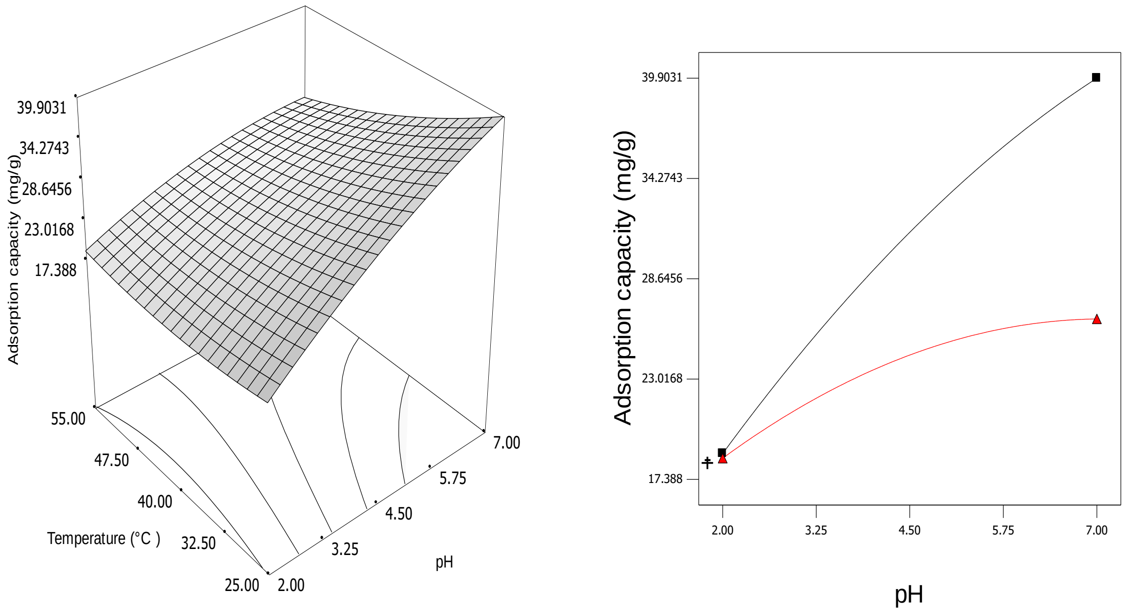
(a) (b)

Figure 26: The effect of adsorbent dosage and temperature on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where temperature is held at + 55°C and -25°C.

4.3.5.5 Effect of pH and temperature on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure ***27*** depicts the variations in adsorption capacity with the changes in the pH (x_2) and temperature (x_5). The adsorbent dosage (x_1), contact time (x_3) and initial metal concentration (x_5) were kept constant at 4.5, 75 minutes and 300 ppm respectively.

As shown in Figure 27 adsorption capacity increases with an increase in pH but decreases with a decrease in the temperature. A decrease in the adsorption capacity at a higher temperature suggests that the process follows an exothermic nature (Saleh et al., 2014). As the pH value increases the presence of hydrogen atoms in solution decrease and provide less competition for lead ions on the adsorption sites of the activated carbon and this leads to increased adsorption capacities. (Saleh et al., 2013; Rao et al., 2016b). However, at low pH values the lead ions compete with hydrogen atoms for the adsorption sites on the surface of the activated carbon leading to low adsorption capacities. As pH increase at low temperature (25°C) the adsorption capacity increases at a greater extent, however as pH increased at high temperature the adsorption capacity increases at smaller extent at pH of approximately 5.75, an increase in pH does not affect the adsorption capacity.



