REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY ADSORBENT DERIVED FROM WASTE TYRES

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A PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF
CHEMICAL ENGINEERING, FACULTY OF ENGINEERING,
UNIVERSITY OF BENIN, BENIN CITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE
AWARD OF DEGREE OF B.Eng. (HONS) IN CHEMICAL
ENGINEERING

JULY, 2021.

CERTIFICATION

This is to certify that this research project submitted to the Department of Chemical Engineering was carried out by **AGIDI KELVIN MARIO** with Matriculation Number: **ENG1503480** of the Department of Chemical Engineering, University of Benin, Benin City, under the supervision of **Engr. Dr. S.E UWADIAE**. This work has not been presented for the award of a degree in any other university and all the sources of information used in this research project have been appropriately acknowledged.

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ACKNOWLEDGEMENTS

My special acknowledgement goes to God Almighty whose plans and purposes must surely prevail.

I am particularly grateful to my Supervisor Engr. Dr. S. E. Uwadiae who not only made this work possible but also provided the support and guidance in the entire project. Despite his tight schedule, he took out time to read and correct my entire project work.

Special thanks to my parents and siblings for their unwavering support, admonitions, prayers and love, they were a major support system during the whole process of this research work, I am more than grateful for the love and support.

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ABSTRACT

Chromium is one of the most notorious heavy metals released by various industries such as tanning and leather industries, manufacturing industries, catalyst and pigments, fungicides, ceramics, crafts, glass, photography, electroplating industry and corrosion control application. This study was aimed at sorption of chromium(VI) ion from aqueous solution by adsorbent derived from used tyres.

Waste tyre was collected from Uwelu spare part market in Edo state. The collected tire was washed and rinsed with distilled water to remove debris, oven dried for 3hours at 180^{o}C and ground into powder. This dried powder was carbonized and activated by charging into a muffle furnace for 2hrs at 500^{o}C and then treated with 4M nitric acid. The efficacy of chromium removal of the adsorbent is determined by investigating the various parameters such as adsorbent dose, agitation time and shaking speed. The adsorbent was characterized by Scanning Electron Microscopy (SEM), Energy dispersive X-ray (EDX) and Fourier Transform Infra-Red (FTIR) spectroscopy.

The total pore volume of the adsorbent was observed to bet P/P_0=0.988646762:0.624668 cm^3/g. The percentage of C and O was found to be 30.50% and 20.23%. Analysis of Variance for the response surface quadratic model showed that the Model F-value of 75.25 implies that the model is significant. The Lack of Fit F-value of 0.9763 implies that the Lack of Fit is not significant relative to the pure error. The high R-square value (coefficient of determination) of 0.9898 indicates that the fitted model predicts the metal ion removal with reasonable precision. Based on the identified model, the predicted maximum metal ion removal of 100.874% was obtained at 0.202 g adsorbent dosage, 287.759 rpm shaking speed and 77.931 min contact time. The results indicate that waste tyre activated carbon is an efficient low-cost adsorbent for the removal of chromium (VI) ion from wastewater.

CHAPTER ONE

1.0 INTRODUCTION

1.1. Background of study

High concentration of untreated or poorly treated wastewater containing toxic heavy metals such as Cr, Ni, Cd, Pb, Hg, Zn, Co and Cu from industrial effluents into the natural water bodies is a major environmental Problem because of their high toxicity and their tendency to accumulate through the food chain (Bajpai.,2015). Chromium is one of the most notorious heavy metals released by various industries such as tanning and leather industries, manufacturing industries, catalyst and pigments, fungicides, ceramics, crafts, glass, photography, electroplating industry and corrosion control application (Agawal., 2015).

Chromium forms three common oxidation states in its compounds, +2, +3, and +6. The +3 and +6 oxidation states are the most commonly observed in chromium compounds, whereas +4, and+5 states are rare. The most prominent example of toxic chromium is hexavalent chromium Cr(VI) (park et al, 2008). International Agency for Research on Cancer (IARC) has classified chromium (VI) in Group 1 (carcinogenic to humans) and metallic chromium and chromium (III) in Group 3 (not classifiable as to their carcinogenicity to humans (Bajpai.,2015). Therefore, the removal of chromium (VI) from wastewater is extremely important before its discharge into the aquatic system, which needs immediate attention. Conventional treatment technologies have been developed to remove Cr (VI) from water and wastewater, including reduction followed by chemical precipitation, ion exchange, membrane separation, electrocoagulation, nanoparticles, dialysis/electro dialysis and adsorption/filtration (Jayswal and Chudasama, 2007). Capital and operational costs often limit efficiency and the effectiveness of these methods, principally, when large volumes of effluents contain relatively low concentrations (Pellegrini *et al.*, 2018).

Most of this method are expensive or ineffective when the metals are dissolve in large volume of solution at a relatively low concentration but in contrast, the adsorption technique is a highly effective method because it is a simple and cost effective method for recovering and eliminating heavy metal ions from dilute solutions (Buliety, 2012). Recently, a variety of cheap materials have been examined as adsorbents for the removal of Cr (VI) from aqueous solution with the aim of finding cheaper alternatives for conventional sorbent materials such as activated carbon which is an expensive adsorbent. Some of the low cost adsorbents include anaerobic sludge apple residue, sawdust, rice Polish, clay, zeolite, fly ash, chitosan, waste tea, seaweeds, polyaniline coated on sawdust and waste tyres which is the focus of this research
Environment waste such as tyre waste is problem to the to the environment has typical properties (large surface area, high cation exchange capacity, chemical stability and a layer structure) that make them good adsorbents (Nik *et al.*, 2021).

1.2. Statement of Problem

Heavy metals pollution has become one of the major problems in the environment today especially in waste water which is toxic to both human beings and aquatic life. The metal that is been study in this research is chromium VI. We are also using waste tyres which are not biodegradable and cause menace in the environment as an adsorbent to remove this heavy metal from aqueous solution. This research work is to address this environment problem by using waste tyre as an absorbent in removing this heavy metal (Chromium VI) from aqueous solution.

1.3 Aim and Objectives

The aim of this study is to use adsorbent derived from waste tyres for the removal of chromium (VI) from aqueous solution.

The objective of this study is as follow i To investigate the effect of contact time, pH, adsorbent dosage and shaking on the removal of chromium ions from aqueous solutions.

ii To determine the physical properties such as pore size distribution of the waste tyres

iii To determine the chemical properties such as functional group and pH at zero potential

iv To assess the feasibility of waste tyres as adsorbent in the removal of chromium ions from aqueous solutions.

1.4. Scope

The scope of this study is to test the adsorption the chromium (VI) ion using tyres waste as an adsorbent. The influence of experimental parameters such as adsorbent dosage contact time, pH, initial concentration and mesh size were studied to optimize the condition for maximum Chromium (VI) removal with the use of Atomic Adsorption Spectrophotometer for analysis.

1.5. Relevance of the Study

The adverse consequence of heavy metals on the environment and human health cannot be over emphasis and quantify.

Waste tyre has a non-biodegradable waste material have also cause a lot of damages to the environment as a result of improper disposal which lead to blockage of drainage that cause flooding problem and prevent proper remediation of the soil.

The use of waste tyre as an absorbent will lead to the removal of this non-biodegradable waste from the environment and also will be use to remove chromium (vi) ion from aqueous solution.

This will lead to a cleaner environment and also a source of cheap absorbent for heavy metals removal making the environment heathier for both plants and human since the material is a waste product and can be source locally at a very low cost.

This will also make the land (soil) to be more fertile for crop to produce well since the non-biodegradable material that negatively has been removed from the environment.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Heavy metals/ metalloids in the environment

The term ‘heavy metal/metalloid’ denotes any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Arruti *et al.*, 2010). It is a general collective term, which generally applies to a group of metals and metalloids with an atomic density greater than 4g/cm^3 (Mansourri and Madani, 2016). Most of the heavy metals are classified as hazardous pollutants due to their toxicity. These metals/metalloids are major pollutants in ground water, industrial effluent, marine water, and even treated waste water. The important toxic metals/metalloids (i. e. Cd, Hg, As, Cr, Zn, and Pb) find its way to the water bodies through waste water (Valavanidis and Vlachogianni, 2020; Onuegbu *et al.*, 2013). In a global context, the major problem of surface water pollution is heavy metal discharge from industrial activities (Ayeni, 2014; Kalavrouziotis and Koukoulakis, 2016). The development of industrial sector in the African continents is the primary cause of heavy metals being released into water, air and soil in all countries

Most industries are the point source of heavy metals (Nazir, 2015); these industries include electroplating, chemical and petrochemical, metal and mining, leather, textile, ceramic, cement, fertilizer, tanneries, batteries, paper, pesticides and others. These industries release their wastewater containing various harmful heavy metals without treatment into the environment (Mucha and Kulakowski, 2016). These harmful toxic chemicals include elements such as uranium (Ur), selenium (Se), zinc (Zn), silver (Ag), gold (Au), nickel (Ni), cadmium (Cd), mercury (Hg), copper (Cu), chromium (Cr), arsenic (As), lead (Pb) and others. Their presence even at low concentrations, affects the health of humans and other living organisms (Jaishankar *et al.*, 2014). The fact that these elements are highly soluble in water and not easily degradable by soil, makes their presence in water bodies more alarming

(Kalavrouziotis and Koukoulakis, 2016). Therefore, it is important to treat heavy metals discharge from industrial wastewater, with affordable and technically feasible methods which initiates the need for exploring cost-effective, simple and efficient removal techniques using locally available materials.

