

Removal Of Chromium from An Aqueous Solution Using River Sediment from Kashere, Gombe State, Nigeria.

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Abstract: The removal of chromium by river sediment was carried out under laboratory condition and a good consideration on experimental parameters like temperature, time, pH, concentration and dosage was put in place. pH 7.0 was applied while pseudo first order and pseudo second order are the only kinetics models selected on this research and also isotherms such as Langmuir and Freundlich adsorption isotherms were also involved. The result of the experiment showed that the removal of chromium followed pseudo second order due to highest value of correlative coefficient R^2 ranging from 0.9998 to 1.000 approximately. Also adsorption capacity of chromium at equilibrium q_e was high with value of 4.66 to 8.69 in pseudo second order compared with 7.931 of pseudo first order and the R^2 value of Langmuir is 0.9998 and value of R^2 from Fruindlich 0.9591 which is lower than that of Langmuir and so the adsorption process followed Langmuir because it showed monolayer adsorption process due to the high value of R^2 .

Keywords: Chromium, Sediment, Adsorption.

INTRODUCTION

Toxic metals are often discharged by a number of industrial processes and this can in turn lead to the contamination of fresh water and marine environment (Low et al., 2000; Braukmann, 1990; Raji & Anirudhan, 1997; Yu et al., 2011; Kargar et al., 2012; Mzoughi and Chouba, 2012). Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater (Valdman et al., 2001; Ghaderi et al., 2012; AlimohammadKalhori et al., 2012; Ashraf et al., 2012). Unlike organic pollutants, majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products, and result in a number of environmental problems (Kalswarn & Yu, 2001; Yan & Viraraghavan, 2001; Nasrabadi et al., 2010; Haruna et al., 2011; Serbaji et al., 2012; Ogundiran et al., 2012). Due to their non-biodegradability and persistence, metals can accumulate in the environment elements such as food chain and thus may pose a significant danger to human health (Yeti et al., 1998; Kortenkamp et al., 1996; Bakkaloglu et al., 1998; Okuku and Peter, 2012; Mhadhbi et al., 2012; Divis et al., 2012). Chromium

(VI) compounds known as chromates and dichromates enter waters from many industrial processes such as electroplating, leather tanning, metal finishing, paints and pigments etc (Sharma, 2001; Hu et al., 2003). Chromium (VI) is the most water soluble and easily enters the living cells. As determined by the National Toxicology Programme (NTP), the International Agency for Research on Cancer (IARC), Cr (VI) is a human carcinogen. It also causes skin irritation resulting in ulcer formation. Overexposure to Cr(VI) leads to liver damage, pulmonary congestion and oedema. Research on toxicological effect of chromium on water bodies concluded that high concentration of Cr(VI) in water is lethal to various fishes. Generally Cr (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, concentration, ion exchange, reverse osmosis, electro dialysis, solvent extraction and evaporation etc (Iqbal et al., 2002; Dean et al., 1972; Sengupta & Clifford, 1986; Geselbarcht, 1996; Schnoor, 1997:

STATEMENT OF THE PROBLEM

In most of the mining area where mining activities are commonly practiced the interaction of solid mineral and water source is inevitable. In essence water bodies such as rivers and lakes are mainly used for domestic purposes with heavy metals. As such, there is a need for a cheap and flexible process for the removal of this heavy metal from the aqueous/water to be used domestically.

HEAVY METALS

“Heavy metal” is a general communal term assigned to the collection of metals and metalloids having atomic density greater than 4000 kg/m³ and specific gravity greater than five (Garbarino et al., 1995). They are the natural component of earth crust. Most of the heavy metals other than cadmium, mercury and lead are essential micro nutrients needed for living beings at lower concentration, but at higher concentration they can lead to severe poisoning.