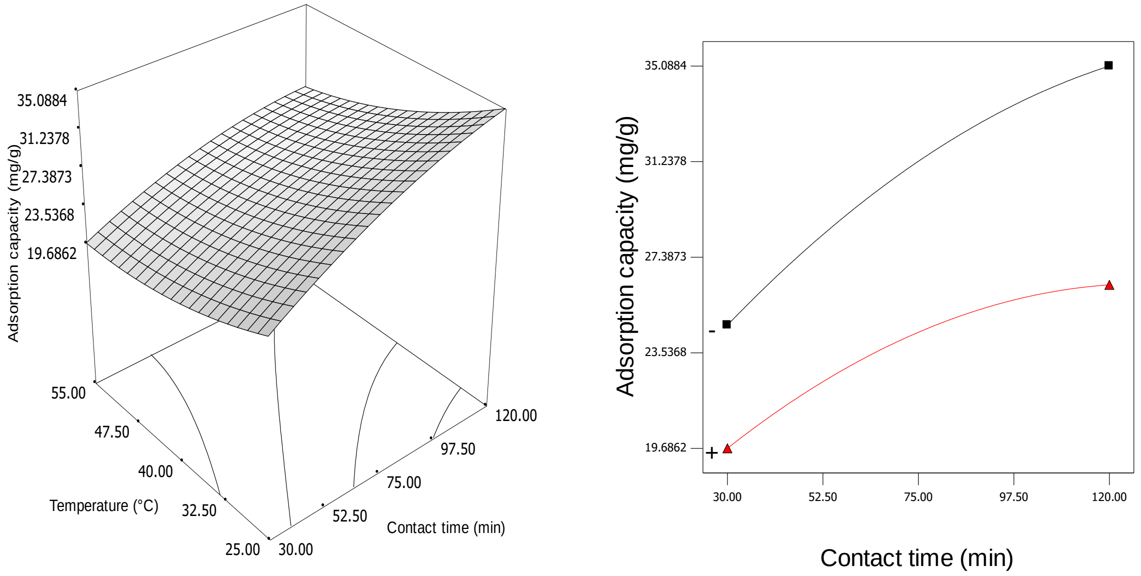
(a) (b)

Figure 27: The effect of pH and temperature on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where temperature is held at + 55°C and -25°C.

4.3.5.6 Effect of contact time and temperature on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 28 depicts the variations in adsorption capacity with the changes in the contact time (x_3) and temperature (x_5). The adsorbent dosage (x_1), pH (x_2) and initial metal concentration (x_5) were kept constant at 0.55g/100ml, 75 minutes and 300 ppm respectively.

As shown in Figure 28, the adsorption capacity increases with an increase in contact time and decreases with an increase in temperature. At low contact time, the adsorption there is no enough time for the metals ions to adhere to the activated carbon to but as the contact time increases there is adequate time available for the metal ions to adhere to the adsorption sites on the surface of the activated carbon and this will in return result in adsorption capacity (Uçar et al., 2015). As the contact time is increased both the adsorption capacities at high temperature and low temperature increases.



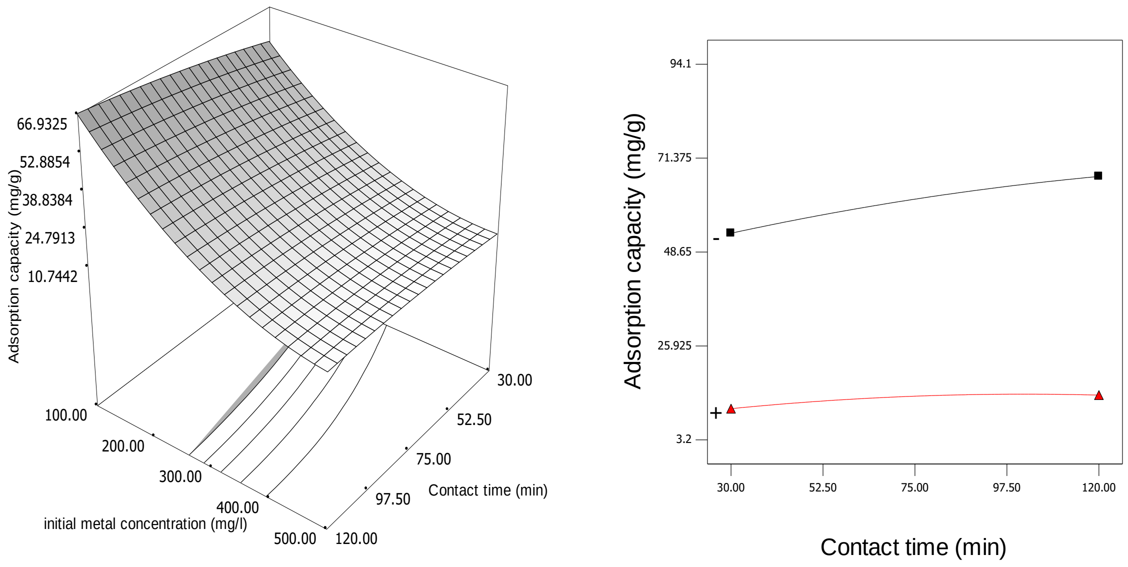
(a) (b)

Figure 28: The effect of contact time and temperature on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where temperature is held at + 55°C and -25°C.