2.2. Chromium

Chromium is a major toxic contaminant even at low concentrations, which entered the water streams through various industrial operations. Sources of chromium contamination include disposal of chromium containing wastes and releases from electroplating processes (Unceta *et al.*, 2010). The stable forms of Cr are the trivalent Cr (III) and the hexavalent Cr (VI) species; although there are various others valence states which are unstable and short lived in biological systems. In its hexavalent form Cr(VI) is well known due to its health-related issues in humans including carcinogenic and mutagenic risks (Bokare, 2011). Moreso, chromium can lead to cancer in the lungs and digestive tract. Cr (VI) is considered the most toxic form of Cr, which usually occurs associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions (Bianco *et al*., 2018; Alemayehu *et al*., 2011). Cr (III) is less mobile, less toxic and is mainly found bound to organic matter in soil and aquatic environments (Brasili *et al*., 2020). The speciation of chromium in contaminated environments becomes critical for understanding its fate and exposure.

2.2.1. Sources of chromium

The potential sources of chromium(VI) wastes are effluents from metallurgy, electroplating, leather tanning, textile dyeing, paint, ink and aluminum manufacturing industries (Bianco *et al.*, 2018) Cr (III) and Cr (VI) are released to the environment primarily from stationary point sources resulting from human activities. Chromium is released due to environmental as well as occupational sources (Alves et al., 2012). Environmental sources of chromium includes airborne emissions from chemical plants and incineration facilities, cement dust, contaminated landfill, effluents from chemical plants, asbestos lining erosion, road dust from catalytic converter erosion and asbestos brakes, tobacco smoke (Yusuf et al., 2013). Occupational sources of chromium include anti-algae agents, antifreeze, cement, chrome alloy production, chrome electroplating (soluble Cr(VI), copier servicing, glassmaking, leather tanning (soluble Cr[III]), paints/pigments (insoluble Cr[VI]), photoengraving, porcelain and ceramics manufacturing, production of high-fidelity magnetic audio tapes, textile manufacturing, welding of alloys or steel, and wood preservatives.

2.2.2. Uses of chromium

Chromium has a wide range of uses in metals, chemicals, and refractories industries. The followings are some of the more common uses of chromium in the world today (Rajaganapathy *et al*., 2011).

- Magnetic tape (used in audio cassettes and high-class audio tapes) is made from a magnetic compound of chromium.
- Wood preservative by using salts of chromium (VI). Different compounds of chromium are used to make different colored pigments and dyes.
- Stainless steel, used in many applications, an alloy of iron with chromium.
- Alloys of iron, nickel and chromium are very strong and handle very high temperatures which are used in jet engines and gas turbines.
- Chromium is fairly hard and is resistant to corrosion. Therefore, many things are coated with chromium.

Chromium compounds are highly toxic to plants and are detrimental to their growth and development. Although some crops are not affected by low Cr concentration (3.8 x 10-4 μM), Cr is toxic to higher plants at 100 μM. kg-1 dry weight. The impact of Cr contamination in the physiology of plants depends on the metal speciation, which is responsible for its mobilization, subsequent uptake and resultant toxicity in the plant system. Cr toxicity in plants is observed at multiple levels, from reduced yield, through effects on leaf and root growth, to inhibition on enzymatic activities and mutagenesis (Becquer *et al*., 2003; Onuegbu *et al*., 2013).

2.3. Conventional methods for treatment of water

A variety of conventional treatment technologies, based on the principle of precipitation, ion exchange, electrolysis, solvent extraction, reverse osmosis, membrane and biosorption process have been proposed and is tested for removal efficiency of different pollutants from potable water as well as industrial effluent (Gupta et al., 2016; Moussavi and Barikbin, 2010). Each technique provides a different and unique approach and perhaps provides certain advantages over others for a particular situation. But these process are not very popular because one or more disadvantage. However, when large volumes of water containing toxic elements are to be treated, it would, be of great advantage if the method would provide reliable results without involving much cost and working efforts.

2.3.1. Precipitation

Chemical precipitation of heavy metals and metalloids as their hydroxides using lime or sodium hydroxide is widely used in this process. Lime is generally used for precipitation purpose due to its low cost and easy control pH in the range of 8-10. The efficiency of the process depends on a number of factors, which include the ease of hydrolysis of metal and metalloids ions, nature of the oxidation state, pH, and presence of complex forming ions, standing time and filtering characteristics of the precipitate. This method has been used for the removal of metals and metalloids such as iron, copper, chromium, arsenic, cadmium and zinc from the effluents of the industries (Ajay, ,2016; Prathima, 2012; Park *et al*., 2010). Carbonate precipitation used to precipitate metal and metalloids ions using calcium or sodium carbonate is very limited. Tchobanoglous *et al*. (2003) reported improved results for carbonate precipitation of cadmium and lead from electroplating effluents.

2.3.2. Chemical reduction

Certain ions such as arsenite, chromate and dichromate have least tendency for precipitation and cannot be removed efficiently by any other removal technology. On the other hand, adsorption is a feasible process but there isn't many adsorbent available for removal of arsenite and dichromate ions since arsenite and dichromate are very selective towards bio-adsorption. To overcome these difficulties, researchers are working on chemical reduction methods. In recent year chemical methods of arsenite and chromate reduction using zero-valent metal like iron (Fe), aluminum (Al) and magnesium (Mg) have been studied intensively. In reducing waters, arsenite is found in some form of arsenious acid which ionizes according to the equations (Jones *et al*., 2019).

2.3.3. Bio-sorption/Adsorption

The term "biosorption or adsorption" includes the uptake a gaseous or liquid components of mixtures from the external and/or internal surface of porous solids biosorbents or adsorbents. In chemical engineering, biosorption or adsorption is called the separation process during which specific components of one phase of a fluid are transferred onto the surface of a solid biosorbent or adsorbent (Chojnacka, 2010; Alpat *et al*., 2010). The bio adsorption of various substances on solids is due to the increased free surface energy of the solids due to their extensive surface (Bilba *et al*., 2008). According to the second law of thermodynamics, this free energy has to be reduced. This is achieved by reducing the surface tension via the capture of extrinsic substances. The term "sorption" is used to describe every type of capture of substances from the external surface of solids, liquids, or mesomorphs as well as from the internal surface of porous solids or liquids. Most of the heavy metals are efficiently removed by adsorption method (Jayswal and Chudasama, 2007).

Adsorption is a conventional but efficient technology for the removal of toxic pollutants from wastewaters. So, there is a need to develop low cost and easily available activated carbon adsorbents for the removal of heavy metal ions from the aqueous environment. The main advantages of this technique are the reusability of material, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time. Removal of chromium (VI) ions from water was reported to be efficient by activated carbon prepared from saw dust, rice husk, raw rice bran, ethylenediamine-modified rice hull, coconut husk fibers, hazelnut shell, modified saw dust, maple saw dust, sugarcane bagasse, agricultural waste, cow dung, activated sludge, cow dung, fly ash, coconut shell charcoal, coniferous leaves, pine needles etc (Park *et al*., 2010; Oliveira *et al*., 2011; Noroozi *et al*., 2007). *Eichhornia crassipes* (family Pontederiaceae) commonly known as water hyacinth, is an aquatic weed found abundantly (Pellegrini *et al.*, 2018). The disposal of this weed is a major problem all over the world because of its vigorous growth in water bodies. Activated carbon prepared from *Eichhornia crassipes* root biomass, and its use for the removal of chromium (VI) ions from water has not been reported (Ndimele, 2012). In view of the above facts it is worth to prepare the activated carbon from the root and subsequently use the material to remove the chromium (VI) from water. Depending on the type of bonding involved, sorption can be classified as follows.

2.3.3.1. Physical Adsorption

In physical sorption (or physisorption), no exchange of electron is observed; rather, intermolecular attraction between favorable energy sites take place and are therefore independent of the electronic properties of the molecules involved. The biosorbate is held to the surface by relatively weak van der Waals forces and multiple layers may be formed with approximately the same heat of biosorption. The heat of biosorption for physisorption is at most a few kcal/mole and therefore this type of adsorption is stable only at temperature below 50 °C.

2.3.3.2. Chemical Adsorption

Chemical Adsorption (or chemisorption) involves an exchange of electron between specific surface sites and solute molecules, and as a result, a chemical bond is formed. Chemisorption is characterized by interaction energies between the surface and adsorbate comparable to the strength of chemical bonds (tens of Kcal/mol), and is consequently much stronger and more at high temperatures than physisorption. Generally, only a single molecular layer can be adsorbed.

2.3.3.3 Electrostatic Adsorption (ion exchange)

This is a term reserved for Coulomb attractive forces between ions and charged functional groups and is commonly classified as ion exchange. Ion exchange is a process in which solid material takes up charged ions from a solution and release an equivalent amount of other ions into the solution (Jayswal and Chudasama, 2007). The ability to exchange ions is due to the properties of the structure of the materials. The exchanger consists of a matrix, with positive or negative excess charge. This excess charge is localized in specific locations in the solid structure or in functional groups. The charge of the matrix is compensated by the counter ions, which can move within the free space of the matrix and can be replaced by other ions of equal charge sign (Noroozi *et al*., 2007). The pores sometimes contain not only counter ions but also solvent. When the exchanger is in contact with the liquid phase, the solvent can travel through the exchanger and cause “swelling” to an extent that depends on the kind of counter ions. Some electrolytes can also penetrate into the exchanger along with the solvent.

As a result, there are additional counter ions, called co-ions, which have the same charge sign as fixed ions. Normally, exchanger has many open areas of variable size and shape that are altogether called “pores.” Only a few inorganic exchangers contain pores of uniform cross section.

2.4. Production and Adsorption Capacity of Activated Charcoal

Activated carbon can be prepared using this process. Fire wood or any other compatible wood is dried at about 105-115◦C for 24 hours, then placed in an oven which is sealed and heated at a rate of about 5◦C/min from room temperature gradually to 450◦C. Simultaneously, N2 is passed into the oven at a rate of 3 dm^3/min for 1 and half hour. For the carbonization process, the char will be soaked in a concentrated NaOH solution. Then later on it is oven-dried and activated. The activated products are then cooled to room temperature and washed clean with distilled water. The resulting sample is then decanted into a container containing 0.1 mol/dm^3 HCl (250cm^3) and stirred rigorously for 1 hour. Then finally it is washed with hot water until neutral pH is obtained within the range of 6-7. On an average about 20 – 25 g solvent per 100 g activated carbon can be adsorbed when effective adsorption takes place using activated charcoal. If the adsorbent is a poor adsorber, the temperature or the air humidity increase, then capacity will decrease. Impregnated activated carbon, are prepared differently. Adsorption can be done in a bed composed of activated carbon. An adsorption zone is then formed around bed, which when saturated moves the air inlet to the outlet. When the air gets to the saturation zone at 100% input concentration level it leaves the zone at the lowest possible vapor pressure in equilibrium relation with the activated carbon.

