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## Effect of Bed height on Chromium (III) and Manganese (IV) Fixed-bed Column Adsorption from Crude Oil Contaminated Water from Okuru River in Ogali, Eleme, Rivers State, Nigeria

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doi: [https://doi.org/10.37745/ijep.13/vol12n14974\\_](https://doi.org/10.37745/ijep.13/vol12n14974_)

Published December 18 2023

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**Citation:** Lawrence M.O. and Ogori B. (2024) Effect of Bed height on Chromium (III) and Manganese (IV) Fixed-bed Column Adsorption from Crude Oil Contaminated Water from Okuru River in Ogali, Eleme, Rivers State, Nigeria, *International Journal of Environment and Pollution Research*, 12(1),49-74

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**ABSTRACT:** *The removal of Cr (III) and Mn (IV) fixed-bed column adsorption from crude oil contaminated water was evaluated using atomic absorption spectrophotometer (AAS). Activated carbon prepared from sorghum (bicolor) chaff was used to adsorb Cr (III) and Mn (IV). The evaluated physicochemical properties of the activated carbon were pH (6.30), bulk density (0.33 g/cm<sup>3</sup>), moisture content (4.40%), Iodine Adsorption Ratio (0.28 mol/g), porosity (13.00), attrition factor (11.00%), and surface area (797.4 m<sup>2</sup>/g). Optimum percentage adsorption and equilibrium adsorption capacity for the effect of pH, inlet flow rate, bed height, inlet concentration and particle size gave, (89.796, 90.116, 93.046) % and (2.245, 2.253, 2.326) mg/g, (74.720, 84.990, 91.346) % and (2.277, 2.275, 2.284) mg/g, (88.192, 89.994, 90.190) % and (2.205, 2.249, 2.255) mg/g, (88.934, 90.002, 90.634) % and (2.223, 2.250, 1.266) mg/g, (91.346, 89.964, 88.936) % and (2.284, 2.249, 2.223) mg/g for Cr (III) and (84.630, 87.830, 82.507) % and (1.269, 1.317, 1.238) mg/g, (47.770, 74.425, 83.790) % and (0.239, 0.744, 1.257) mg/g, (85.590, 84.023, 83.167) % and (1.284, 1.260, 1.248) mg/g, (82.473, 83.790, 85.230) % and (1.237, 1.257, 1.278) mg/g, (88.497, 87.220, 84.420) % and (1.327, 1.308, 1.266) mg/g for Mn (IV) respectively. The results therefore, shows that percentage adsorption increases with the effects mentioned and the kinetic data fitted well to the model for the effect of bed height.*

**KEYWORDS:** Fixed-bed column adsorption, Chromium (III), Kinetics, Manganese (IV), Bed height, Okuru River

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### INTRODUCTION

Water is critical to the existence of the human race and aquatic life. This is because it is a resource for ecosystem sustainability, delivering life-sustaining functions to people, animals, and plants. However, the discharge of heavy metals such as chromium and manganese into aquatic

environments via crude oil has become a source of concern in Nigeria over the previous few decades. According to many sources, water contamination can result in low profitability, bad living circumstances, and even the death of living beings (Garba et al., 2010).

Crude oil water contamination has been a major concern in the Niger Delta region of Nigeria through oil exploration and exploitation activities from petroleum companies like Shell Nigeria. Their technological processes generate and increased pollution of the Niger Delta environment, through sabotage, accidental spillages, leaks from producing wells, storage tanks, gathering lines, pipelines, flow stations, refineries and industrial dump sites (Onwuka et al 2021). A lot of crude oil spills and wastewater are discharged without treatment into the waterbodies like Okuru River in Ogali, Eleme, Rivers State. Consequences of this are severe health challenges to human such as blindness in children, kidney failure, cancer, lungs related diseases, mutation, and even death. Aquatic habitats are also not left out. Bio-accumulation of heavy metals in the bodies of aquatic animals can be transferred to human through consumption (Enegide C., and Chukwuma K. C., 2018).

Eleme is a community in Rivers State, Nigeria which is one of the oil producing and agro-ecological areas of Nigeria's Niger-Delta region, a region rich in natural resources such as good weather and agricultural land. Despite the fact that agricultural productivity in that region is quite low given its vast resource endowment, it is the country's greatest oil producing zone. It is the foundation of Nigeria's oil and gas industry, accounting for more than 90% of the country's GDP (T.A. Abii and P.C. Nwosu, 2009). The toxicity of heavy metals in the environment is still major concerns of human life; because they accumulate in living tissues throughout the food chain which has humans at its top. Therefore, treatment of water and waste water containing heavy metals is very demanding (Prabakaran and Arivoli, 2013).

Adsorption, wet oxidation, solvent extraction, precipitation, ultrafiltration, reverse osmosis, ion exchange, chemical coagulation, flocculation, membrane technologies, electrolytic recovery, and flotation are the most commonly cited heavy metal removal technologies. Adsorption is the most recommended approach among these possibilities, and activated carbon is the most effective adsorbent commonly used to treat waste water containing various classes of metal ions, since it is a low-cost commercial activated carbon. (El-Sayed et al, 2011, Prabakaran and Arivoli, 2013, and Jameel and Hiend, 2012).

Despite these wide methods, they have disadvantages, which include incomplete metal removal requirement and expensive equipment. Recently many researchers in the world investigated low-cost adsorbents with high metal binding capacities. Hence, agricultural by-products have been widely used for treatment of water containing heavy metal (Jameel and Hiend, 2012). This work, presents the use of sorghum bicolor chaff which is an agricultural industrial waste product as adsorbent for the removal of Cr (III) and Mn (IV) and the study of the effect of bed height on their removal.

## LITERATURE REVIEW

### Crude Oil Contaminated Water

Crude oil is a mixture of comparatively volatile liquid hydrocarbons (compounds composed mainly of hydrogen and carbon), though it also contains some nitrogen, sulfur, and oxygen. Crude oil is found accumulated in various porous rock formations in Earth's crust and is extracted for burning as fuel or for processing into chemical products. Crude oil exploration and exploitation is very lucrative, and a major revenue earner in Nigeria. But, like most industrial activities, it produces environmental hazards that are "slow poisons," in that they often take months and years to cause disease and death. This is unlike the contamination of water, food, and the environment with micro-organisms, which immediately results in ill health (Ordinioha B. and Brisibe S., 2013). Crude oil is a colloidal mixture of huge number of hydrocarbon and non-hydrocarbon. The source material for nearly all petroleum products is crude oil. Spill, leaks and other releases of gasoline, diesel, fuels, heating oils and other petroleum products often result in the contamination of soil and water. Hydrocarbon forms over 90 percent of petroleum oil are grouped according to their chemical structures such as straight, branched and cyclic alkanes and aromatics. The non-hydrocarbon components of petroleum include (O<sub>2</sub>, N, S ---) and some metals related porphyrin oxygen containing compounds e.g. naphthenic acid, carboxylic acid, esters, ketones, phenols etc. Oil pollution occurs when oil is introduced into the environment directly or indirectly by men's impacts resulting in unfavorable change in such a way that safety and welfare of any living organisms is endangered. Crude oil if spilled into the water spreads over a wide area forming a slick and oil in water immediately begins to undergo a variety of physical, chemical and biological changes including evaporation of high volatile fractions, dissolution of water-soluble fractions, photochemical oxidation, drill, emulsification, microbial degradation and sedimentation (Edema N., 2012)

