EFFECT OF PARTICLE SIZE ON CHROMIUM (III) AND MANGANESE (IV) REMOVAL FROM A TANNERY WASTEWATER

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Abstract

The removal of chromium (III) and manganese (IV) from a tannery wastewater was evaluated using atomic absorption spectrophotometer (AAS). Activated carbon prepared from sorghum (bicolor) chaff was used to remove chromium (III) and manganese (IV). The evaluated physicochemical properties of the activated carbon were pH (6.30),bulk density (0.33 g/cm^3), moisture content (4.40%), Iodine Adsorption Ratio (0.28 mol/g), porosity (13.00), attrition factor (11.00%), and surface area (797.4 m^2/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 chromium (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 manganese (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 particle size.

Keywords: Column absorption, chromium (III), kinetics, manganese (IV), particle size, tannery wastewater

1. INTRODUCTION

Pollution is one of the most important problems around the world today in which thousands of millions of world inhabitants suffer health problems related to industry and atmospheric pollutants. Recent years have witnessed significant attention being paid to the problems of environmental contamination by wide variety of chemical pollutants including heavy metals. Heavy metals enter into our environment from both natural and anthropogenic sources. They contaminate food source and accumulate in both agriculture products and seafood through water, air and soil pollution (Olayowola, 2013).

Toxic heavy metals contamination of industrial waste water is an important environmental problem. Many industries such as leather, electroplating, pigments, metallurgical processes and mining industries release various concentrations of heavy metals. Metal ions such as chromium and manganese are commonly detected in both natural and industrial effluents (El-Sayed et al, 2011). 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. The danger of these heavy metals is due to poisoning, cancer and brain damage. Therefore, treatment of water and wastewater containing heavy metals is very demanding (Prabakaran and Arivoli, 2013).

The treatment technologies more frequently cited for removal of heavy metals are carbon adsorption, wet oxidation, solvent extraction, precipitation, ultrafiltration, reverse osmosis, ion exchange, chemical coagulation, flocculation, membrane technologies, electrolytic recovery and flotation. Among these options, adsorption is most preferred method and activated carbon is most effective adsorbent widely employed to treat waste water containing different classes of metal ions, recognising the economical drawback of 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 particle size on their removal.

2. LITERATURE REVIEW

2.1 Heavy Metals

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include; mercury (Hg), manganese (Mn), cadmium (Cd), arsenic (As), Chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our body via food, water and air. As trace elements, some heavy metals (copper, selenium, zinc) are essential to maintain the metabolism of the

human body. However, at higher concentrations they can lead to poisoning (Cussler, 1997). 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, in the same situation, don't bring 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 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 (Rashmi and Pratima, 2013).

2.2 Tannery Effluent

The processing of hides and skins into leather is carried out in an aqueous medium, hence the discharged water from pits, drums or paddles containing several soluble and insoluble constituents constitute the effluent from the tannery. Based on different studies of the material balance in leather production, the processing of 1000 kg of wet-salted raw hide into chrome-tanned upper or upholstery leather, result in the production of 200 kg of the products, 30-40 cm^3 wastewater and considerable amount of solid wastes and by-products. Materials in tannery effluent may include bits of flesh, hide scraps, hair, blood, manure, salts, soluble proteins, suspended lime, sulphites and sulphides, amines, arsenic, tannins, soda ash, sugars, mineral acids, dyes and other organic and inorganic compounds (Oremusová, 2007).

2.3 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated carbon, synthetic resins and water purification (Buba, 2004).

2.3.1 Column Adsorption Kinetic Models
Thomas kinetic model
Thomas kinetic model is one of the most general and widely used kinetic model. The model is applicable in system with a constant flow rate and no axial dispersion, and its behaviour matches the Langmuir isotherm and the second-order reversible reaction kinetics. The model has the following form;

$$\frac{C}{C_o} = \frac{1}{1+\exp[\frac{k_T(qm - C_o V)}{Q}]} \qquad (1)$$

Where, k_T is rate constant (L/mmolh)
Q is flow rate (L/h)
m is mass of the bed (g)

V is effluent volume (L)

The linearization of equation (1) yields;

$$\ln\left[\left(\frac{C_o}{C}\right) - 1\right] = \frac{k_T qm}{Q} - \frac{k_T C_o t}{Q} \tag{2}$$

From the linear dependence of versus t, the removal capacity, q, and rate constant k_T can be determined (Marina et al 2011).