2.5. Activated charcoal from waste tires as treatment for waste water

Several methods have been deployed by different chemist to effectively extract activated charcoal from waste tires; we will explore two among such popular methods. In his method carbonaceous adsorbents was prepared by reaction of HCl, HNO3, and NaOH aqueous solutions in an atmosphere of N^2. Next, these adsorbents are characterized by their texture and tested as adsorbents of phenol, paminophenol, pnitrophenol, of metals in aqueous solutions. The result is a carbonaceous pyrolous adsorbent that is used for the removal of heavy metals such as mercury and lead from liquid solutions in this case waste water. The tire obtained activated carbon was used for the removal of Cu (II) and Pb (II) ions from wastewater collected from domestic water waste. The prepared adsorbent was by scanning electron microscopy method. For optimization purposes, factors such as pH value, time, concentration of solution and mass adsorbent were effectively studied.

Using whatever method, the general production of adsorbent from waste tires follows the following steps

- Cleaning and washing of raw material
- Drying
- Pyrolysis
- Oxidation
- Re-washing
- Re-drying
- Oxidation
- Activation
- Final Washing and drying
- Sieving

2.5.1. Factors affecting the efficiency of activated charcoal when treating heavy metals in waste

Few factors affect the production of activated charcoal, (Mousavi et al.,2011). In the year 2010 did a research on used ash of waste tire rubber as an adsorbent in the removal of heavy metal ion from liquid phase. They conducted Batch adsorption studies on the effect of pH, temperature, and effect of contact time in the adsorption of heavy metals using activated charcoal, their conclusion showed that these factors contribute in many ways in the adsorption process. They discovered that removal of heavy metals by adsorbents in this case activated charcoal depends largely on the pH of its initial concentration. Batch equilibrium studies were carried out in using pH values to ascertain this. Manchon-Vizuete et al.,2005 did another research using waste tires to prepare carbonaceous products and these carbonaceous products were used as an adsorbent for the removal of mercury from liquid solution. The adsorption of mercury was studied from its kinetic and equilibrium characteristics. In their research paper they concluded that adsorption capacity of tyre towards mercury increases when the adsorbent is consecutively heated and cured chemically. While using activated charcoal as an adsorbent to treat waste water it is necessary that we observe the optimal conditions as determined by these stated researches and more, to be able to treat waste water effectively and optimally remove all heavy metals in the waste water.

2.6. Factors Affecting Adsorption

There are many factors that affect adsorption process, these factors include surface area, temperature, pressure, nature of adsorbent amongst many others. A few of these factors are explained below.

2.6.1. Temperature

Adsorption is an exothermic process, Hence, according to Le Chatelier's principle at given pressure low temperature favours adsorption. If the temperature is increased, adsorbate molecules get removed from the adsorbent and this process is called desorption. Thus, adsorption is inversely proportional to the temperature. This is true for physical adsorption. In chemical adsorption, due to high energy of activation, the extent of adsorption increases initially and decreases as the temperature increases further.

2.6.2. Nature of Adsorbent

Since adsorption is a surface phenomenon, adsorption increases with the increase in the surface area of the adsorbent. More finely divided or rougher the surface of adsorbent, the greater will be the surface area and hence the greater will be the adsorption. Metal catalysts in the finely divided form, colloidal form, rough surfaces, activated adsorbent provides more surface area.

Chemisorption is preferential and more specific. A gas will be chemisorbed on a given surface only if it can provide large surface area. E.g. hydrogen gas is adsorbed by nickel but not by iron. The chemical nature of the adsorbent should be such that it can cause chemisorption of adsorbate on the adsorbent.

2.6.3. Nature of Adsorbate

In case of adsorption of gases by solids, it has been found that more easily liquefiable and highly water-soluble gases are adsorbed more readily due to greater van der Walls forces. Hence ammonia, hydrogen chloride, chlorine and Sulphur dioxide are more adsorbed than hydrogen, nitrogen and oxygen. (Eric Van dijk et al.,2013)

In physical adsorption, the extent of adsorption depends on the boiling point of the gases. Gases are adsorbed on solids more readily than liquids.

porous and finely powdered solid e.g. charcoal, fullers earth, adsorb more as compared to the hard non-porous materials. Due to this property powdered charcoal is used in gas masks.

2.6.4. Concentration of Adsorbate

When liquid is adsorbed on solid, at higher concentration of adsorbate, the extent of adsorption is greater, provided that the temperature is kept constant. The concentration of adsorbate has a similar type of effect as that of pressure.

2.6.5. Adsorption Isotherm

An adsorption isotherm is a relation between the ex\\tent of adsorption (amount of a substance adsorbed per unit of an adsorbent) and the equilibrium pressure or concentration at a constant temperature. Actually, it is a curve obtained by plotting extent of adsorption (amount of a substance adsorbed per unit mass of an adsorbent) against the equilibrium pressure or concentration at a constant temperature.

2.6.6. Surface area of the solid adsorbent

The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. larger the surface area of the adsorbent, greater is the extent of adsorption. Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

2.6.7. Effect of pressure on the adsorbate gas

An increase in the pressure of the adsorbate gas increases the extent of adsorption. At low temperature, the extent of adsorption increases rapidly with pressure. Small range of pressure, the extent of adsorption is found to be directly proportional to the pressure. At high pressure (closer to the saturation vapor pressure of the gas), the adsorption tends to achieve a limiting value. (Jasen et al.,2013)

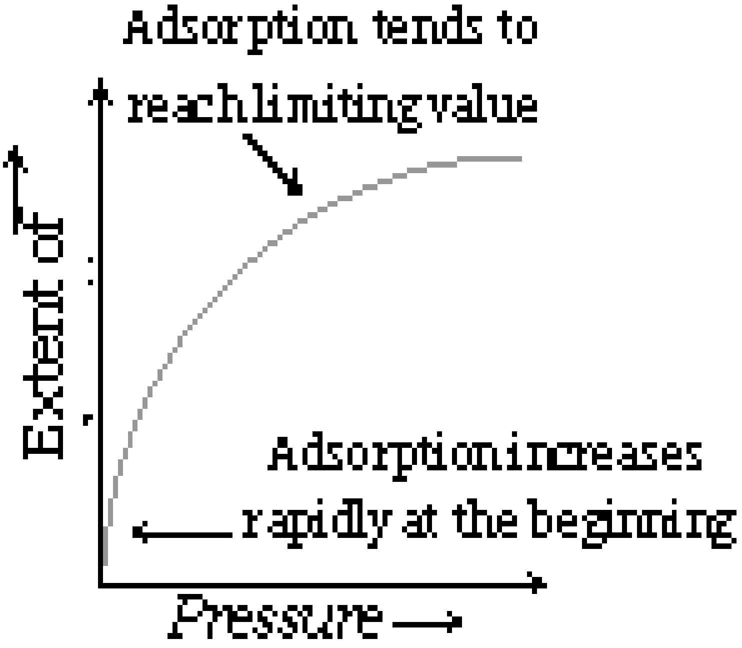


Figure 2. 1: Relationship between Extent of adsorption and Pressure

2.7. Applications of Adsorption

The phenomenon of adsorption finds a number of applications. Few of them are-

1. **Production of high vacuum:** Adsorption process is used in the production of vaccum by using cultivated charcoal in Dewar's flask.
2. **Gas masks:** Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used by miners and sanitation workers to adsorb poisonous gases such as methane and carbon monoxide.
3. **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
4. **Removal of colouring matter from solutions:** Animal charcoal removes colours of solutions by adsorbing coloured impurities. For example, crude sugar is decolourised by adsorption of colouring matter by charcoal.

5. **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
6. **Separation of inert gases:** Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
7. **In curing diseases:** A number of drugs are used to kill germs by getting adsorbed on them.
8. **Froth floatation process:** A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.
9. **Adsorption indicators:** Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point
10. **Chromatographic analysis:** Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields such as separation and purification of mixtures of substances.
11. Ion-exchange resins, which work on adsorption principle, are used for softening hard water.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1. Material and Reagents

The waste tyre was collected from Uwelu spare part market at Egor local government in Edo state Nigeria. Only the sides of the tyre was cut from the whole since the side walls are thread free. It was this side wall of the tyre that was used to prepared the absorbent and all the analytical grades chemicals and reagents were purchase from mosaic chemicals Nigeria Ltd, Benin city, Edo state Nigeria.

3.1.1. Materials and their Uses

The chemicals and reagents used for this work were purchase from mosaic chemical Nigeria (Ltd) and were all analytical grades. They are presented in the Table 3.1.

Table 3.1: List of chemicals and their uses

Chemical	**Use**
Nitric acid	For activation
Hydrochloric acid	For pH adjustment
Sodium hydroxide	For pH adjustment
Distilled water	For washing and preparation of solution
Chlorofoam	For iodine test
Wijs solution	For iodine test
Sodium thiosulphate (Na2S2O3)	For iodine number test titration
Phenolpthalein	Use as indicator
Potassium dichromate	Use as the absorbat

3.1.2 List of Equipment and Apparatus Used

The equipment and apparatus used for this work was from chemical engineering laboratory and are presented in the Table 3.2..