4.3.5.7 *Effect of contact time and initial metal concentration on the adsorption of lead on activated carbon derived from waste tire pyrolytic char*

Figure 29 depicts the variations in adsorption capacity with the changes in the contact time (x3) and initial metal concentration (x4). The adsorbent dosage (x_1), pH (x_2) and temperature (x5) were kept constant at 0.55g/100ml, 4.5 and 40°C respectively.

As shown in Figure 29 there is a slight increase in the adsorption capacity as the contact time is increased at 100 ppm and 500 ppm. However, as the initial metal concentration increases there is a decrease in the amount of adsorption capacity achieved. This can be explained as follows at low initial metal concentration there is low competition for the adsorption sites on the surface of the activated carbon, this means there will be more adsorption taking place hence a higher adsorption capacity is expected at low initial metal concentration. However, at high initial metal concentration there is more completion for the adsorption active site and eventually the adsorption site of the activated carbon derived from waste tire pyrolytic char becomes saturated and hence there will be a reduction in the adsorption capacity. This is in excellent agreement with the results obtained by Rao et al., 2016. As the adsorption dosage is increased, there is a slight increase in the adsorption capacities at both low and high metal initial concentration.



(a) (b)

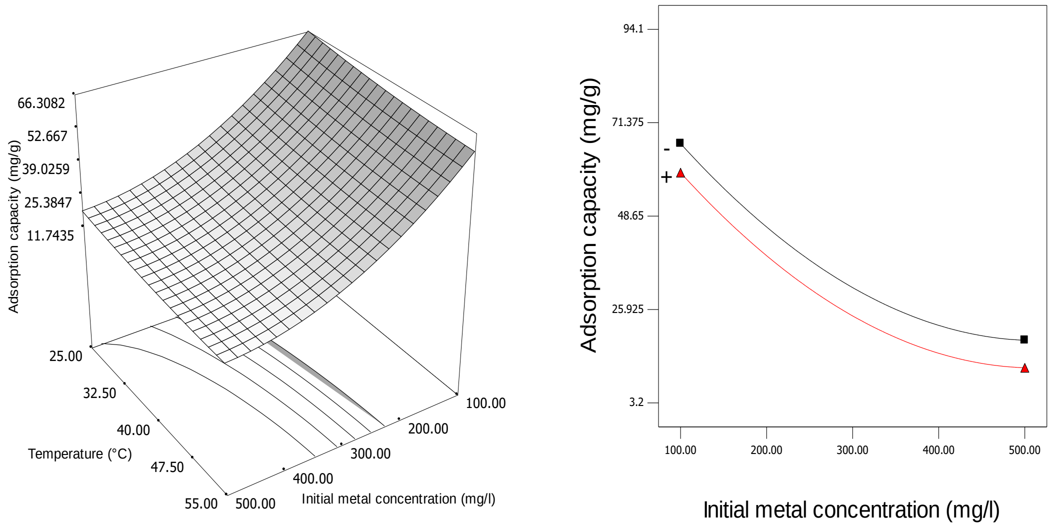
Figure 29: The effect of contact time and initial metal concentration on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where initial metal concentration is held at + 500 mg/l and – 100mg/l.

4.3.5.8 Effect of temperature and initial metal concentration on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 30 depicts the variations in adsorption capacity with the changes in the temperature (x5) and initial metal concentration (x4). The adsorbent dosage (x_1), pH (x_2) and contact time (x3) were kept constant at 0.55g/100ml, 4.5 and 75 minutes respectively

As shown in Figure 30, as the as the initial metal concentration increases there is a decrease in the amount of adsorption capacity achieved. This can be explained as follows at low initial metal concentration there is low competition for the adsorption sites on the surface of the activated carbon, this means there will more adsorption taking place hence a higher adsorption capacity is expected at low initial metal concentration. However, at high initial metal concentration there is more completion for the adsorption active site and eventually the adsorption site of the activated carbon derived from waste tire pyrolytic char becomes saturated and hence there will be a reduction in the adsorption capacity. This is in excellent agreement with the results obtained by Rao et al. 2016.