2.4 Physicochemical properties of adsorbents

2.4.1 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) (Bates, 1954). 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).

$$pH = -\log[H^+]$$

where $[H^+]$ is activity of H^+ ions in mole/liter

2.4.2 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^3) (Adie et al 2013).

2.4.3 Porosity

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

2.4.4 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).

2.4.5 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).

2.4.6 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).

2.4.7 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).

2.3.8 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 forma granular material (Ahile et al 2015).

3. MATERIALS AND METHODS

3.1 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 wastewater was collected from Gashash Tannery Company, Bompai Industrial Estate, Kano, Kano State, Nigeria.

3.2 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 mm 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 ^{o}C-600 ºC 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.

3.4 Determination of Physicochemical Properties of Adsorbent
3.4.1 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).

3.4.2 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 (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);

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

3.4.3 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 ^{o}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

3.4.4 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.

$$IAR\ (mol/g) = M_{S_2O_3^{2-}}(V_b - V_s)/2m_a$$

Where $M_{S_2O_3}^{2-}$ 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 2010a).

3.4.5 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).

$$Porosity = V_i - V_f$$

3.4.6 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);

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

3.4.7 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

3.5 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 wastewater 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) (Hanen and Abdelmottaleb, 2013).

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

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

Where, C_o 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

3.5.1 Effect of pH
The effect of pH on adsorption was studied by adjusting the pH of the wastewater 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.

3.5.2 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.

3.5.3 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.

3.5.4 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 wastewater by collecting it at three different levels from the container where bed height, inlet flow rate, pH and particle size were kept constant.

3.5.5 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 μm, 90 μm and 180 μm. Each study was done where the bed height, inlet flow rate, pH, and inlet concentration of the solution were kept constant.

4. RESULT AND DISCUSSION
4.1 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^3)	0.33
Moisture content (%)	4.40
Iodine Adsorption Ratio (mol/g)	0.28
Porosity	13.00
Attrition Factor (%)	11.00
Surface area (m^2/g)	797.4

4.1.1 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 absorbent for this study is weakly acidic. This indicates high percentage adsorption

4.1.2 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^3 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.

4.1.3 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.

4.1.4 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.

4.1.5 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.

4.1.6 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.

4.1.7 Surface Area

The surface area of absorbent measures 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^2/ g.

4.2 Adsorption Analysis of Chromium (III)

4.2.1 Effect of pH on percentage adsorption of Chromium (III) (Cr^{3+})

Table 4.2: Effect of pH on the removal of Cr^{3+}

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^{3+} from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

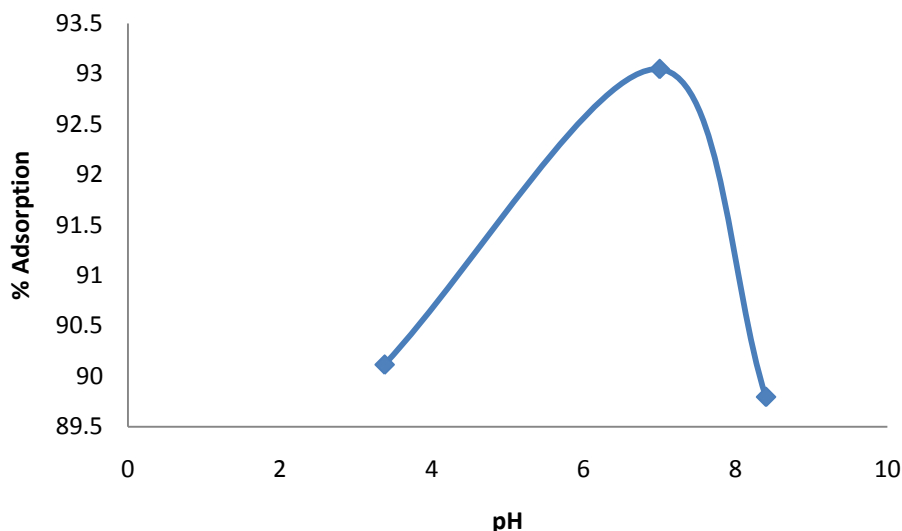Figure 4.1: Effect of pH on percentage adsorption of Cr^{3+} from tannery wastewater.