Table 3.2: List of equipment and their uses

Equipment and apparatus	**Uses**
Orbital shaker	Use for shaking samples
Beakers	They are used for pouring, mixing and keeping of reagents
Conical flask	It is used for shaking and titration
Furnace	For carbonization
Burette	For titration of iodine number
Retort stand	For holding burette during titration
Weighing balance	Use to evaluate the mass of a substance
Volumetric cylinder	For measurement of samples and reagents
Round bottom flask	Use for boiling during iodine number test
Heating Mantle	For heating

3.2. METHODS

3.2.1. Preparation of Aqueous Solutions

Stock solutions (1000mg/l) of Cr (VI) was prepared by dissolving 5.75g of analytical grade potassium dichromate ($K_2Cr_2O_7$) in 1000mL in distilled water. Working solutions were obtained by diluting the stock solutions with appropriate amounts of distilled water. The concentration of metal ions in solutions was analyzed by Atomic Absorption Spectrophotometer.

3.2.2 Preparation of Adsorbent Precursor

The collected waste tyre was thoroughly washed with detergent and rinsed with deionized water to ensure that there were no soil particles and other debris remaining on the surface of the tyres. This was then thoroughly rinsed with distilled water. Thereafter the tyre material was oven dried at 80 ^oC for 2h. The tyres were cut into smaller pieces with a sharp knife and were further dried in the oven at 100 ^oC for 1hour. The tyre was then ground into powder and was made uniform by milling the particles to the same size by sieving using 50um mesh size.

3.2.3 Carbonization and Activation of Adsorbent

Waste tyre was carbonized and activated via a modified previously reported method (Lakshmi *et al.*, 2018) The prepared waste tyre was charged into muffle furnace to carbonize at 500^{o}C for 2 hours. Then, it was removed from the furnace and cooled in desiccators. The material was then treated with 4M nitric acid solution to remove the ash content and was then washed with deionized water. The product was finally dried in an oven at 120°C for 6h.

3.2.4 Determination of Point of Zero Charge

The method employed in the determination of point of zero charge of the adsorbent is as reported by Flores-Cano *et al.*,2016. The point of zero charge is generally described as the pH at which the net charge of total particle surface (that is adsorbent's surface) is equal to zero. Acid-base titration procedure was adopted. Several neutralization solutions were prepared by adding 10 mL of 0.1M HCl and NaOH titrating solutions into a 50 mL volumetric flask and fillingo the mark with 0.1 M NaCl solution. The initial pH of the titrating solutions ranged from 2 to 12.

0.1 g of the adsorbent and 25 mL of a titrating solution were added into a stoppered vial and left in contact for 24 h. The final pH of the solution was recorded using a pH meter. The initial pH values of the neutralizing solutions without adsorbent were also measured using the remaining 25 mL of the neutralizing solution against the pH of the solution, were plotted in the same figure for the titrating solution without adsorbent and titrating solution with adsorbent, and the intersection of these curves was the pH for the point of zero charge.

3.2.5 Characterization of Adsorbent

The functional groups, surface morphology, structure and surface area of adsorbent were determined using FTIR Spectrophotometer, SEM-EDX and BET.

3.2.6. Batch Adsorption Studies

The adsorption studies for evaluation of the adsorbent for removal of the Cr(VI) ions from aqueous solutions was carried out in triplicate using the batch adsorption procedure (Brasil *et al.*, 2006). For these experiments, varying adsorbent doses were placed in a 250 ml conical flasks containing 50.0 ml of aqueous solutions of Cr(VI) with an initial concentration of 40mg/L which were agitated at varying agitation speeds and at different contact times at a fixed pH greater than the point of zero charge which have been determined

The metal ion uptake and the percentage removal of metal ion were calculated by applying the Equations (3.1) and (3.2), respectively:

$$q = \frac{(C_o - C_f)}{m} * V \qquad (3.1)$$

$$\%\, metal\ ion\ removal = \frac{(C_o - C_f)}{C_o} * 100 \qquad (3.2)$$

Where q is the amount of metal ion adsorbed by the adsorbent (mg/g); *C*o is the initial ion concentration in contact with the adsorbent (mg/L), *C*f is the metal ion concentration at time, t (mg/L) C_f is the metal ion concentration after the batch adsorption ,V is the volume of aqueous solution put in contact with the adsorbent in Land m is the adsorbent dose in g.

3.2.7 Experimental Design for Metal Ion Removal

The Box-Behnken design was employed in the design of experiments involving three variables in metal ion uptake from the solution. This resulted in generation of 17 experimental runs. The selected process parameters for the adsorption of Cr(VI) were contact time, shaking speed and adsorbent dosage. The coded and actual variable levels are displayed in Table 3.3

Table 3.3: Coded and actual levels of the factors for three factors Box-Behnken design

Variables	Symbol	Coded and actual levels		
		-1	0	+1
Adsorbent Dosage (^{g})	X_1	0.2	0.7	1.2
Shaking speed (rpm)	X_2	100	200	300
Contact time (min)	X_3	20	50	80

The Design Expert 8.0.6 (Stat-case, Inc. Minneapolis, USA), a statistical software was used to develop the experimental design using the central composite design in Table 3.3 above to generate 30 experimental runs. The experiments were therefore performed in the laboratory in a random manner in other to avoid any systematic bias in the outcomes.

3.2.7 Modelling and Optimization Using RSM

Response surface Methodology (RSM) was used to model and optimize the uptake of Cr(VI) from aqueous solution. The data obtained from the adsorption experiments were analyzed statistically so as to fit the quadratic polynomial equation (model) generated by The Design Expert 8.0.6 (Stat-case, Inc. Minneapolis, USA). To correlate the response variable (metal ion uptake) to the independent variables (adsorbent dose, shaking speed and contact time), multiple regression was be used to fit the coefficient of the polynomial model of the response. The fitted polynomial equation is as follows;

$$Y_i = b_o + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum b_{ii} X_i^2 + e_i \qquad (3.2)$$

Y_i is the predicted response or dependent variable (bioethanol yield)

X_i and X_j are the independent variables

b_o is the offset term\intercept value

b_i and b_{ij} are the single and interaction effect coefficients and e_i is the experimental error term/ random error

The Design Expert 8.0.6 (Stat-case, Inc. Minneapolis, USA) thereafter developed the regression model in terms of the actual values that describes the production of ethanol from the sawdust. The optimal values of the independent variables for the production of bioethanol from sawdust were obtained by solving equation 3.1 and the yield at these optimum conditions predicted by the model was also recorded.

Table 3.4: Experimental design matrix for Cr(VI) removal from aqueous solution

		Factor 1	**Factor 2**	**Factor 3**
STD	**Run**	**A:Adsorbent Dosage**	**B:Shaking Speed**	**C:Contact time**
		(g)	(rpm)	(mins)
10	1	0.7	300	20
14	2	0.7	200	50
17	3	0.7	200	50
8	4	1.2	200	80
13	5	0.7	200	50
16	6	0.7	200	50
7	7	0.2	200	80
3	8	0.2	300	50
11	9	0.7	100	80

4	10	1.2	300	50
6	11	1.2	200	20
5	12	0.2	200	20
9	13	0.7	100	20
15	14	0.7	200	50
12	15	0.7	300	80
1	16	0.2	100	50
2	17	1.2	100	50

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1. Characterization of Waste Tyre activated carbon (WTAC)

The following analysis explained below were carried out for the characterization of the waste tyre activated carbon which was used for the batch adsorption studies involving the removal of chromium (VI) from aqueous solution. A pH of 8 of the adsorbent was obtained. This was in line with a report by Evbuomwan et al., (2013) that carbons of 6-8 is acceptable for most adsorption applications.

4.1.1 Point of Zero Charge: The point of zero charge (pHpzc) of the WTAC was estimated to be 7 as shown in the Figure 4.1.

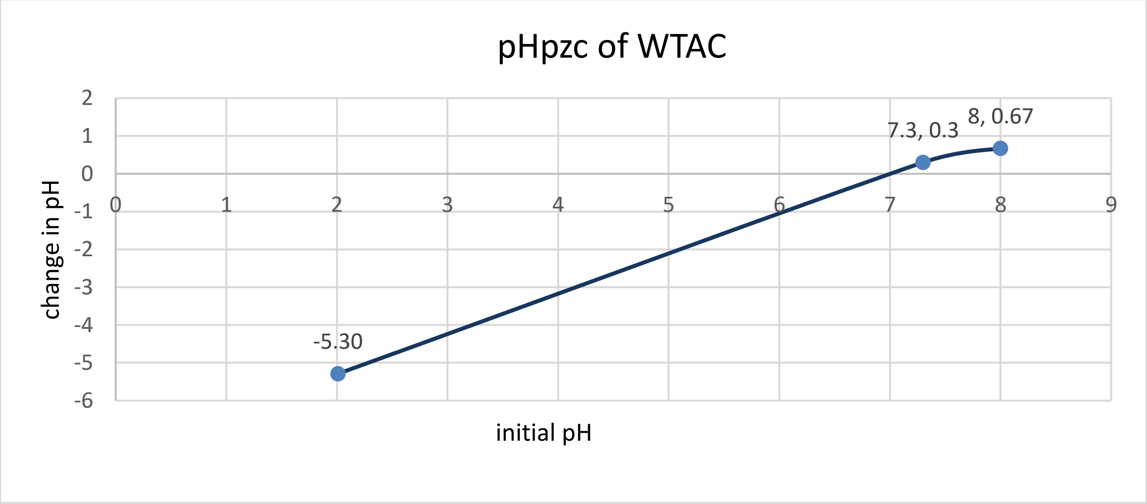


Figure 4. 1: Plot of Point of Zero Charge (pHpzc) of WTAC

In the Figure 4.1 , a plot of final pH against initial pH is represented for the WTAC adsorbent. The point of zero charge (pHpzc) of the sample represents the point where the plot of final pH versus initial pH (represented by the curve) intersects with the line at which the final pH equals to the initial pH (represented by the straight line). The pHpzc occurs when there is no change in the pH after contact with the adsorbent (Ekpete and Horsfall, 2011).

This implied that a pH above the point of zero charge of the WTAC will result in a negatively charged adsorbent surface which will have a greater affinity towards the Chromium (VI) ions.