Nigeria is the largest oil producer in Africa and the eleventh largest producer of crude oil in the world. Prospecting and extraction of petroleum occur in over 50% of the Niger Delta region, resulting in a cornucopia of access roads, pipelines, wells, gas flaring, dredged spoils and flow stations that are often located near homes, schools, farms, waterbodies and within communities. Oil spills are common throughout the area, as a consequence of pipeline corrosion, poor maintenance of infrastructure, spills or leaks at the well heads, human error, theft of oil and intentional vandalism. The amount of oil that is spilled in the Niger delta is unknown (Nriagu et al., 2016). A report by (Jernelov, 2010) estimated that the total spillage was between 9 and 13 million barrels over 50 years—roughly 1.5 million tons per year, equivalent to one Exxon-Valdez spill annually for half a century. The collective impacts of these pervasive massive spills on the environment and local inhabitants are worsened by seasonal floods which transfer the oil pollution to farmlands and occupied areas. Currently, hundreds of thousands of people who live in the Niger delta are being exposed to crude oil contamination near their homes, farmlands, fishing grounds and in their drinking water and foods but the consequences of such exposure on their health are unknown.

### **Heavy Metals Water Pollution**

Water pollution is the contamination of water by foreign matter that deteriorates the quality of the water. As the term applies, liquid pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short liquid-containing areas. It involves the release of toxic substances, pathogenic germs, substances that require much oxygen to decompose, easy-soluble substances, radioactivity, etc. that becomes deposited upon the bottom and their accumulations will interfere with the condition of aquatic ecosystems. According to the water cycle, naturally, water around us will be absorbed to the land (soil) and rivers will stream from the upstream to the downstream and released to the sea. In normal situation organic pollutants are biodegraded by microbes and converted to a form that brings benefits to the aquatic life. And for the inorganic pollutants, like heavy metals, in the same situation, do not bring too much hazards because they are widely dispersed and have almost no effect to the environment which they are released to. Some of the pollutants like manganese, lead, arsenic, mercury, chromium especially hexavalent chromium, nickel, barium, cadmium, cobalt, selenium, vanadium, oils and grease, pesticides, etc are very harmful, toxic and poisonous even in parts per billion range. However heavy metal pollution of surface and ground water sources results in considerable soil pollution and pollution increases when mined ores are dumped on the ground surface for manual dressing and during crude oil exploration and exploitation activities (Rashmi V. and Pratima D., 2013).

### **Chromium**

Chromium is one of the major trace heavy metal pollutants in the environment. Chromium in environmental waters typically comes from industrial pollution sources, including crude oil exploration and exploitation activities, tanning factories, steel works, wood preservation and artificial fertilizers. It is widely known that the toxicity and biological activity of the element not only depends on the total amount, but also on its chemical form. Chromium species exist mainly in two different oxidation states in environmental water. Cr (VI) and Cr (III), which have contrasting physiological effects. Cr (III) is considered as an essential trace element for the maintenance of an effective glucose, lipid and protein metabolism in mammals. On the other hand, Cr (VI) can be toxic for biological systems and cancerogenic in humans. Therefore, speciation of Cr (VI) and Cr (III) is necessary for evaluating the toxicological behaviour of chromium (Oremusová J., 2007).

### **Manganese**

Manganese is a very abundant, widely distributed in the earth's crust. It does not occur naturally in the native state, the most important manganese-containing minerals being oxides, silicates and carbonates, while the most common is pyrolusite (MnO<sub>2</sub>). Manganese also occurs in most iron ores, in coal and in much lower concentrations, in crude oil. Manganese is used mostly in metallurgical processes, but it is also used in the manufacturing of dry-cell batteries, glass, fertilizers and in the leather and textile industries. Organic carbonyl compounds are used as fuel-additives and smoke inhibitors. Manganese is released into the atmosphere by both natural and anthropogenic processes, mostly in the form of coarse particles, through wind erosion, road dusts, agricultural and building activities and quarry processes. In the form of fine particles, it is released

into the atmosphere by natural ore smelting and fossil-fuel combustion. Manganese is also emitted by the manufacturing of ferroalloys and other industrial processes. Since it has a low volatility, manganese settles mostly in the immediate vicinity of its source of release (Amal H.M., 2018).

### Adsorption

The “adsorption” was suggested by Bois-Reymond but given into the world by Kayser, which is defined as an increasing concentration of a specific compound at the surface of interface of the two phases. These specific compounds are transporting from one phase to another and thereafter adhered into surface. It is considered to be a complex phenomenon and depends mostly on the surface chemistry or nature of the sorbent, sorbate and the system conditions in between the two phases. It is the most inexpensive and efficient process for treatment of water or wastewater; therefore, it has been widely used for the removal of solutes from solutions and harmful chemicals from environment. It required less investment in terms of the initial cost and land, simple design, no other toxic effect and superior removal of organic waste constituent, compared to the other conventional treatment in water pollution control (Dabrowski 2001; Selim et al., 2014).

### Column Adsorption Kinetic Models

#### Bed-Depth Service-Time kinetic model

The bed depth service time (BDST) model describes the relationship between  $C/C_0$  and  $t$  in a continuous system. The experimental data can be modeled by establishing a term called service time, which was defined as the time required for the effluent concentration to reach 1mg/L of the adsorbate. The bed height ( $Z$ ), and service time ( $t$ ), have a linear relationship which was given by BDST model written as;

$$t = \frac{N_o Z}{C_o V} - \frac{1}{k_a C_o} \ln\left(\frac{C_o}{C} - 1\right)$$

Where,  $C$  is the breakthrough adsorbate concentration (mg/L)

$N_o$  is the sorption capacity of bed (mg/L)

$V$  is the linear velocity (cm/min)

$k_a$  is the rate constant ( $Lmg^{-1}min^{-1}$ )

This simplified and design model ignores the intra-particle mass transfer resistance and external resistance directly (Rajeshkannan et al., 2013).

### Physicochemical Properties of Adsorbents

#### pH

Adsorbent, given in terms of pH values, is a measure of the active acidity or hydrogen ion ( $H^+$ ) activity of the adsorbent solution. pH is define as the negative logarithm of the hydrogen ion concentration (activity) [10]. It is well known that solution of pH is an important factor controlling the surface charge of adsorbent and the degree of ionization of the adsorbate in aqueous solution (El-Kholy et al 2013).

$$\text{pH} = -\log[\text{H}^+]$$

where,  $[\text{H}^+]$  is activity of  $[\text{H}^+]$  ions in mole/liter

### **Bulk Density**

Bulk density is one of the parameters that describe the quality of an adsorbent. It predicts the filterability of an adsorbent. High values of bulk density portend good quality adsorbent. Bulk density is the measure of the weight of a material per unit volume expressed in grams per centimetre cube (g/cm<sup>3</sup>) (Adie et al 2013).

### **Porosity**

Porosity of an adsorbent is a measure of the void in the adsorbent; and the greater the porosity of given adsorbent, the greater would be the relative size of molecules it can adsorb onto its crystal structure. Thus, the ion exchange or adsorption characteristics of adsorbent are determined also by the size and geometry of its pore spaces (Adie et al 2013).