A decrease in the adsorption capacity at a higher temperature suggests that the process follows an exothermic nature (Saleh et al., 2014). Similar results were obtained by Rao et al. (2016) on their work on the adsorption of lead ions onto waste tire derived activated carbon and activated carbon from biomass. Another possible explanation for these results is that the adsorption sites on the surface of the activated carbon are more activate at lower temperatures than at elevated temperatures where the adsorptive forces between the activated carbon and lead ions are weaker. Another study reported that this behavior is a result of lead ions escaping from the solid phase at higher temperatures (Guyo et al., 2015).



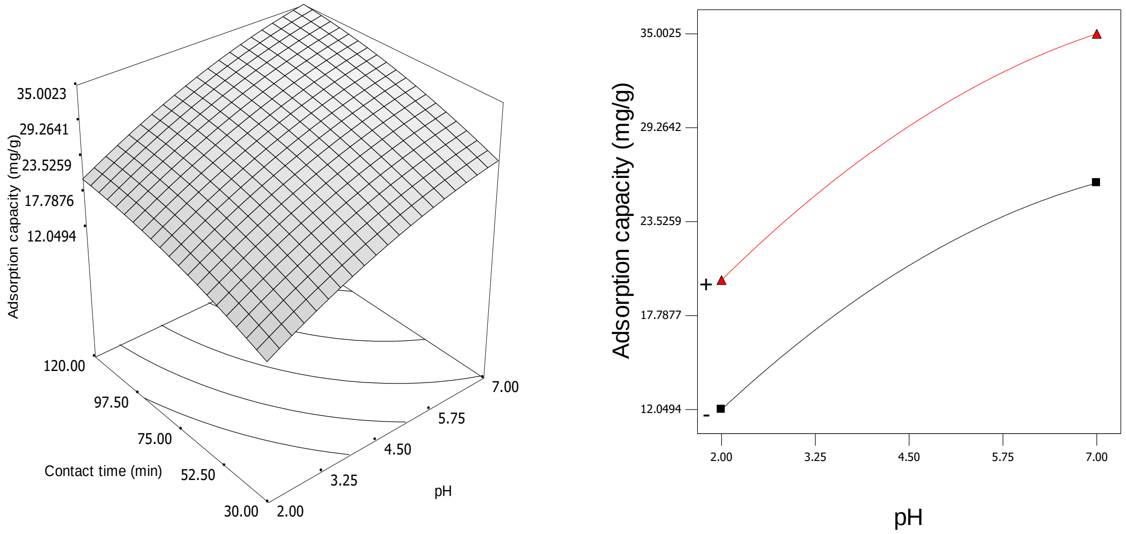
(a) (b)

Figure 30: The effect of temperature and initial metal concentration on the adsorption capacity of lead onto activated carbon derived from waste tyre char (a) Surface response plot (b) two-dimensional plot where the temperature is held at + 55°C and 25°C.

4.3.5.9 Effect of pH and contact time on the adsorption of lead on activated carbon derived from waste tire pyrolytic char

Figure 31 depicts the variations in adsorption capacity with the changes in the pH (x_2) and contact time (x_4). The adsorbent dosage (x_1), initial metal concentration (x4) and temperature (x5) were kept constant at 0.55g/100ml, 300 ppm and 40°C respectively.

Figure 31 below demonstrates the combined effect of contact time and the pH value of the solution on the adsorption capacity of the activated carbon for lead ions adsorption. The effect of both variables has been explained in the previous sections. For reference, the discussion of the effect of these two variables can be found under sections 4.3.5.1 and 4.3.5.6. From Figure 31, the optimum points obtained for the two variables are 7 and 120 min respectively for the pH value of the solution and the contact time.



(a) (b)

Figure 31: The effect of pH and contact time on the adsorption capacity of lead onto activated carbon derived from waste tire pyrolytic char (a) Surface response plot (b) two-dimensional plot where pH is held at + 7 and - 2.