Figure 4.1 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 are 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.

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

Table 4.3: 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 4.3 shows the results of the effect of inlet concentration on the adsorption of chromium (III) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.2: Effect of inlet concentration on percentage adsorption of Cr (III) from tannery wastewater.
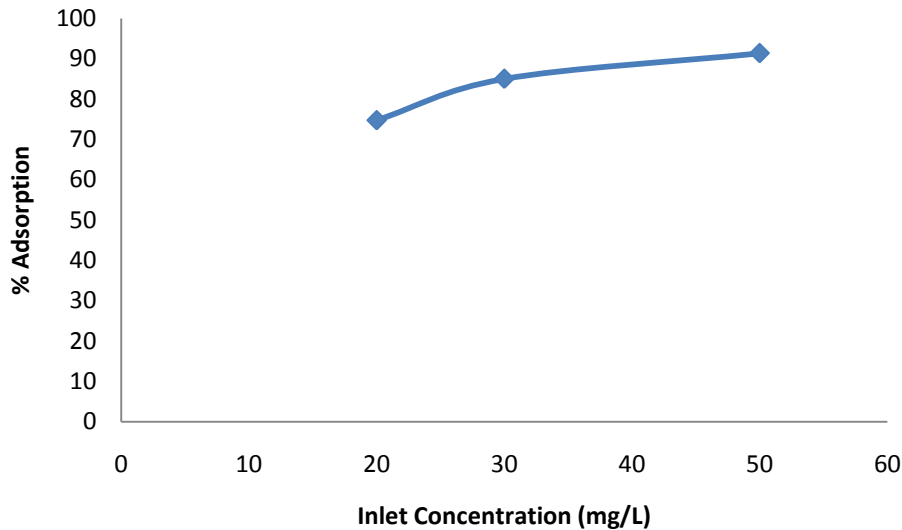

Figure 4.2 shows that the percentage adsorption of Cr (III) increases with increase in inlet concentration. This is due to an increase in the gradient of concentration which is the driving force of the phenomenon of adsorption. Hence, it can be deduced that, at lower inlet concentration 20 mg/L, the 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 %.

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

Table 4.4: 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 4.4 shows the result of the effect of inlet flow rate on the adsorption of Cr (III) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.3: Effect of inlet flow rate on percentage adsorption of Cr (III) from tannery wastewater.
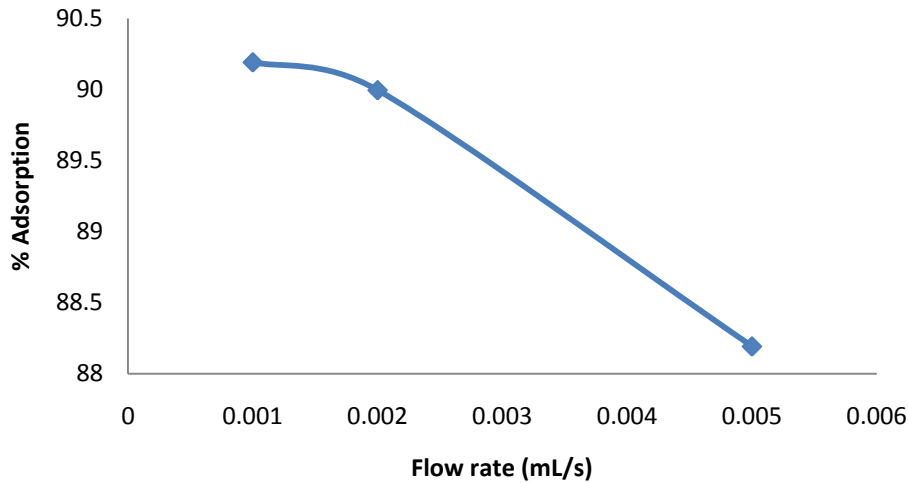

Figure 4.3 shows that at the lowest inlet flow rate of 0.001 mL/sec, relatively high percentage adsorption of 90.190 % of Cr (III) was observed. Hence, at the highest flow rate 0.005 mL/sec, the percentage adsorption of Cr (III) was 88.192 %, low. This behaviour can be explained by insufficient residence time of the tannery wastewater in the column. The residence time decreases with the increase of the flow of the tannery wastewater in the column.