4.1.2. BET analysis

The BET surface area and pore size distributions of the prepared waste tyre adsorbent before treatment with Cr (VI) was determined. The BET surface area of the prepared raw adsorbent without treating it with Cr (VI) was 38.320 m^2/g. More so, the total pore volume of the adsorbent was observed to bet P/P0=0.988646762:0.624668 cm^3/g

4.1.3. Surface Morphology of Waste Tyre Ash Adsorbent by SEM Analysis

Surface morphology characterization was carried out on tyre ash using SEM at 10000× magnification as shown in figure 4.1 below.

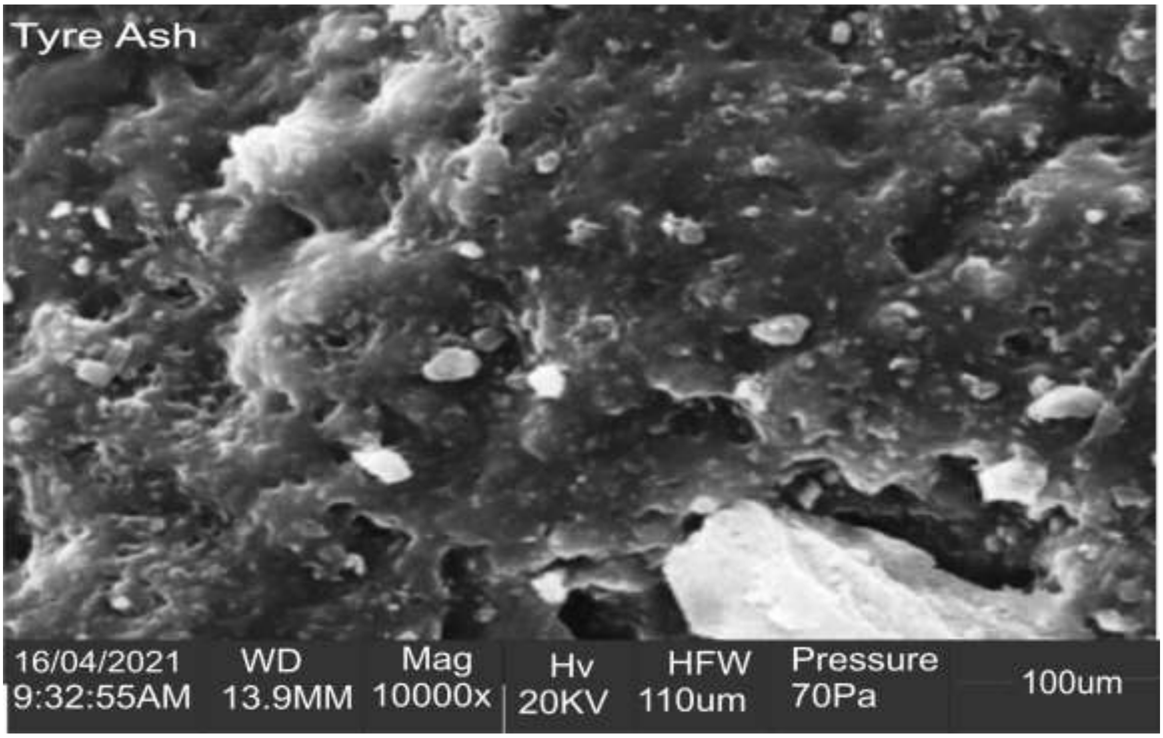


Figure 4. 2: Surface Morphology of waste tyre using SEM

The surface texture and porosity of the sample was determine using SEM. The SEM result of the activated carbon as shown in fig 4.1 reveals the morphological and microstructure characteristics favorable for MB dye adsorption. The result shows that the activated carbon has a rough surface and it is porous. The particles represent presence of varied mixture of mesopores and micropores which is in accordance with the studies of Nazile (2021) who reported that scanning electron microscopy (SEM) analysis on the microstructure of improved clay was porous, had rough surfaces and particle presence was mixture of microspore and mesospores. The particles represent presence of varied mixture of mesopores and micropores. Fernandes *et al.* (2017) also reported the presence of mesopores and micropores in rice husk ash.

4.1.4 EDX Analysis

The elemental composition of the waste tyre activated carbon WTAC was investigated by EDX analysis. The percentage of the various elements found in WTAC is given in Table 4.1.

Table 4. 1: Elemental Composition of Adsorbent

Element	**Wt %**
C	30.50
O	20.23
Na,	0.35
Al	3.20
S	20.49
K	3.20
Ca	0.63
Zn	10.00
Cl	4.20
Fe	2.20
LOI	5.00

The percentage of C and O was found to be 30.50% and 20.23%, and the high quantity of C confirms the synthesis of activated carbon, whereas O may be present as surface functional groups of activated carbon or as oxides. Additionally, some other elements, including Na (0.35%), Al (3.20%), S (20.49%), K (3.20%), and Ca (0.63%), Zn (10.00%), Cl (4.20%), Fe (2.20%) which may be present as oxide impurities or as mineral clays which may be added to rubber as fillers, out of these sulfurs may be present in the tire waste in elemental form.

Percentage mass loss was calculated for the sample. Mass losses are given as percentage loss on ignition at each of the separate temperature steps, and the loss on ignition (LOI) is 5%.The LOI which is part of an elemental analysis of a sample is used as quality test for a sample.s (Nik *et al*., 2021) has reported similar outcome in the use of waste tyre ac magnetic activated carbon (M-AC) using tyre ash and its potential investigation for adsorption of Cr (VI) from wastewater.

4.2 Statistical Analysis

The statistical analysis of metal ion removal from solution was carried out on the experimental values obtained from the Box Behkhen design. The combined factors and responses obtained from the experiment are shown in Table 4. 2 below.

Table 4. 2: Experimental design matrix and obtained responses

Run	**Experimental Factors**			**Response**
	X1:Adsorbent Dosage	**X2:Shaking Speed**	**X3:Contact time**	**Metal ion removed**
	(g)	(rpm)	(min)	%
1	0.7	200	50	85.18
2	0.7	100	80	78.23
3	0.7	100	20	94.75
4	0.7	200	50	83.53
5	1.2	200	20	98.45
6	1.2	100	50	93.68
7	1.2	300	50	96.35
8	0.2	200	80	91.33

9	0.7	200	50	84.69
10	0.2	300	50	98.98
11	0.2	100	50	91.33
12	1.2	200	80	93.35
13	0.2	200	20	99.38
14	0.7	300	80	94.85
15	0.7	200	50	82.68
16	0.7	200	50	83.89
17	0.7	300	20	92.85

4.2.1. ANOVA Analysis

The identified equation of the response surface model that relates the metal ion removal to the process variables in terms of coded factors is shown below.

$$Y = +84.10 + 0.1013X_1 + 3.13X_2 - 3.46X_3 - 1.25X_1X_2 + 0.7375X_1X_3 + 4.63X_2X_3 + 8.22X_1^2 + 2.77X_2^2 + 3.31X_3^2 \qquad (4.1)$$

Where:

Y_1= Metal ion removed

X_1 = Adsorbent Dosage

X_2 = Shaking Speed

X_3 = Contact time

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Table 4. 3: Model Summary Statistics

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	6.16	0.2607	0.0901	-0.2152	811.82	
2FI	6.32	0.4016	0.0425	-0.6927	1130.88	
Quadratic	0.9881	0.9898	0.9766	0.9216	52.39	Suggested

Table 4. 4: Analysis of Variance (ANOVA) for the Response Surface Quadratic Model

Source	Sum of Squares	DF	Mean Square	F-value	p-value	
Model	661.24	9	73.47	75.25	< 0.0001	significant
X_1	0.0820	*1*	0.0820	0.0840	*0.7804*	
X_2	78.38	*1*	78.38	80.27	*< 0.0001*	
X_3	95.70	*1*	95.70	98.01	*< 0.0001*	
$X_1 X_2$	6.20	*1*	6.20	6.35	*0.0398*	
$X_1 X_3$	2.18	*1*	2.18	2.23	0.1791	
X_2 *X3*	85.75	*1*	85.75	87.82	*< 0.0001*	
X_1^2	284.72	*1*	284.72	291.60	*< 0.0001*	
X_2^2	32.21	*1*	32.21	32.99	0.0007	
X_3^2	46.08	*1*	46.08	47.20	0.0002	

Residual	6.83	7	0.9764			
Lack of Fit	2.89	3	0.9631	0.9763	*0.4872*	*not significant*
Pure Error	3.95	*4*	0.9864			
Cor Total	668.08	16				

The Model F-value of 75.25 implies that the model is significant. P-values less than 0.0500 indicate model terms are significant. In this case X_2, X_3, X_1X_2, X_2X_3, X_1^2, X_2^2 and X_3^2 are significant model terms while X_1 and X_1X_3 are non-significant terms. Values greater than 0.05 indicate the model terms are not significant.

The Lack of Fit P-value of 0.4872 implies that the Lack of Fit is not significant relative to the pure error. There is a 48.72% chance that a Lack of Fit F-value this large could occur due to noise. Therefore, a non-significant lack of fit is good.

Table 4. 5: ANOVA Fit Parameters

Parameter	Value
R-Squared	0.9898
Adj R-Squared	0.9766
Pred R-Squared	0.9216
Adeq Precision	27.4074
Std. Dev.	0.9881
Mean	90.82
Coefficient of variation% (CV).	1.09

The high R-square value (coefficient of determination) of 0.9898 indicates that the fitted model predicts the metal ion removal with reasonable precision. The Predicted R^2 of 0.9216 is in reasonable agreement with the Adjusted R^2 of 0.9766; i.e. the difference is less than 0.2.

The small value, 1.09% for the coefficient of variance (CV). indicates a high reproducibility for the model. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 27.407 indicates an adequate signal. This model can be used to navigate the design space. The ANOVA therefore shows that fitting of the model to the experimental data has a high quality.