### **Attrition Factor**

This is also known as percent abrasion resistance. It is an indicator of the mechanical strength of an adsorbent for aqueous phase applications. It describes the ability of the adsorbent to, not only maintain its physical integrity during the adsorption process but also its ability to withstand frictional forces imposed by back washing. Previous investigations have revealed that for an adsorbent, particularly the low cost ones to be considered for economic purposes, it should possess not only impressive adsorption properties, but also a high resistance to abrasive forces in batch and column applications. Low abrasion resistance leads to loss of adsorbent particle integrity and formation of dust particles, resulting in the reduction in the rate of filtration, and in the amount of the adsorbent (Adie et al 2013).

### **Surface Area**

Surface area of an adsorbent usually measures the extent of pore surface developed within the matrix of the adsorbent. Its value indicates the functionality of an adsorbent. Its value indicates the functionality of an adsorbent based on the principle that greater the surface area, the higher the number of available adsorption sites. A large surface area is therefore, a necessary requirement for a good adsorbent (Adie et al 2013).

### **Iodine adsorption ratio (IAR)**

This is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level of an adsorbent to adsorb iodine hence higher degree indicates higher activation. IAR is a measure of the microspore content of the activated carbon by adsorption of iodine from solution. The higher the iodine adsorption ratio, the higher the efficiency of adsorption of the adsorbent (Itodo et al, 2010).

### **Moisture Content**

This is the quantity of water contained in a material. Moisture content is used in a wide range of scientific and technical areas, and is expressed as a ratio, which can range from zero (completely dry) to the value of the materials' porosity at saturation. It can be given on a volumetric or mass (gravimetric) basis (Rajeshkannan et al, 2013).

### **Particle size**

Particle size is a notion introduced for comparing dimensions of solid particles (flecks), liquid particles (droplets), or gaseous particles (bubbles). The notion of particle size applies to colloidal particles, particles in ecology, particles present in granular material (whether airborne or not), and particles that form granular material (Ahile et al 2015).

### **Materials and Methods**

#### **Sample Collection**

The sorghum bicolor chaff used in this work was collected from Benue Brewery Nigeria Limited, Gboko-Makurdi Road, Makurdi, Benue State, Nigeria and the crude oil contaminated water was collected from Okuru River in Ogali, Eleme, Rivers State, Nigeria.

#### **Sample Preparation**

The sorghum bicolor chaff was washed clean of dust with water, soaked in clean water for about 4 hours. The sorghum bicolor chaff was collected in the form of a paste and it was filtered using a wire mesh while washing the residue each time with distilled water. The cleaned residue (sorghum bicolor chaff) was air-dried. The residue was reduced into particle size (powdered form) with the aid of a porcelain mortar and pestle, from which was further passed through 354  $\mu$ m mesh to retain a good, uniform and finer particles. The residue was steeped in 1.0 M phosphoric acid for 24 h at room temperature and it was washed with distilled water and air-dried at room temperature. The sorghum bicolor chaff was carbonized at 500 °C- 600 °C using a muffle furnace and crucibles for 20 min. The carbonised sorghum chaff was allowed to cool, washed with distilled water to remove ash particles and kept in air-tight plastic container prior to analysis.

#### **Determination of Physicochemical Properties of Adsorbent**

##### **Determination of pH**

1 g of the adsorbent sample was weighed and steeped in 100 mL of distilled water and was then placed on a magnetic stirrer and stirred for 4 h. The mixture was then filtered and pH of the filtrate was determined using a pH meter (Itodo et al 2010).

##### **Determination of bulk density**

2 g of the adsorbent sample was placed into a 10 mL graduated measuring cylinder and compacted by tapping on the bench top until an expected volume;  $V$  ( $\text{cm}^3$ ) was occupied by the mass,  $m$  (g). The cylinder was tapped on the bench top until the volume of the sample stop decreasing. The mass and volume were recorded and the density was calculated (Itodo et al 2010);

$$\rho = \frac{\text{Mass}}{\text{Vol. occupied}}$$

#### Determination of moisture content

An empty dry crucible was weighed. 5 g of the sample was weighed into the empty clean dry crucible and the weight of the crucible and sample was noted. The crucible was transferred into an oven for 1 h 30 min for drying at 105 °C. After drying, it was transferred into a desiccator to cool and then reweighed (Itodo et al 2010).

Calculation:

$$\% \text{ moisture content} = \frac{M_3 - M_2}{M_2 - M_1} \times 100$$

Where,  $M_1$  = weight of the empty dry crucible

$M_2$  = Weight of the crucible and sample before drying

$M_3$  = Weight of the crucible and sample after drying

#### Determination of iodine adsorption ratio (IAR)

1.0 g of adsorbent was weighed into a beaker and 25 mL of 0.05 M iodine solution added. The mixture was stirred vigorously for 10 min and filtered by means of a funnel impregnated with glass wool at the stem. A 20 mL of the resulting filtrate was then titrated with 0.1 M sodium thiosulphate solution to a persistent pale-yellow colour. 5 mL of freshly prepared starch indicator solution was added to give a dark-blue solution and titration with thiosulphate resumed slowly until a colourless solution appeared. The procedure was repeated two more times and the average was taken. The titration was carried out with 20 mL portion of the 0.05 M iodine solution not treated with the adsorbent to serve as blank. The blank titration was repeated two more times. The iodine adsorption ratio,

IAR, was calculated using the expression

$$\text{IAR (mol/g)} = M_{\text{S}_2\text{O}_3^{2-}} (V_b - V_s) / 2m_a$$

Where  $M_{\text{S}_2\text{O}_3^{2-}}$  is the molarity of thiosulphate solution (M),  $V_b$  the average volume of thiosulphate used for blank titrations (mL),  $V_s$  the average volume of thiosulphate used in titration of adsorbent treated aliquots (mL), and  $m_a$  the mass (g) of adsorbent used (Itodo et al 2010).

#### Determination of porosity

3.0 g of the adsorbent was weighed into 100 mL beaker. 100 mL (initial volume,  $V_i$ ) of distilled water was added and left to stand for 48 h. The adsorbent was then filtered out and the filtrate (final volume,  $V_f$ ) was measured. The porosity was calculated using the expression (Adie et al 2013).



$$\text{Porosity} = V_i - V_f$$

#### Determination of Attrition Factor

1.0 g of adsorbent was placed in 50 mL of distilled water. It was stirred with a magnetic stirrer for 2 h. The solution was filtered and the residue was dried and weighed. Percentage of attrition was calculated as (Adie et al 2013);

$$\text{Attrition (\%)} = \left( \frac{\text{initial weight of adsorbent (g)} - \text{final weight of adsorbent (g)}}{\text{initial weight of adsorbent (g)}} \right) 100$$

#### Determination of surface area

1.0 g of the adsorbent was weighed and stirred in 100 mL of 0.1 M of HCl. Then a 30 g of NaCl was added while stirring the suspension and then the volume was made up to 150 mL with deionized water. The solution was titrated with 0.1 M NaOH and the volume, V, was recorded (Nwabanne and Igbokwe, 2012). The surface area according to this method was calculated as;

$$S = 32V - 25$$

Where, S = surface area of the adsorbent, V = volume of NaOH

#### Fixed-Bed Column Adsorption Studies

Fixed-bed column adsorption studies were conducted on sorghum (bicolor) chaff in a glass adsorption column with inner diameter of 2.4 cm and a height of 24 cm, packed with a known quantity of the adsorbent. The crude oil contaminated water at a known concentration was introduced into the column by gravitational flow. The desired inlet flow rate was regulated as the adsorption studies was subjected to different conditions such as pH, bed height, inlet concentration, inlet flow rate and particle size. Samples were collected at regular time intervals and analysed using Atomic Absorption Spectrophotometer (AAS model-PGAA500) (Hanan and Abdelmottaleb, 2013).