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

Table 4.5: 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 4.5 shows that the result of the effect of bed height on the adsorption of Cr(III) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.4: Effect of bed height on percentage adsorption of Cr (III) from tannery wastewater.
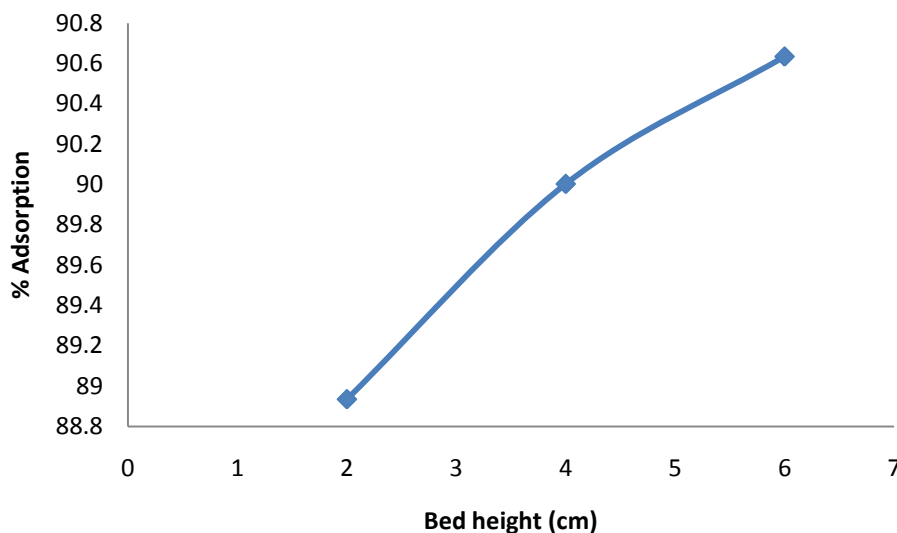

Figure 4.4 shows that the percentage adsorption of Cr (III) increases with increase in the bed height. This is because higher bed height contains more adsorbent; therefore, more binding sites would be available. It can be deduced that, the percentage adsorption of Cr (III) was 88.934 % when the lowest bed height was 2 cm and the percentage adsorption of Cr (III) was 90.634 % when the highest bed height was 6 cm.

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

Table 4.6: Effect of particle size on the removal of Cr (III)

Particle size (μm)	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 4.6 shows the result of the effect of particle size on the adsorption of Cr (III) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.5: Effect of particle size on percentage adsorption of Cr (III) from tannery wastewater.
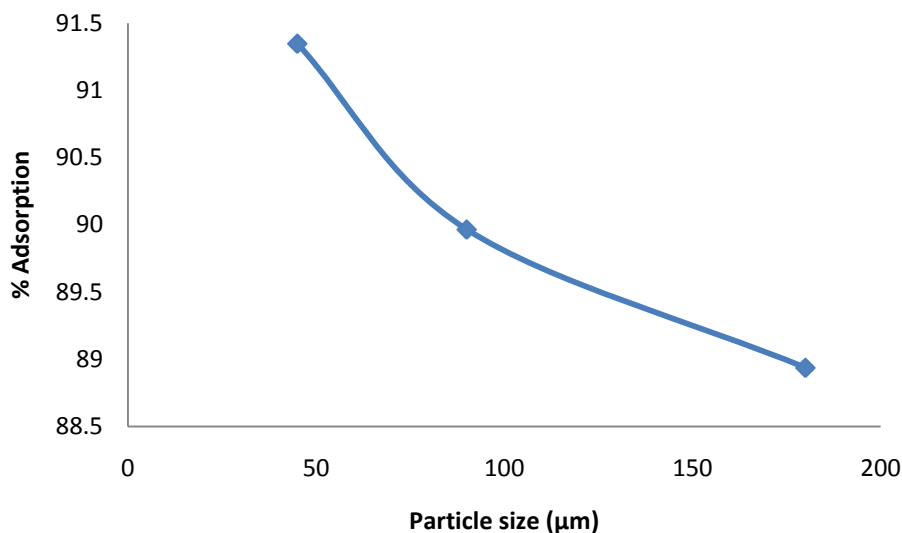

Figure 4.5 shows that the percentage adsorption of Cr (III) increases with the decrease in particle size of the adsorbent. This is due to the fact that when, the particle of the adsorbent is finer (reduced), its internal pore structure is highly developed and this gives a better access to the surface 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 %.