4.3.6 Process optimization

In RSM once the appropriate model has been established it is possible to optimize the response variable. In this study, the method of optimization applied is the numerical method. In numerical optimization, it is important to select the goal or objective function for each variable and the response (Amini et al., 2008).The goals for each variable are set as of maximum, minimum, in range, target, equal to or none for the response only. To optimize the process, the goals for the process variables where set as in range of 0.1 to 1g/100ml for adsorbent dosage, in a range of 2 to 7 for the pH value of the solution, in a range of 30 to 120 min for contact time, in a range of 100 to 500 mg/l for initial metal concentration, minimum for temperature, and maximum for adsorption capacity. From Figure 32 it is visible that by applying numerical optimization a high adsorption capacity of 93.1762 mg/g can be achieved by operating the process parameters at 0.97 g/100ml for adsorbent dosage, 100 mg/l for initial metal concentration, 115.27 min for contact time and 25℃ for temperature. For this optimization, the desirability obtained is 0.994 which symbolizes that the response does not fall outside of the desirable limits and this suggests that the optimized operating conditions can be relied on in achieving the optimum adsorption capacity provided by the model. Figure 32 gives an elaborate overview of the process optimization of all the parameters used.

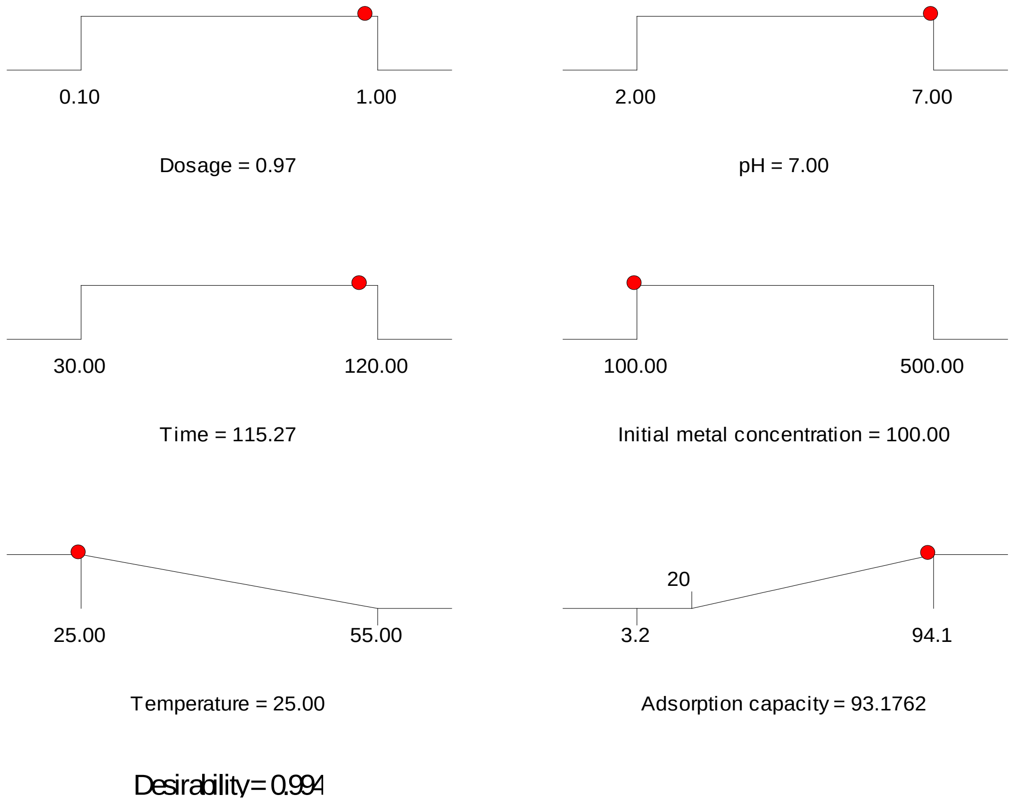


Figure 32: Numerical optimization desirability ramps for the optimization of six goals (Adsorbent dosage, pH, contact time, initial metal concentration, temperature, and adsorption capacity).