The percentage adsorption of Cr (III) and Mn (IV) was calculated using the expression;

$$A = \frac{C_0 - C_t}{C_0} \times 100$$

Where,  $C_0$  and  $C_t$  are the Cr (III) and Mn (IV) concentrations in mg/L initially and at a given time t

The amount of Cr (III) and Mn (IV) adsorbed in mg/g at time t was computed by using the equation;

$$q_t = \frac{(C_o - C_t)V}{m}$$

Where,  $q_t$  is the amount adsorbed at  $t$ ,  $V$ , volume of metal ion solution in mL,  $m$ , mass of adsorbent in g

### **Effect of pH**

The effect of pH on adsorption was studied by adjusting the pH of the crude oil contaminated water with acetic acid and NaOH solution to 3.38, 7.00 and 8.40, where inlet flow rate, inlet concentration, bed height and particle size were kept constant. A pH meter was used to measure the pH of the solution.

### **Effect of inlet flow rate on adsorption**

The effect of influent flow rate on adsorption was determined by varying the influent flow rate from 0.001 mL/s, 0.002 mL/s and 0.005 mL/s with a constant bed height, pH, inlet concentration and particle size.

### **Effect of inlet concentration on adsorption**

The effect of inlet concentration on adsorption of Cr (III) and Mn (IV) was determined by varying the inlet concentration of the crude oil contaminated water by collecting it at three different levels from the container where bed height, inlet flow rate, pH and particle size were kept constant.

### **Effect of particle size on adsorption**

The effect of particle size on fixed bed column adsorption of Cr (III) and Mn (IV) was determined on adsorbent particles of sizes 45  $\mu\text{m}$ , 90  $\mu\text{m}$  and 180  $\mu\text{m}$ . Each study was done where the bed height, inlet flow rate, pH, and inlet concentration of the solution were kept constant.

### **Effect of bed height on adsorption**

Adsorption of Cr (III) and Mn (IV) in a fixed bed column with bed heights 2 cm, 4 cm and 6 cm were determined at a constant inlet flow rate, pH, inlet concentration and particle size.

## RESULT AND DISCUSSION

### Physicochemical Analysis

The physicochemical properties of sorghum (bicolor) chaff sample collected from Benue brewery Nigeria Limited are summarized in Table 4.1.

Table 4.1: Physicochemical properties of sorghum (bicolor) chaff adsorbent

Properties	Values
pH	6.30
Bulk density (g/cm <sup>3</sup> )	0.33
Moisture content (%)	4.40
Iodine Adsorption Ratio (mol/g)	0.28
Porosity	13.00
Attrition Factor (%)	11.00
Surface area (m <sup>2</sup> /g)	797.4

### pH

This is the negative logarithm of hydrogen ion concentration. An increase in pH of adsorbent increases its capacity to adsorb cation, particularly adsorbents derived from agricultural residues indicates an optimum metal ion uptake level at pH >4.00. the pH of 6.30 shows that the adsorbent for this study is weakly acidic. This indicates high percentage adsorption

### Bulk Density

This is the mass of the adsorbent that occupies a volume in other words it gives the volume of activity of an adsorbent. It predicts the filterability of an adsorbent. From the result, 0.33 g/cm<sup>3</sup> the adsorbent has low bulk density and hence a high adsorption capacity. The low bulk density value of this adsorbent is due to the decrease in the attractive forces holding the particles together, therefore producing larger surface area.

### Moisture content

This is the amount of moisture present in the adsorbent. The amount of moisture present in this adsorbent was determined to be 4.40 %, a value far lower than 50.00 % upper limit for adsorbents. This implies that the adsorbent can be stored for a long period without significant microbial activity being observed.

**Iodine Adsorption Ratio (IAR)**

This is a fundamental parameter usually used to characterise the performance of an adsorbent. It is a measure of the micro-pore content of the adsorbent by adsorption of iodine from solution. IAR value for this study determined was 0.28 mol/g.

**Porosity**

This is a measure of the void in the adsorbent; and the greater the porosity of a given adsorbent, the greater would be the relative size of molecules it can adsorbed onto its crystal structure. In this study, the adsorbent has a porosity of 13.00, which shows great promise for adsorption applications.

**Attrition Factor**

This is an indicator of the mechanical strength of an adsorbent for aqueous phase applications. It describes the ability of the adsorbent to, not only maintain its physical integrity during the adsorption process but also its ability to withstand frictional forces. Low attrition leads to loss of adsorbent particle integrity and formation of dust particles, resulting in the reduction in the rate of filtration and in the amount in the adsorbent. Percentage attrition for the adsorbent determined was 11.00 %, a value interpretive of good mechanical strength, implying its potential for low degradability during analysis.

**Surface Area**

The surface area of an adsorbent measure the extent of pore surface developed within the matrix of the adsorbent. Its value indicates the functionality of an adsorbent based on the principle that the greater the surface area, the higher the number of available adsorption sites. A large surface area is therefore, a necessary requirement for a good adsorbent. The investigated adsorbent gave a surface area value of 797.4 m<sup>2</sup>/ g.

**Adsorption Analysis of Chromium (III)**

Effect of pH on percentage adsorption of Chromium (III) (Cr<sup>3+</sup>)

Table 4.2: Effect of pH on the removal of Cr<sup>3+</sup>

pH	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
3.380	4.942	90.116	2.253
7.000	3.477	93.046	2.326
8.400	5.102	89.796	2.245

Table 4.2 shows the results of the effects of adsorption of pH on the adsorption of Cr<sup>3+</sup> from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

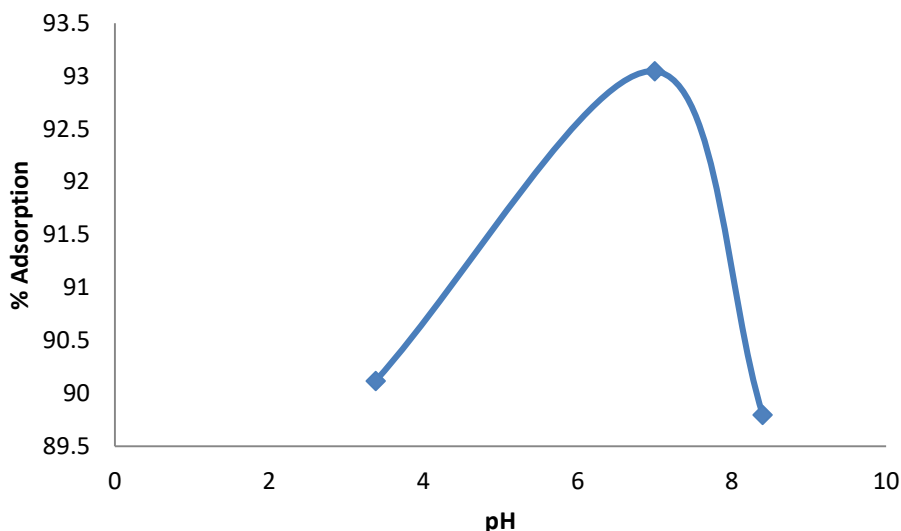


Figure 1: Effect of pH on percentage adsorption of  $\text{Cr}^{3+}$  from crude oil contaminated water.