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

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

Table 4.7:   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 4.7 shows the results of the effects of adsorption of pH on the adsorption of Mn^{4+} from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.6: Effect of pH on percentage adsorption of Mn^{4+} from tannery wastewater.
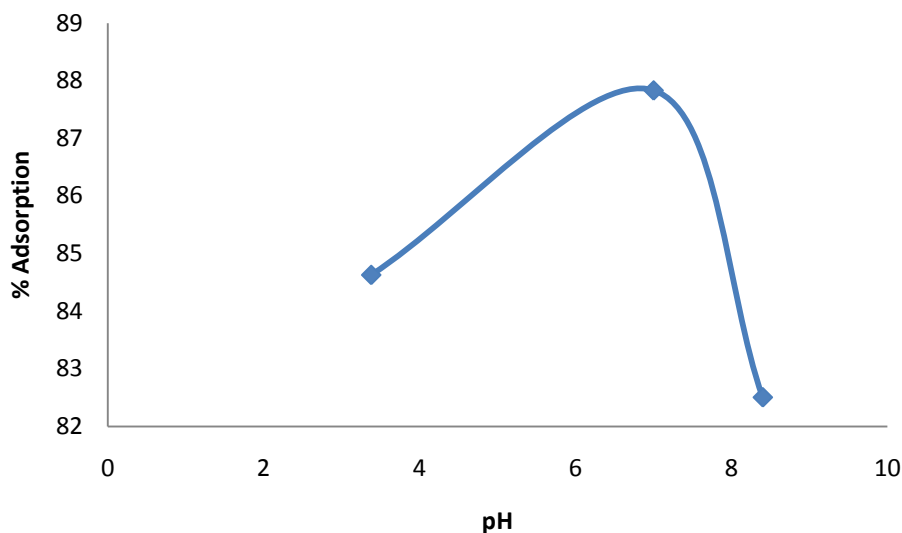

Figure 4.6 shows that the lowest percentage adsorption of Manganese (IV) was 82.507 %, when the pH was 8.40, but the highest percentage adsorption of Manganese (IV) was 87.830 %, when the pH 7.00 was used. As a result, the percentage adsorption of Manganese (IV) has been found to increase with increase 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.

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

Table 4.8: 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 4.8 shows the results of the effect of inlet concentration on the adsorption of Manganese (IV) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.7: Effect of inlet concentration on percentage adsorption of Mn (IV) from tannery wastewater.
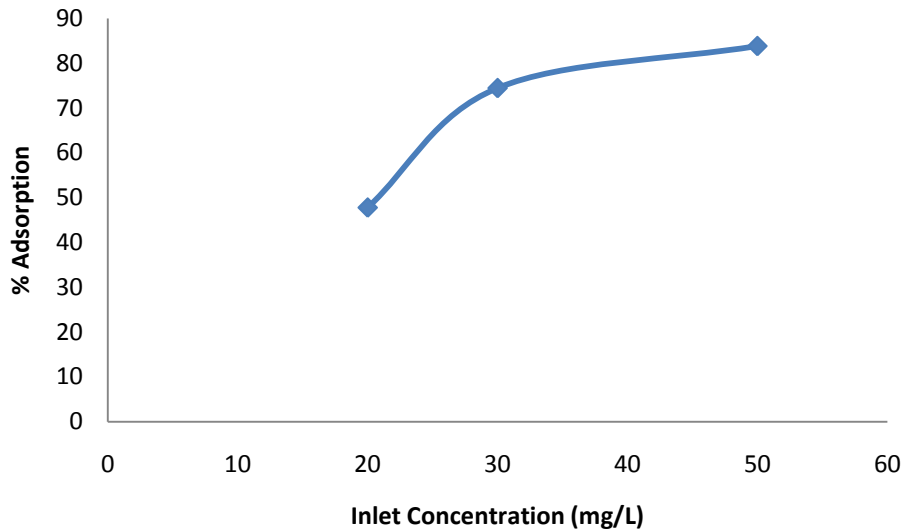

Figure 4.7 shows that the percentage adsorption of Mn (IV) increases with increase in inlet concentration. This is due to an increase in the gradient of concentration which is the driving force of the phenomenon of adsorption. Hence, it can be deduced that, at lower inlet concentration 10 mg/L, the percentage adsorption of Mn (IV) was 47.770 % and at higher inlet concentration 30 mg/L, the percentage adsorption of Mn (IV) was 83.793 %.