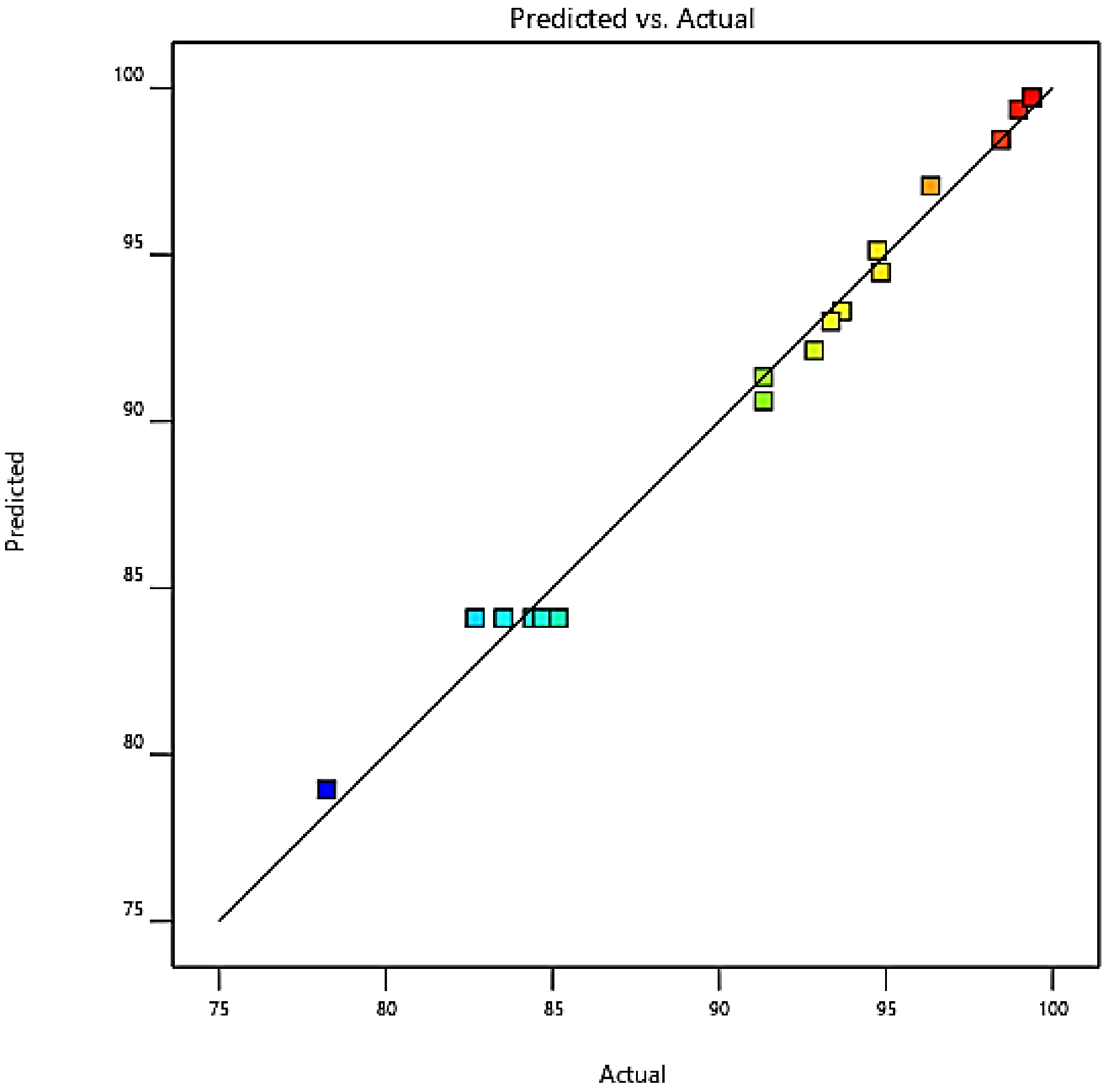


Figure 4. 3: Predicted vs actual experimental values

4.1.2: Effect of process variables on metal ion removal

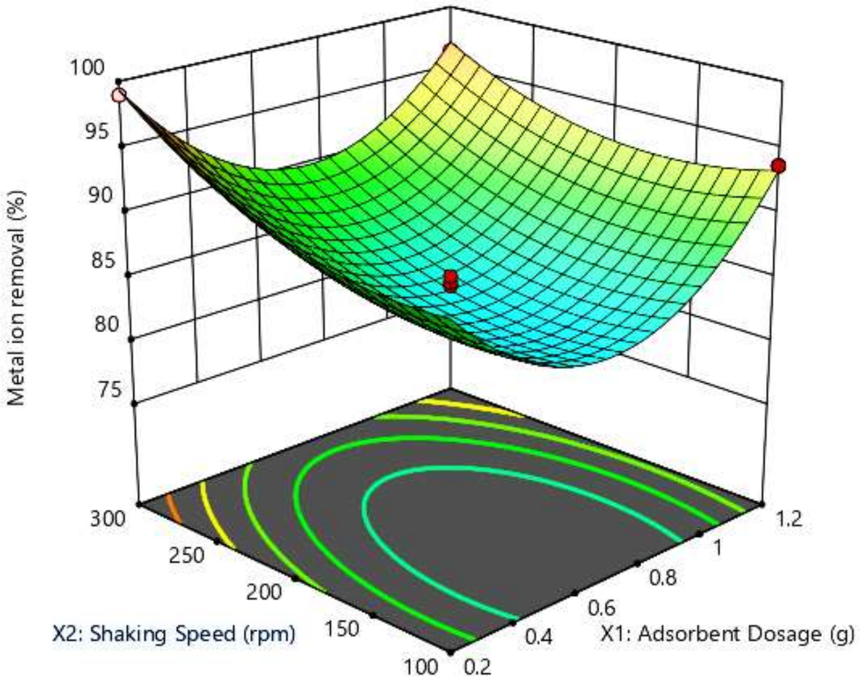


Figure 4. 4: 3D Response surface plot of Shaking Speed and Adsorbent Dosage interaction effect on chromium ion removal

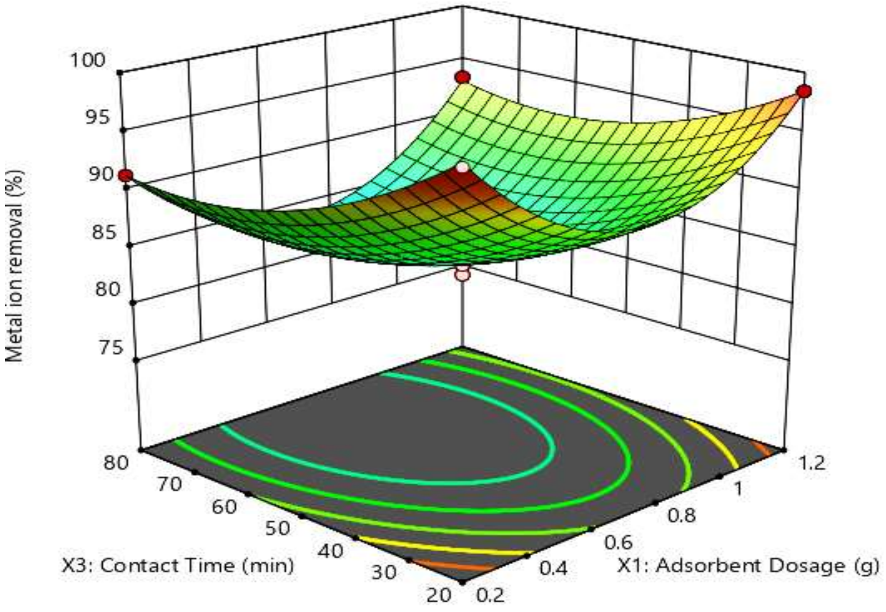


Figure 4. 5: 3D Response surface plot of contact time and adsorbent dosage interaction effect on metal ion removal