Figure 1 shows that the lowest percentage adsorption of chromium (III) was 89.796 %, when the pH was 8.40, but the highest percentage adsorption of chromium (III) was 93.046 %, when the pH 7.00 was used. As a result, the percentage adsorption of chromium (III) has been found to increase with increase in pH to obtain a maximum around 7.00, but it is observed that it decreases at pH 8.40. this is because the adsorption characteristics of the adsorbent is influenced by ion exchange and precipitation. Though it is expected that adsorption should increase with increase in pH since there is no competition at the adsorption site between hydrogen ion and chromium (III), but the presence of hydroxyl ion necessitates the precipitation of chromium (III) ion.

### Effect of inlet concentration on percentage adsorption of chromium (III)

Table 3: Effect of inlet concentration on removal of chromium (III)

Inlet concentration (mg/L)	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
20.000	5.056	74.720	2.247
30.000	4.503	84.990	2.275
50.000	4.327	91.346	2.284

Table 3 shows the results of the effect of inlet concentration on the adsorption of chromium (III) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

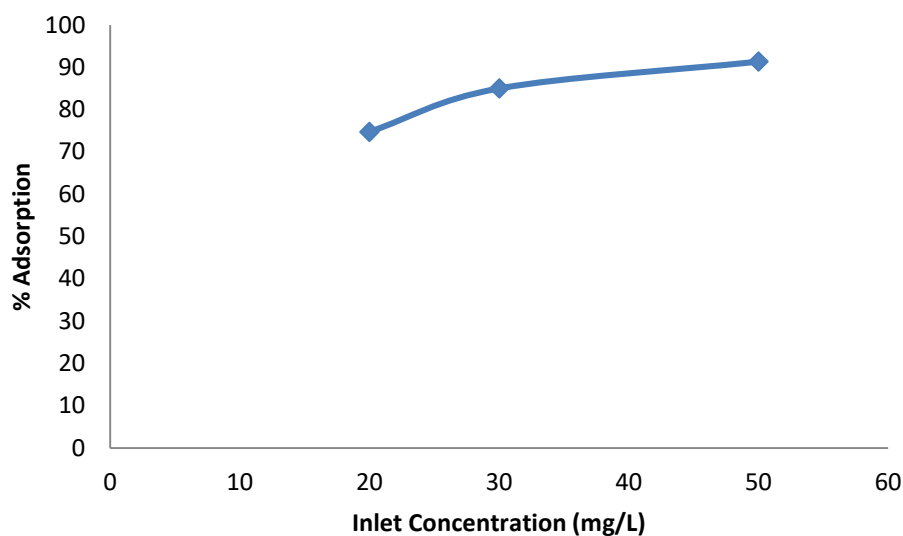


Figure 2: Effect of inlet concentration on percentage adsorption of Cr (III) from crude oil contaminated water.

Figure 2 shows that the percentage adsorption of Cr (III) increases with increase in inlet concentration. This is due to an increase in the gradient of concentration which is the driving force of the phenomenon of adsorption. Hence, it can be deduced that, at lower inlet concentration 20 mg/L, the percentage adsorption of Cr (III) was 74.720 % and at higher inlet concentration 50 mg/L, the percentage adsorption of Cr (III) was 91.346 %.

#### Effect of inlet flow rate on percentage adsorption of Cr (III)

Table 4: Effect of inlet flow rate on the removal of Cr (III)

Inlet flow rate (mL/sec)	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
0.005	5.904	88.192	2.205
0.002	5.016	89.994	2.249
0.001	4.905	90.190	2.255

Table 4 shows the result of the effect of inlet flow rate on the adsorption of Cr (III) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

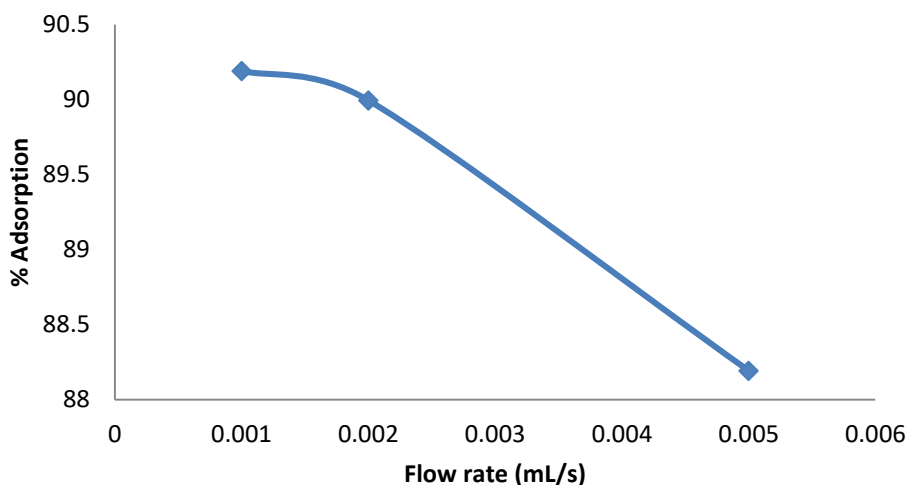


Figure 3: Effect of inlet flow rate on percentage adsorption of Cr (III) from crude oil contaminated water.

Figure 3 shows that at the lowest inlet flow rate of 0.001 mL/sec, relatively high percentage adsorption of 90.190 % of Cr (III) was observed. Hence, at the highest flow rate 0.005 mL/sec, the percentage adsorption of Cr (III) was 88.192 %, low. This behaviour can be explained by insufficient residence time of the crude oil contaminated water in the column. The residence time decreases with the increase of the flow of the crude oil contaminated water in the column.

### Effect of bed height on percentage adsorption of Cr (III)

Table 5: Effect of bed height on the removal of Cr (III)

Bed height (cm)	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
2.000	5.533	88.934	2.223
4.000	4.999	90.002	2.250
6.000	4.683	90.634	1.266

Table 5 shows that the result of the effect of bed height on the adsorption of Cr (III) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

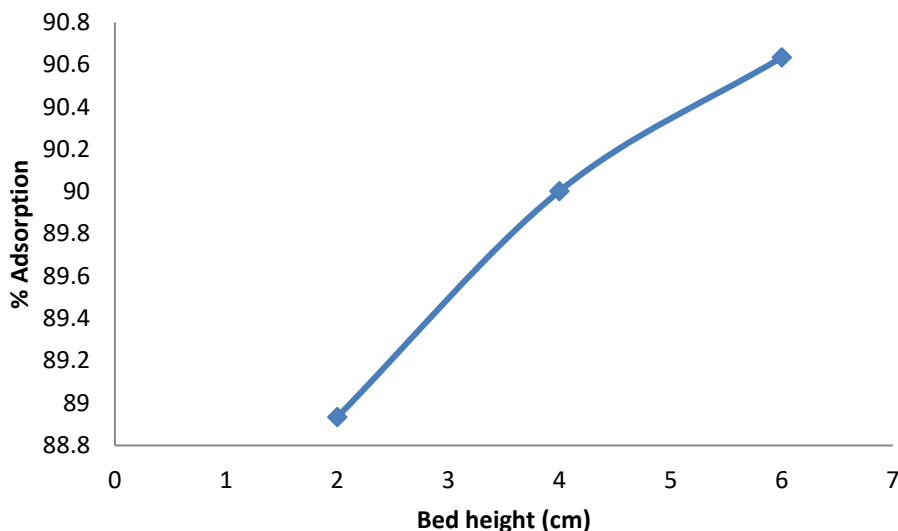


Figure 4: Effect of bed height on percentage adsorption of Cr (III) from crude oil contaminated water.