CONCLUSION

The present study was done to produce activated carbon from waste tire pyrolysis char using chemical activation with KOH. It was required to characterize the activated carbon produced and compare its characteristics with those of the raw char. It was further required to investigate the effect of 5 process parameters on the adsorption capacity of the activated carbon produced for lead ions adsorption using RSM central composite design. FTIR and TGA analysis proved that activating the waste tire pyrolysis char with KOH results in changes being made in the characteristics of the activated carbon, the analysis further showed that using KOH as the activating agent improves the adsorption characteristics of the activated carbon produced by enhancing the presence of the oxygen containing functional groups on the surface of the activated carbon and also showed that the activation process leads in the release of some matter from the char which might imply the formation of pores on the activated carbon. From performing the adsorption studies using CCD it was possible to determine the effect of process parameters on the adsorption capacity of the waste tire derived activated carbon for lead ions removal. By further applying the numerical optimization method under CCD it was possible to determine the optimum operating conditions for the process parameters to achieve maximum adsorption capacity of the activated carbon produced through chemical activation with KOH.

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GENERAL CONCLUSION

The main objective of this study was to determine the beneficiation of waste tire activated carbon prepared by chemical activation with KOH as an adsorbent for the removal of lead ions from aqueous solution. The study was carried out by applying characterisation techniques on the waste tire activated carbon and the waste tire pyrolysis char which was the activated carbon precursor for this study. A comparison was done between the waste tire activated carbon and the waste tire pyrolysis char in order to determine if the activated carbon had improved adsorption characteristics due to activation with KOH. Adsorption experiments were performed using both the waste tire activated carbon and the waste tire pyrolysis char using a one factor at a time experimental design to compare the performance of the waste tire activated carbon and the waste tire pyrolysis char and to also determine the effect process variables have on the removal efficiency of lead ions from aqueous solution. Adsorption isotherms, kinetics and thermodynamics were studied to determine the mechanism for the adsorption of lead ions. Response surface methodology was used to determine the combined effect of process variables on the adsorption of lead ions onto waste tire activated carbon and to optimize the process.

The SEM micrographs showed that there was an improvement in the surface morphology of the waste tire activated carbon produced due to chemical activation with KOH. Proximate analysis indicated a decrease in the volatile matter and the ash content of the waste tire activated carbon which implies development of pore on the waste tire activated carbon. XRF analysis showed a decrease in the inorganic matter which was originally present in the waste tire pyrolysis char. The BET surface area analysis showed that there was a slight increase in the internal surface area of the waste tire activated carbon after activation and the analysis also showed a slight increase in the micro pore volume of the waste tire activated carbon after activation. The XRD analysis indicated that waste tire activated carbon was composed of a crystalline and amorphous structure compared with the waste tire pyrolysis char which was composed of an amorphous structure. FTIR analysis showed that by activating the waste tire char with KOH the presence of oxygen containing functional groups increased which is desired for a good activated carbon for the adsorption of metal ions. TGA analysis further confirmed the results obtained from the proximate analysis by indicating that more volatile matter and ash was removed from the waste tire activated carbon during the activation process.

Adsorption experiments revealed that waste tire activated carbon achieves higher removal percentages of lead ions compared to waste tire pyrolysis char. The adsorption experiments further showed the effect of process variables affecting the adsorption of lead ions onto waste tire activated carbon and the optimum operating conditions were obtained. Performing adsorption experiments using Response Surface Methodology by a CCD method showed the combined effect of the process variables on the adsorption capacity of the waste tire activated carbon for lead ions adsorption. Furthermore, it was possible to determine the optimum operating conditions of the process variables to achieve maximum adsorption capacity of the waste tire activated carbon for lead ions removal by using numerical optimization method under CCD and the optimum operating conditions were found to be adsorbent dosage = 0.97 g/100ml, pH = 7, contact time = 115.27, initial metal concentration = 100 mg/l, and temperature = 25 °C to achieve an adsorption capacity of 93.2 mg/g. The optimum operating conditions obtained under RSM were comparable with those obtained under one factor at a time experimental design which showed that both methods of experimental designs were effective in determining the optimum operating conditions for the adsorption of lead ions onto waste tire activated carbon.