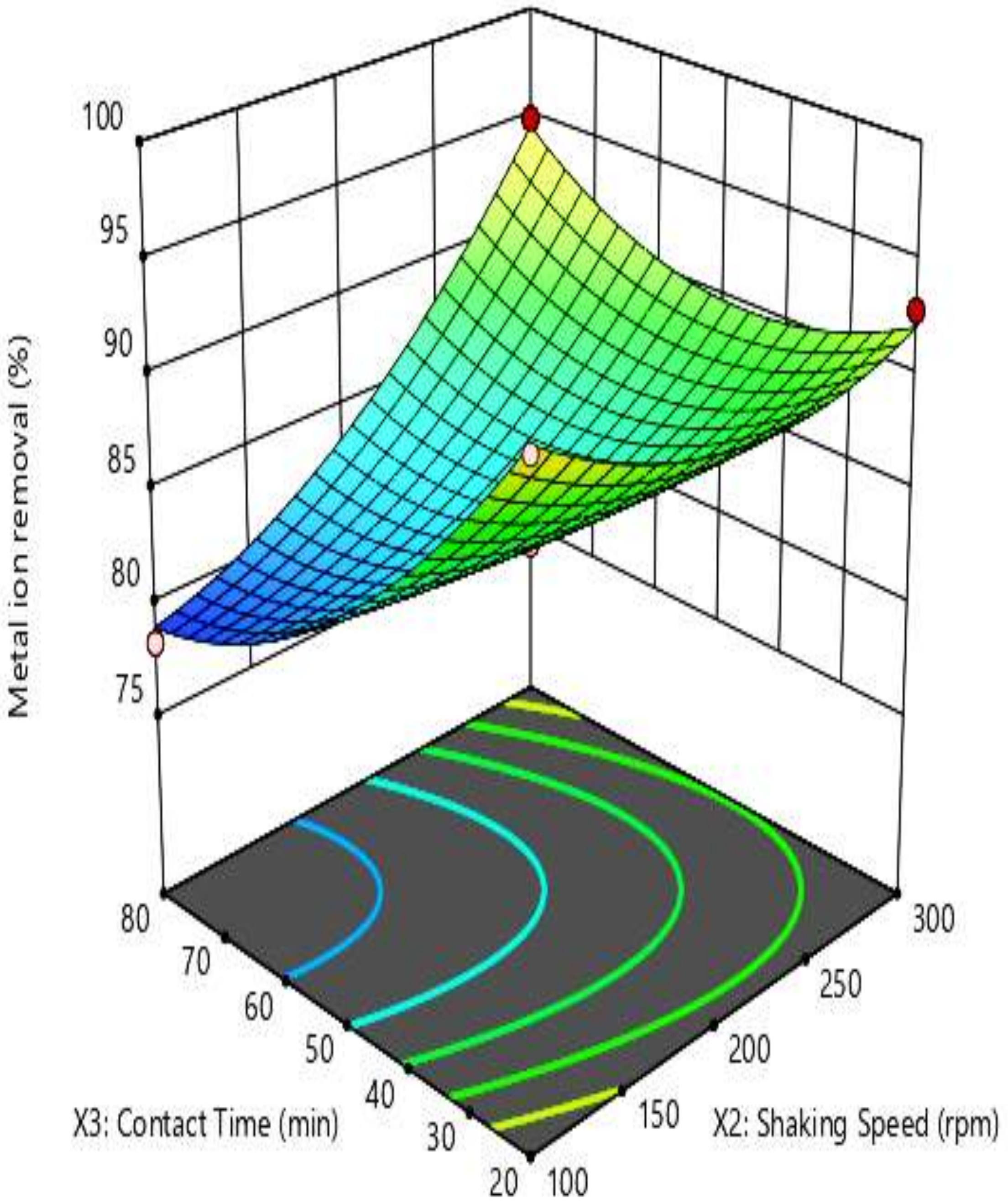


Figure 4. 6: 3D Response surface plot of contact time and shaking speed interaction effect on metal ion removal

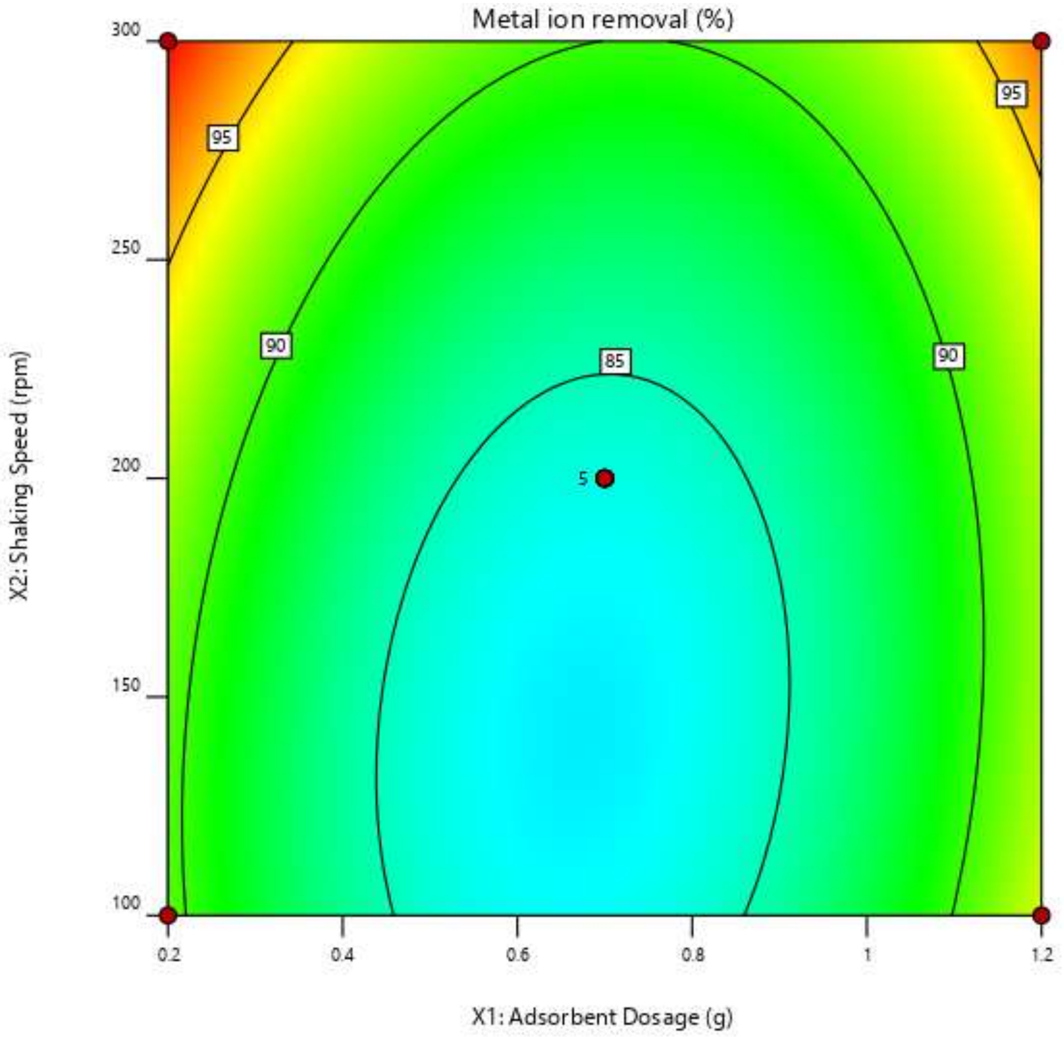


Figure 4. 7: Response surface contour plot of shaking speed and adsorbent dosage interaction effect on metal ion removal

As can be seen from the contour plot above and its corresponding 3D plot in Figure 4.5 above, it is seen that an increase in shaking speed increases the metal ion removal, as at a shaking speed of 100rpm, the metal ion removal was 93%, the metal ion removal decreased slightly at an increase in the shaking speed but this effect was countered by a rapid increase to about 98.7% as seen on the plot at a shaking speed of 300rpm. On the other hand, at an adsorbent dosage of 0.2g, the metal ion removal was 93%, as the adsorbent dosage increases, the metal ion removal reduced drastically, after which an increase was noticed up to about 93.4%.

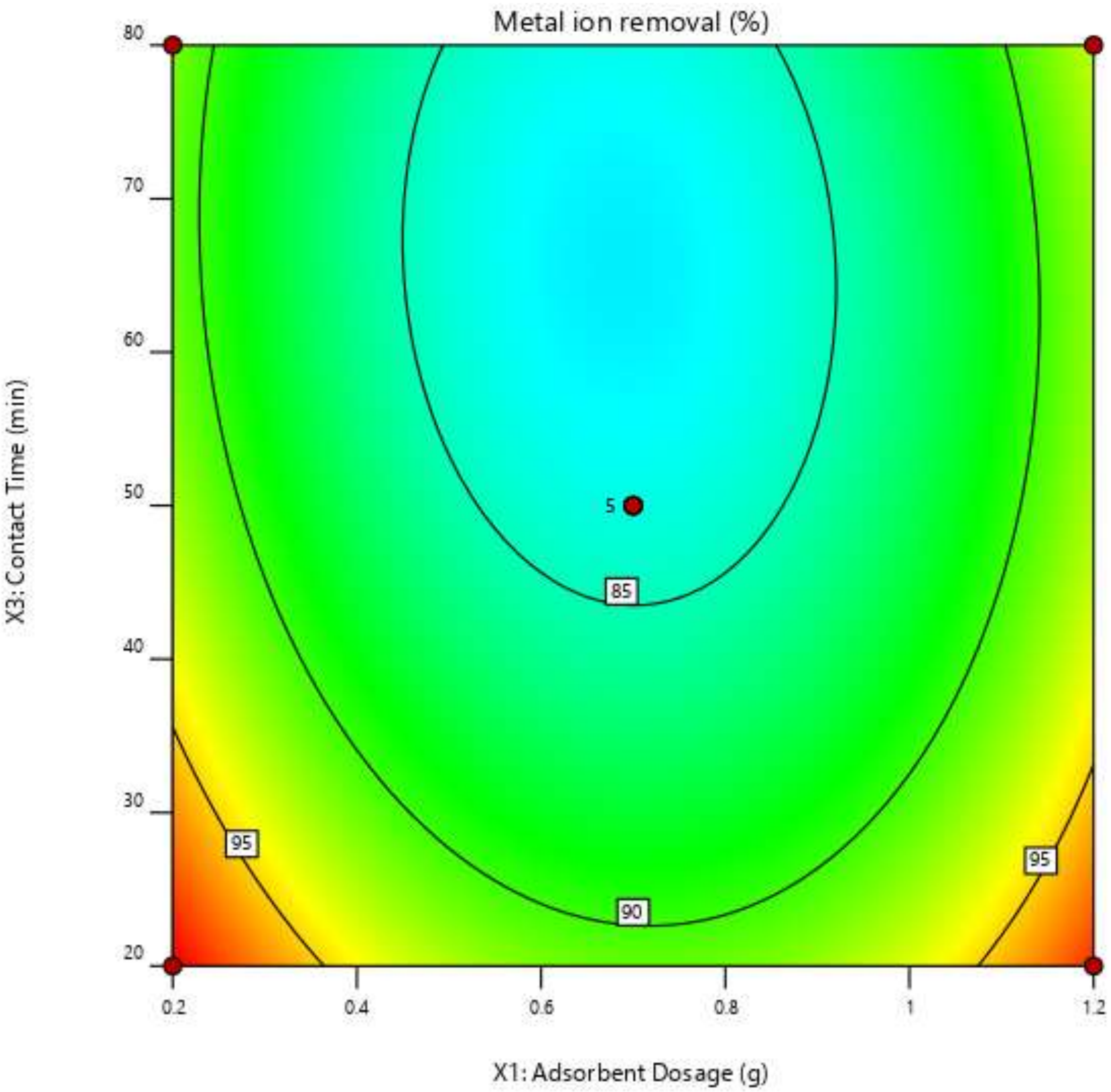


Figure 4. 8: Response surface contour plot of contact time and adsorbent dosage interaction effect on metal ion removal

From the contour plot above and the corresponding 3D plot in Figure 4.6 above, it is seen that an increase in contact time caused a decrease in the metal ion removal. As it can be observed that at a contact time of 20mins, the metal ion removal was at its highest, the metal ion removal reduced gradually as the contact time increases to 80mins, while at an adsorbent dosage of 0.2g, the metal ion removal was 98%, as the adsorbent dosage increases, the metal ion removal reduced drastically, after which an increase was noticed up to about 97.6%.