Figure 4 shows that the percentage adsorption of Cr (III) increases with increase in the bed height. This is because higher bed height contains more adsorbent; therefore, more binding sites would be available. It can be deduced that, the percentage adsorption of Cr (III) was 88.934 % when the lowest bed height was 2 cm and the percentage adsorption of Cr (III) was 90.634 % when the highest bed height was 6 cm.

#### Effect of particle size on percentage adsorption of Cr (III)

Table 6: Effect of particle size on the removal of Cr (III)

Particle size ( $\mu\text{m}$ )	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
45.000	4.327	91.346	2.284
90.000	5.018	89.964	2.249
180.000	5.532	88.936	2.223

Table 6 shows the result of the effect of particle size on the adsorption of Cr (III) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.



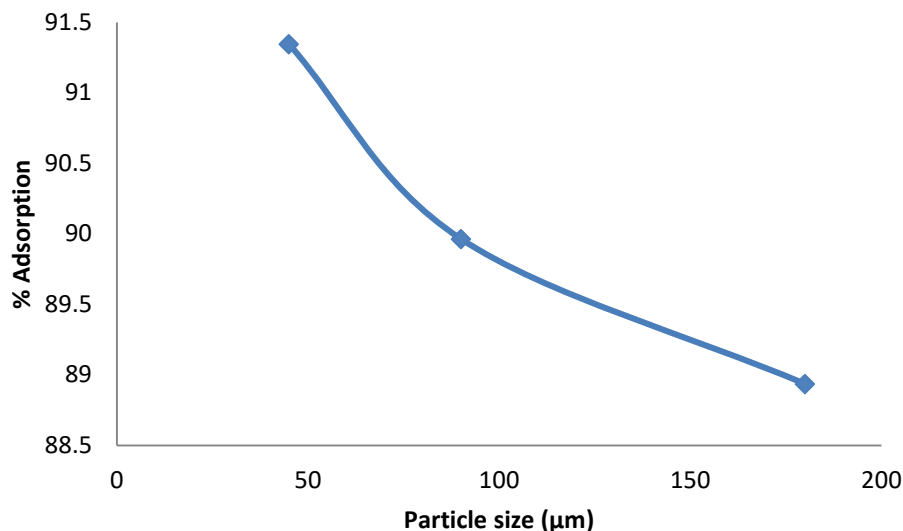


Figure 5: Effect of particle size on percentage adsorption of Cr (III) from crude oil contaminated water.

Figure 5 shows that the percentage adsorption of Cr (III) increases with the decrease in particle size of the adsorbent. This is due to the fact that when, the particle of the adsorbent is finer (reduced), its internal pore structure is highly developed and this gives a better access to the surface area. It can be deduced that at the highest particle size 180 µm, the percentage adsorption was 88.936 % and at the lowest particle size 45 µm, the percentage adsorption was 91.346 %.

#### Adsorption Analysis of Manganese (IV) ( $Mn^{4+}$ )

Effect of pH on percentage adsorption of Manganese (IV) ( $Mn^{4+}$ )

Table 7: Effect of pH on the removal of  $Mn^{4+}$

pH	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
3.380	4.611	84.630	1.269
7.000	3.651	87.830	1.317
8.400	5.248	82.507	1.238

Table 7 shows the results of the effects of adsorption of pH on the adsorption of  $Mn^{4+}$  from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

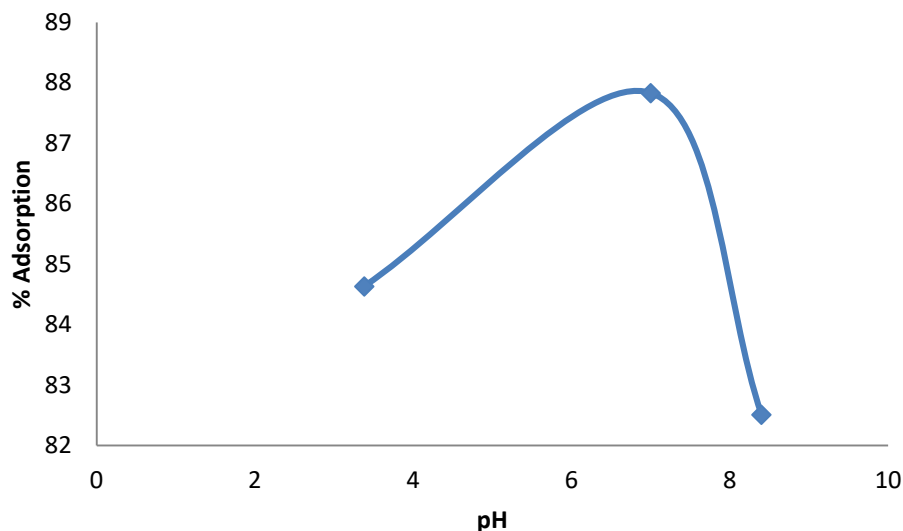


Figure 6: Effect of pH on percentage adsorption of  $Mn^{4+}$  from crude oil contaminated water.

Figure 6 shows that the lowest percentage adsorption of Manganese (IV) was 82.507 %, when the pH was 8.40, but the highest percentage adsorption of Manganese (IV) was 87.830 %, when the pH 7.00 was used. As a result, the percentage adsorption of Manganese (IV) has been found to increase with increase in pH to obtain a maximum around 7.00, but it is observed that it decreases at pH 8.40. This is because the adsorption characteristics of the adsorbent is influenced by ion exchange and precipitation. Though it is expected that adsorption should increase with increase in pH since there is no competition at the adsorption site between hydrogen ion and Manganese (IV), but the presence of hydroxyl ion necessitates the precipitation of Manganese (IV) ion.

#### Effect of inlet concentration on percentage adsorption of Manganese (IV)

Table 8: Effect of inlet concentration on removal of Manganese (IV)

Inlet concentration (mg/L)	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
10.000	5.226	47.770	0.239
20.000	5.115	74.425	0.744
30.000	4.862	83.793	1.257

Table 8 shows the results of the effect of inlet concentration on the adsorption of Manganese (IV) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

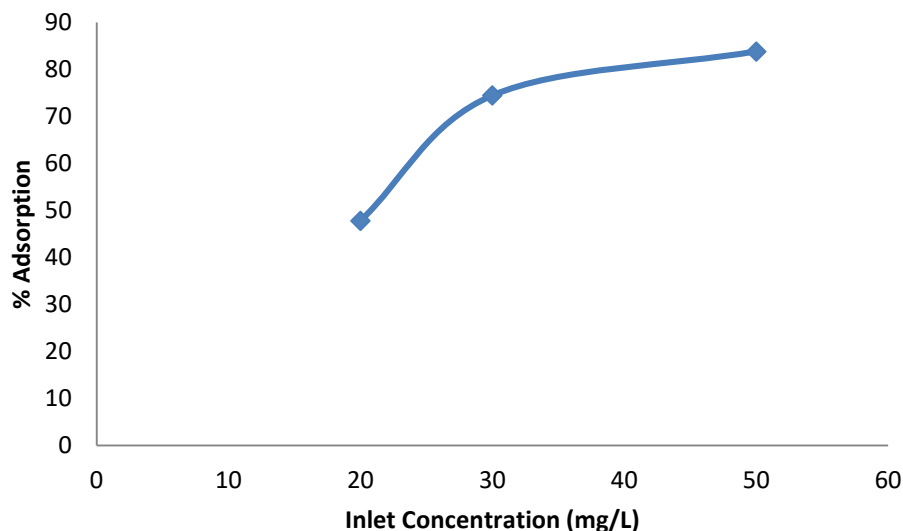


Figure 7: Effect of inlet concentration on percentage adsorption of Mn (IV) from crude oil contaminated water.