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

Table 4.9: 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 4.9 shows the result of the effect of inlet flow rate on the adsorption of Mn (IV) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

Figure 4.8: Effect of flow rate on percentage adsorption of Mn (IV) from tannery wastewater.
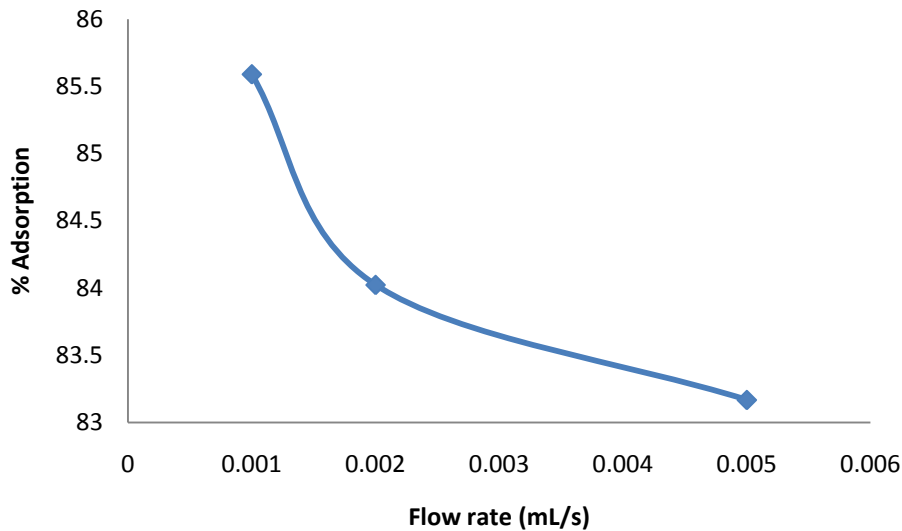

Figure 4.8 shows that at the lowest flow rate of 0.001 mL/sec, relatively high percentage adsorption of 85.590 % of Mn (IV) was observed. Hence, at the highest flow rate 0.005 mL/sec, the percentage adsorption of Mn (IV) was 83.167 % low. This behaviour can be explained by insufficient residence time of the tannery wastewater in the column. The residence time decreases with the increase of the flow of the tannery wastewater in the column.

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

Table 4.10: 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 4.10 shows that the result of the effect of bed height on the adsorption of Mn (IV) from tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

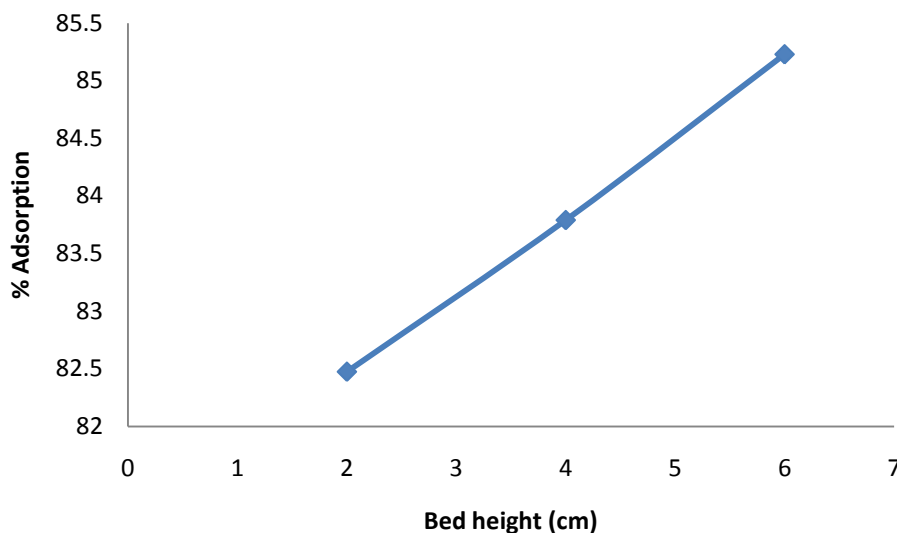Figure 4.9: Effect of bed height on percentage adsorption of Mn (IV) from tannery wastewater.