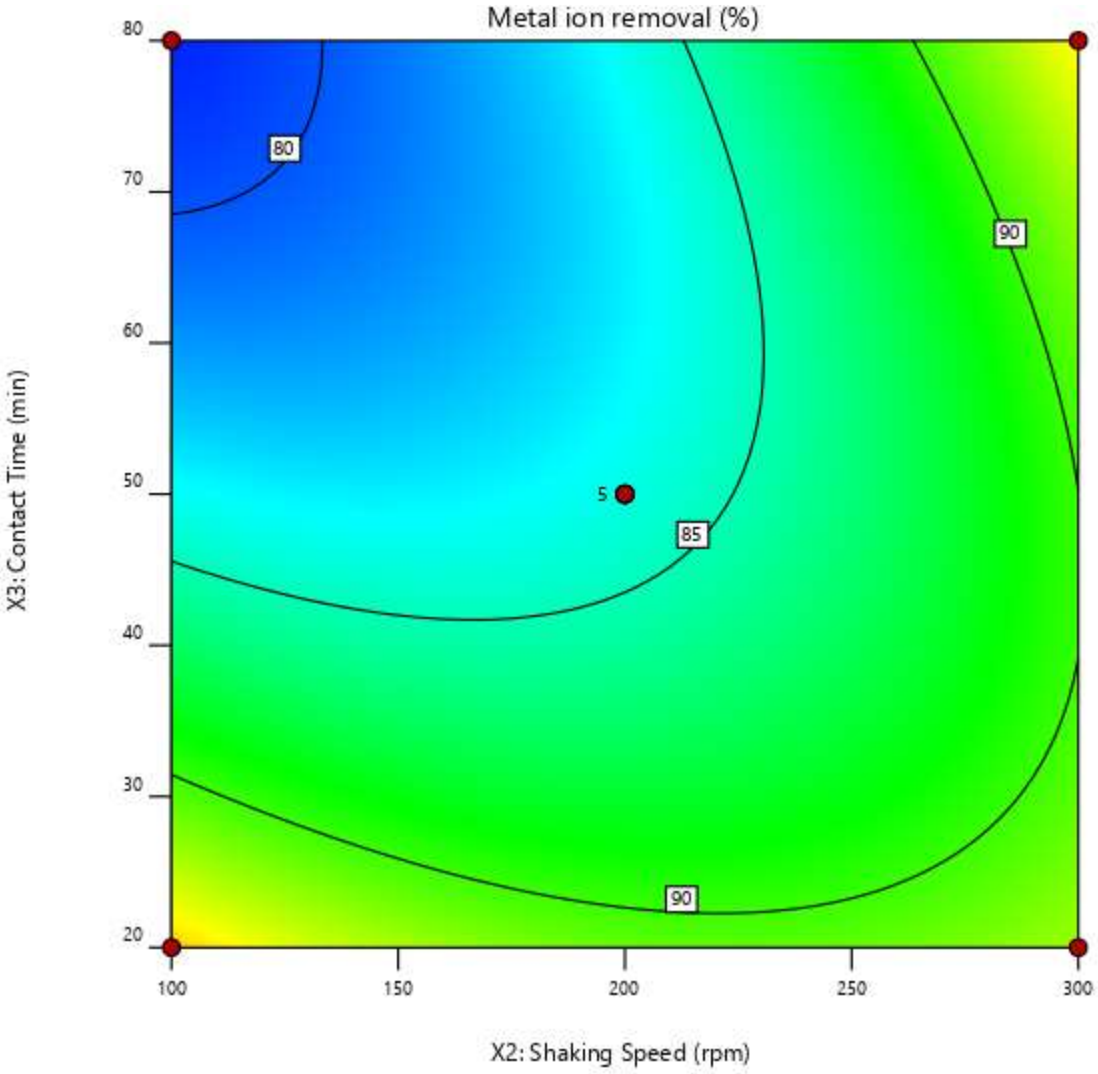
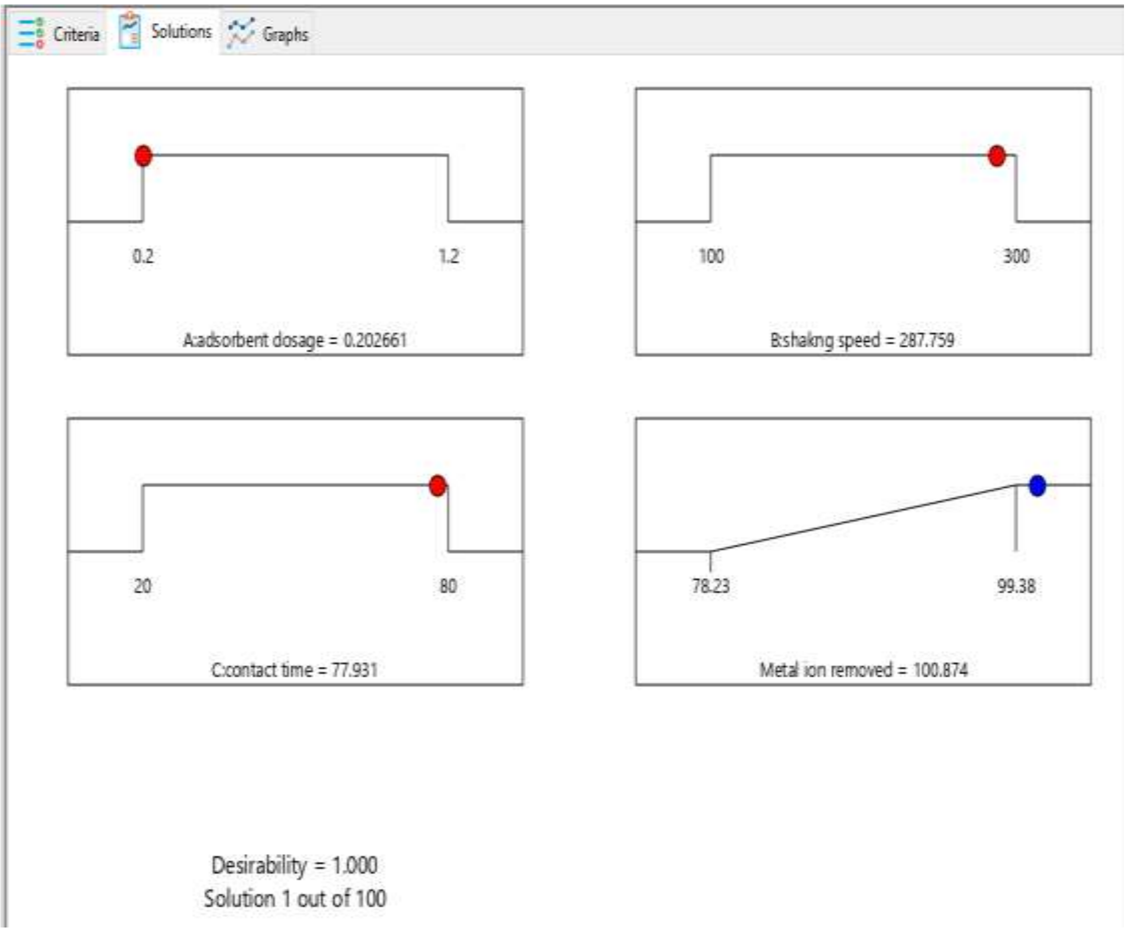


Figure 4. 9: Response surface contour plot of contact time and shaking speed interaction effect on metal ion removal

From the contour plot above and the corresponding 3D plot in Figure 4.7 above, it is seen that an increase in contact time caused a decrease in the metal ion removal. As it can be observed that at a contact time of 20mins, the metal ion removal was at its highest which was about 93.4%, the metal ion removal reduced gradually and finally ends at 77.8% as the contact time increases to 80mins. It is seen that an increase in shaking speed causes little or no decrease to the metal ion removal, as at a shaking speed of 100rpm, the metal ion removal was 92.8%, the metal ion removal decreased slightly at an increase in the shaking speed then followed by an increase to about 92.8% as seen on the plot at a shaking speed of 300rpm

4.1.3: Optimization



A:adsorbent dosage = 0.202661

B:shakng speed = 287.759

C:contact time = 77.931

Metal ion removed = 100.874

Desirability = 1.000
Solution 1 out of 100

Figure 4. 10: Optimization of Metal ion removal

Based on the identified model and the numerical optimization shown above, the predicted maximum metal ion removal of 100.874% was obtained at 0.202661 g adsorbent dosage, 287.759 rpm shaking speed and 77.931 min contact time, and a desirability value of 1 was gotten.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1. Conclusions

The study shows that waste tyre is an effective adsorbent for the removal of chromium VI ions from aqueous solutions, based on the identified model, the predicted maximum metal ion removal of 100.874% was obtained at 0.202661g adsorbent dosage, 287.758rpm shaking speed and 77.931min contact time. The activation of this carbon could increase the economic viability of this recycling process.

5.2 Recommendation

Seeing the results obtained from the experiments carried out in this study, from the 3D and contour graphs analysis and numerical optimization, it is recommended for the case of further studies and experiments to be carried out in the future, that the shaking speed and adsorbent dosage be varied at higher revolutions per minute, as higher shaking speeds and higher adsorbent dosages gave better metal ion removal percentage.

After this experiment and considering the results gotten, it is recommended that this project can be practiced on a commercial scale, as waste tyre has been clearly seen to be a good adsorbent for the removal of Chromium VI.

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