Figure 7 shows that the percentage adsorption of Mn (IV) increases with increase in inlet concentration. This is due to an increase in the gradient of concentration which is the driving force of the phenomenon of adsorption. Hence, it can be deduced that, at lower inlet concentration 10 mg/L, the percentage adsorption of Mn (IV) was 47.770 % and at higher inlet concentration 30 mg/L, the percentage adsorption of Mn (IV) was 83.793 %.

#### Effect of flow rate on percentage adsorption of Mn (IV)

Table 9: Effect of inlet flow rate on the removal of Mn (IV)

Inlet flow rate (mL/sec)	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
0.005	5.050	83.167	1.248
0.002	4.793	84.023	1.260
0.001	4.323	85.590	1.288

Table 9 shows the result of the effect of inlet flow rate on the adsorption of Mn (IV) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

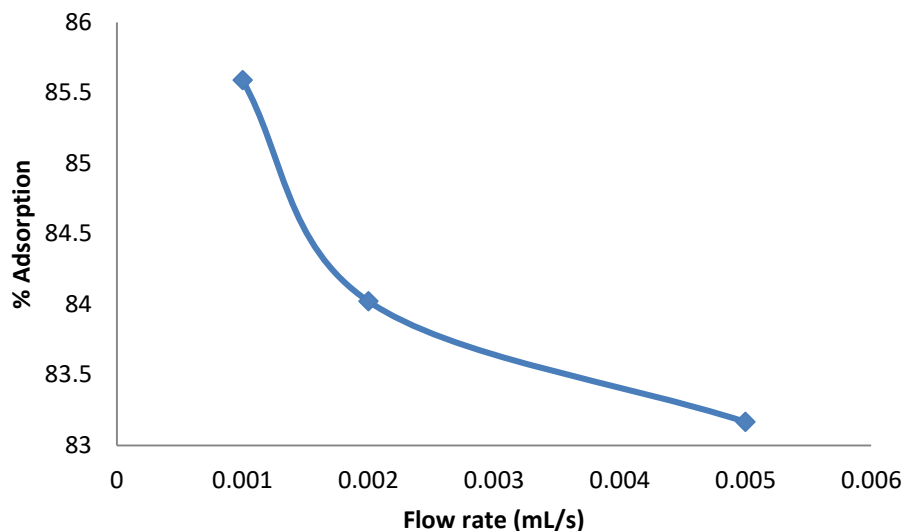


Figure 8: Effect of flow rate on percentage adsorption of Mn (IV) from crude oil contaminated water.

Figure 8 shows that at the lowest flow rate of 0.001 mL/sec, relatively high percentage adsorption of 85.590 % of Mn (IV) was observed. Hence, at the highest flow rate 0.005 mL/sec, the percentage adsorption of Mn (IV) was 83.167 %, low. This behaviour can be explained by insufficient residence time of the crude oil contaminated water in the column. The residence time decreases with the increase of the flow of the crude oil contaminated water in the column.

#### Effect of bed height on percentage adsorption of Mn (IV)

Table 10: Effect of bed height on the removal of Mn (IV)

Bed height (cm)	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
2.000	5.258	82.473	1.237
4.000	4.863	83.790	1.257
6.000	4.431	85.230	1.278

Table 10 shows that the result of the effect of bed height on the adsorption of Mn (IV) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

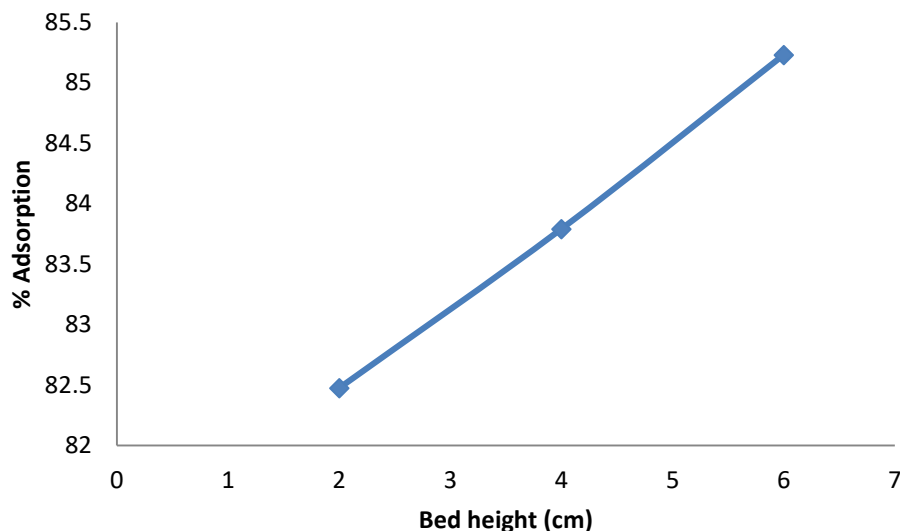


Figure 9: Effect of bed height on percentage adsorption of Mn (IV) from crude oil contaminated water.

Figure 9 shows that the percentage adsorption of Mn (IV) increases with increase in the bed height. This is because higher bed height contains more adsorbent; therefore, more binding sites would be available. It can be deduced that, the percentage adsorption of Mn (IV) was 82.473 % when the lowest bed height was 2 cm and the percentage adsorption of Mn (IV) was 85.230 % when the highest bed height was 6 cm.

#### Effect of particle size on percentage adsorption of Mn (IV)

Table 11: Effect of particle size on the removal of Mn (IV)

Particle size ( $\mu\text{m}$ )	Effluent concentration (mg/L)	Percentage adsorption (%)	Equilibrium adsorption capacity (mg/g)
45.000	3.451	88.497	1.327
90.000	3.834	87.220	1.308
180.000	4.674	84.420	1.266

Table 4.11 shows the result of the effect of particle size on the adsorption of Mn (IV) from crude oil contaminated water and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

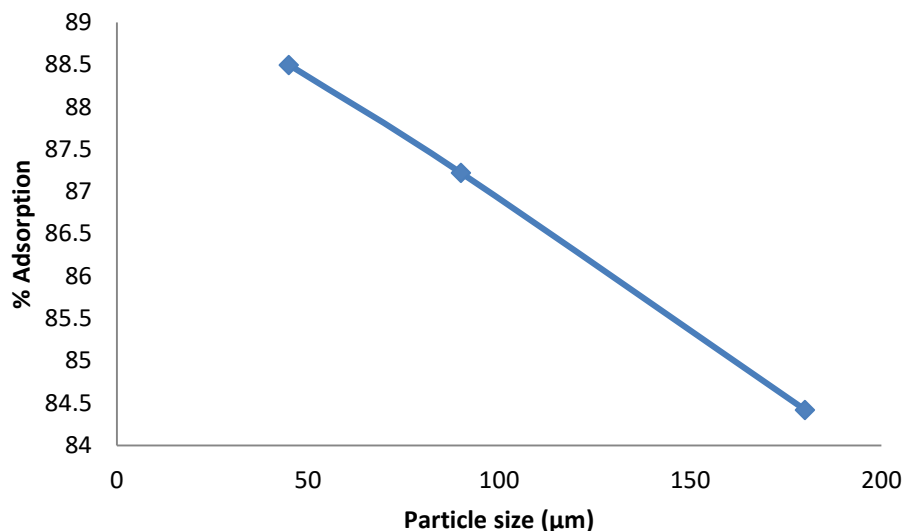


Figure 10 shows that the percentage adsorption of Mn (IV) increases with the decrease in particle size of the adsorbent. This is due to the fact that when, the particle of the adsorbent is finer (reduced), its internal pore structure is highly developed and this gives a better access to the surface area. It can be deduced that at the highest particle size 180  $\mu\text{m}$ , the percentage adsorption was 84.420 % and at the lowest particle size 45  $\mu\text{m}$ , the percentage adsorption was 88.497 %.