Figure 4.9 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.

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

Table 4.11: Effect of particle size on the removal of Mn (IV)

Particle size (μm)	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 tannery wastewater and the corresponding effluent concentration, percentage adsorption and equilibrium adsorption capacity after analysis.

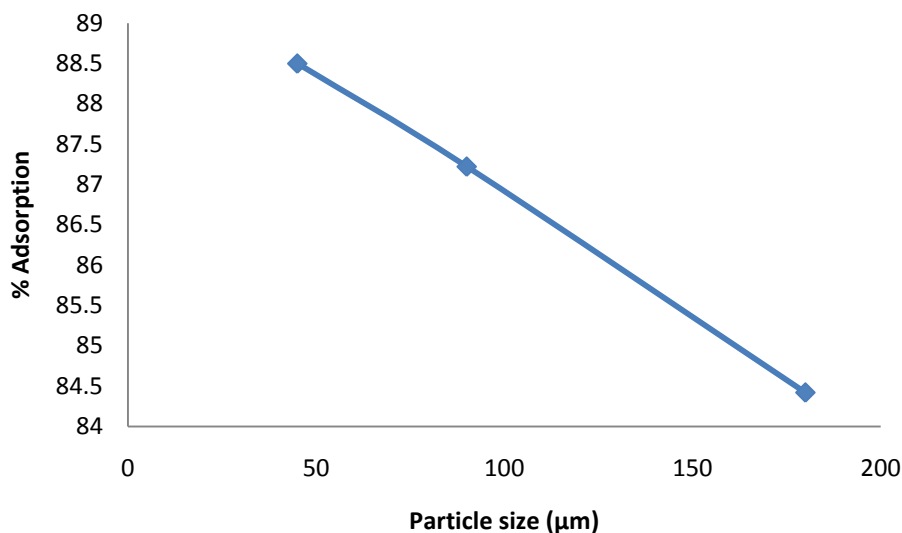Figure 4.10: The percentage adsorption of Mn (IV)

Figure 4.10 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 μm, the percentage adsorption was 84.420 % and at the lowest particle size 45 μm, the percentage adsorption was 88.4 97 %.

4.4 Kinetic adsorption models

4.4.1 Thomas kinetic adsorption model for the adsorption of Cr (III) from tannery wastewater: Effect of particle size

Table 4.12: Thomas kinetic adsorption model on the effect of particle size on Cr (III) adsorption

Particle size (μm)	Inlet concentration Co (mg/L)	Effluent concentration Ce (mg/L)	$\frac{C_o}{C_e}$	$\left(\frac{C_0}{C_e}\right) - 1$	$\ln\left[\left(\frac{C_0}{C_e}\right) - 1\right]$	Time t (sec)
45.000	50.000	4.327	11.555	10.555	2.357	9000.000
90.000	50.000	5.018	9.964	8.964	2.193	7200.000
180.000	50.000	5.532	9.038	8.038	2.084	3900.000

Figure 4.11: Thomas kinetic plot for the adsorption of Cr (III) from tannery wastewater: Effect of particle size
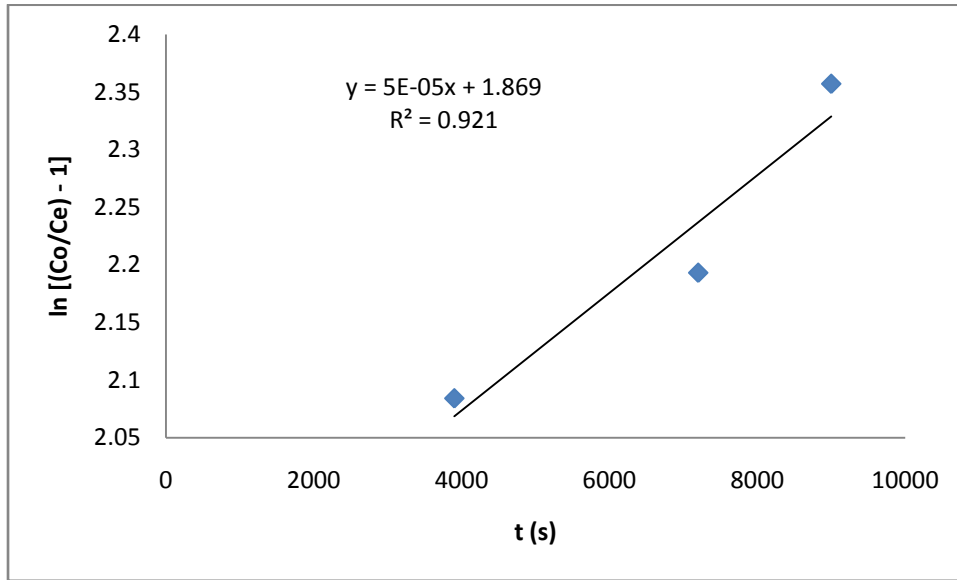