### Kinetic adsorption models

Bed depth service time (BDST) kinetic adsorption model for the adsorption of Cr (III) from crude oil contaminated water: Effect of particle size

Table 12: BDST kinetic adsorption model on the effect of particle size on Cr (III) adsorption

Particle size ( $\mu\text{m}$ )	Inlet concentration $C_0$ (mg/L)	Effluent concentration $C_e$ (mg/L)	Bed height (cm)	Time t (sec)	
45.000		50.000	4.327	2.000	9000.000
90.000		50.000	5.018	4.000	7200.000
180.000		50.000	5.532	6.000	3900.000

Figure 11: BDST kinetic plot for the adsorption of Cr (III) from crude oil contaminated water: Effect of particle size

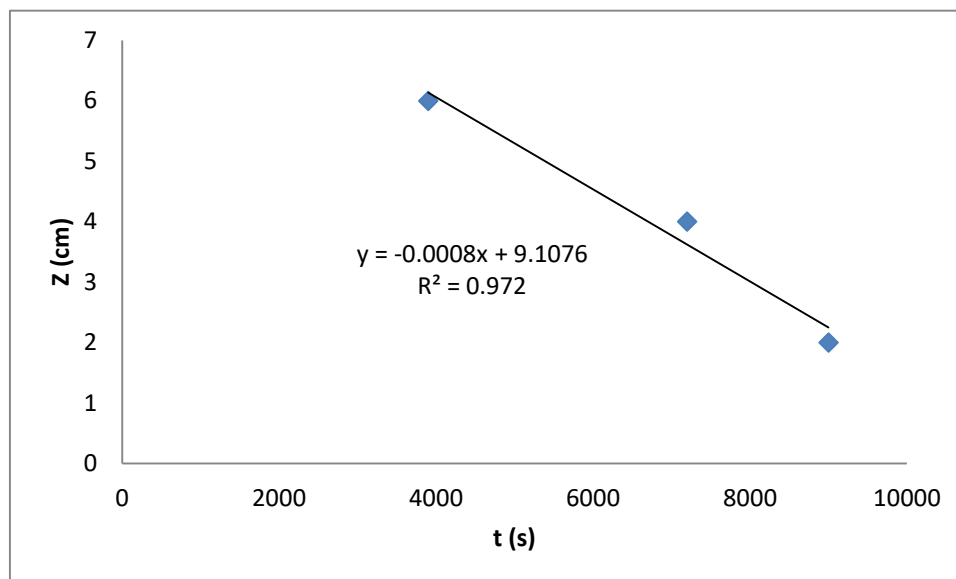


Figure 11 shows that the experimental data are fitted into BDST kinetic model, hence the regression coefficient  $R^2$  value 0.972 is above 0.900.

Bed depth service time (BDST) kinetic adsorption model for the adsorption of Mn (IV) from crude oil contaminated water: Effect of bed height

Table 13: BDST kinetic adsorption model on the effect of particle size on Mn (IV) adsorption

Bed Height (cm)	Inlet concentration $C_0$ (mg/L)	Effluent concentration $C_e$ (mg/L)	Bed height (cm)	Time t (sec)
2.000	30.000	3.451	2.000	9000.000
4.000	30.000	3.834	4.000	7200.000
6.000	30.000	4.674	6.000	3900.000

Figure 12: BDST kinetic plot for the adsorption of Mn (IV) from crude oil contaminated water: Effect of bed height

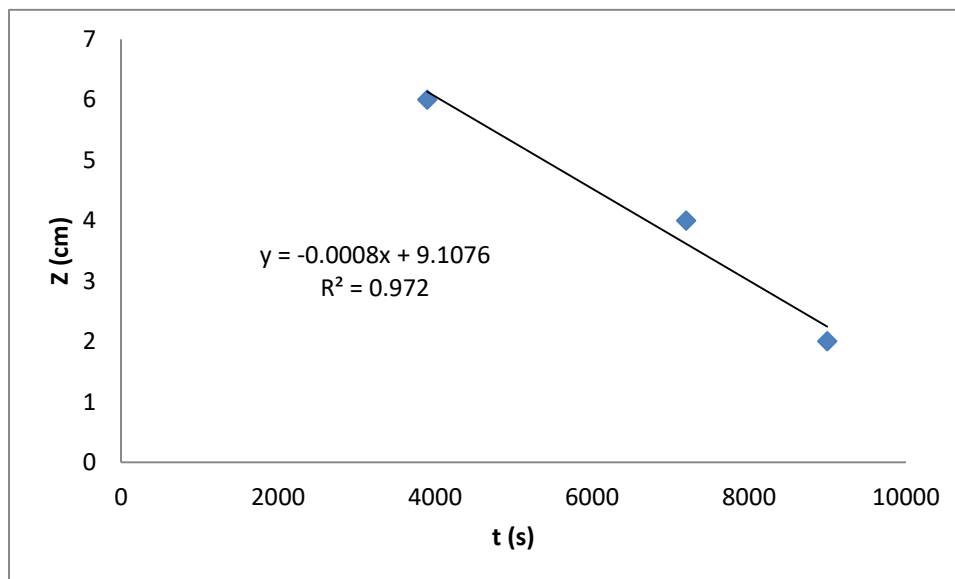


Figure 12 shows that the experimental data are fitted into BDST kinetic model, hence the regression coefficient  $R^2$  value 0.972 is above 0.900.

## CONCLUSION AND RECOMMENDATION

### Conclusion

Based on the experiments conducted in this study, sorghum (bicolor) chaff can be converted into a useful and effective adsorbent and column adsorption is a good potential to remove Cr (III) and Mn (IV) from crude oil contaminated water in practical application, hence higher percentage removal occurs in the pH, 7.00, inlet concentration (50 and 30) mg/L, inlet flow rate, 0.001 mL/s, bed height, 6 cm and particle size 45  $\mu\text{m}$ ; and the experimental data fitted the kinetics.

### Recommendations

The conversion of sorghum (bicolor) chaff which is an agricultural low cost material, into useful products and applications like adsorbent should be encouraged by the Government to remedy environmental pollution.

The concentration of Chromium (III) and manganese (IV) pollutants in crude oil contaminated water is on the increase. It is therefore very important that the Federal Environmental Protection Agency put in place appropriate legislation to guide the disposal of crude oil contaminated water and encourage research activities to develop effective adsorbent that can remove these pollutants.

Oil companies should be more environmental conscious and follow strictly the provisions of the law and standards set by regulatory bodies or agencies to minimize the problems of oil spillage to



the barest minimum. They should also have regular monitoring of oil production activities and facilities and pay adequate compensation to the host affected communities.

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