Figure 4.11 shows that the experimental data are fitted into Thomas kinetic model, hence the regression coefficient R^2 value 0.9215 is above 0.9000.

4.4.2 Thomas kinetic adsorption model for the adsorption of Cr (Mn) from tannery wastewater: Effect of particle size

Table 4.13: Thomas kinetic adsorption model on the effect of particle size on Mn (IV) adsorption

Particle size (μm)	Inlet concentration Co (mg/L)	Effluent concentration Ce (mg/L)	$\frac{C_o}{C_e}$	$\left(\frac{C_0}{C_e}\right) - 1$	$\ln\left[\left(\frac{C_0}{C_e}\right) - 1\right]$	Time t (sec)
45.000	50.000	4.327	11.555	10.555	2.357	9000.000
90.000	50.000	5.018	9.964	8.964	2.193	7200.000
180.000	50.000	5.532	9.038	8.038	2.084	3900.000

Figure 4.12: Thomas kinetic plot for the adsorption of Mn (IV) from tannery wastewater: Effect of particle size
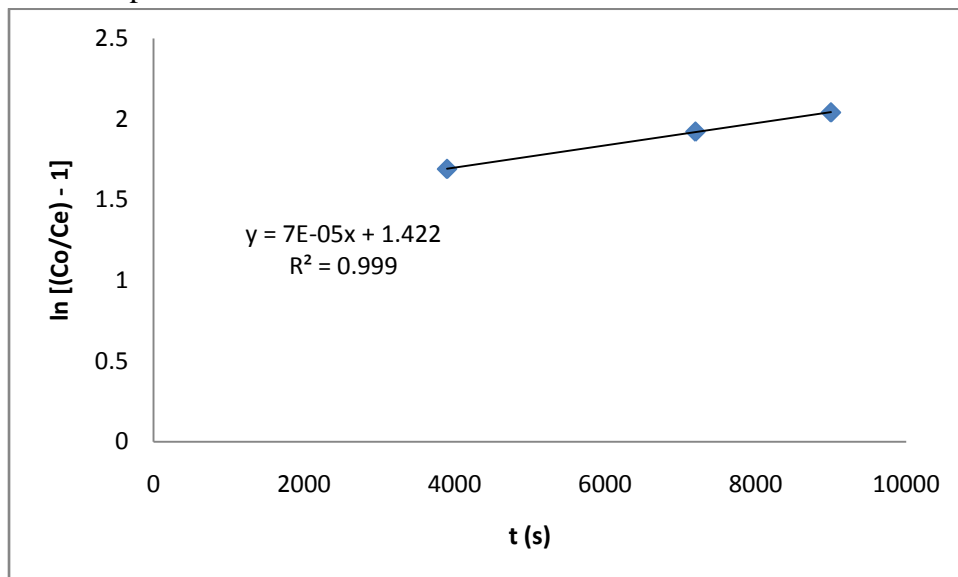

Figure 4.12 shows that the experimental data are fitted into Thomas kinetic model, hence the regression coefficient R^2 value 0.9998 is above 0.9000.

5. CONCLUSION AND RECOMMENDATION

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 tannery wastewater 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 µm; and the experimental data fitted the kinetics. The conversion of sorghum (bicolor) chaff which is a low cost material, into useful products and applications like adsorbent should be encouraged by the Government to remedy environmental pollution.

The concentration of Manganese (IV) and manganese (IV) pollutants in tannery wastewater 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 tannery wastewater and encourage research activities to develop effective adsorbent that can remove these pollutants from tannery wastewater.

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