CHROMIUM

Chromium (Cr) is the seventh most abundant transition metal element occurring naturally on earth. It was first discovered in the year 1797 by a French chemist, Nicholas Louis Vauquelin at the Paris Ecole Des Mines from a Siberian red lead ore (crocoite). A yellow pigment (chromium) produced from crocoite was the first commercially used chromium for paint production. The name “Chromium” was derived from a Greek word “Chroma” meaning colour. Chromium was then discovered in commonly occurring mineral chromite from the Ural Mountains. The major commercially traded forms of chromium materials include chromite ore and ferrochromium (a product of smelted chromite ore). Globally about 77 % of known resources are from South Africa and are also found in other parts of world like Kazakhstan, Zimbabwe, Finland, India, Brazil, Turkey, Albania, Russia, United States and Iran. Based on geological

survey of statistics, India is one among the largest producers of chromite ore in 2009 with greater contribution from Orissa (Sukinda mines) and remaining from the states of Karnataka and Maharashtra.

GENERAL CHARACTERISTICS OF CHROMIUM

Table 1: General information on Chromium *www.wikipedia.com*

Category	Description
Name, Symbol	Chromium(cr)
Atomic number	24
Atomic mass	51.9961 amu
Metalic Category	Transition metal
Melting point	1857.0 c (2130.15k, 3374.6 F)
Boiling point	2672.0 0c(2945.15k,4841.6 F)
Density	293k 7.19g/cm ³
Colour	Grey

Table 1 presents the details of basic information on chromium.

Chromium from chromite ore exists in a wide range of oxidation states (0, +1, +2, +3, +4, +5 and+6). Of the valence states of chromium, the stable and most occurring forms include Cr(0), Cr(+6) and Cr(+3). Elemental chromium (Cr(0)) is a lustrous steel grey metal that does not occur naturally but is used for making steel (ATSDR, 2012). The other valence states like Cr (+5) and Cr(+4) sometimes form unstable intermediates in the conversion of Cr(+6) to Cr(+3).

CHROMIUM CONTAMINATION IN ENVIRONMENT

Chromium append into air, soil and water in the following ways:

- Anthropogenic activities of industries such as electroplating, leather tanning, dyes and pigments, textile, metallurgical, refining and chrome based chemical manufacturer

Burning of natural gas, oil and coal

Improper disposal of mine water from underground and open pit mines

Leachate from solid waste dumps Chromium pollution in the form of Cr(VI) in atmospheric is mainly removed by plunge out and precipitation with the residence time of less than 10 days.

Hence, most of chromium is deposited in water (surface and ground water) and soil sediments (Gheju, 2011). Chromium contamination in many countries is generally caused by leather tanning industries. 160,000 metric tons of chromium per year in US (Cabeza et al., 1998; Brindha and Elango, 2012) and 54 kg of chromium/day in India (Brindha and Elango, 2012) are reported to be generated from US and Indian tanneries respectively. Tannery industrial development is one among the main reason for chromium pollution in India. Though Cr (III) sulfate is used in leather tanning, Cr(VI) is generated due to post tanning processes. Irrespective of strict regulation for treating effluent by common effluent treatment plants, efficiency is not up to the mark to meet the effluent standard recommended by central pollution control board. Ramteke et al (2010) reported that the concentration of Cr(VI) (5.48 mg/l) after treatment by the Common Effluent Treatment Plant (CETP) exceeded the recommended standard value (Inland surface water discharge is 2mg/l (CPCB, 2008)). Based on Indian central pollution control board report (unpublished report), the highly chromium contaminated site in India include: Ranipet (Tamil Nadu) followed by Kanpur (Uttar Pradesh), Vadodara (Gujarat) and Talcher (Orissa). Out of 1200 tanneries (approx.) in India, Tamil Nadu accounts for more than 75 %. Ranipet in Vellore district is a medium-sized community located about 100 miles from Chennai and is found to be the world's fifth largest polluted area. Vast agricultural lands in this region are uncultivable due to pollution. Soil surrounding tannery industries are severely contaminated with chromium concentrations above the maximum threshold limit. The chromium concentration in ground water and surface water are also recorded higher than the recommended limits, compared to other parts of India. Gowd and Govil (2008) reported that chromium levels in surface water in the industrial region of Ranipet were in the range of 2.4 to 1,308.6 µg/l (average of 247.2 µg/l) Apart from tanneries and leather finishing industries located in the vicinity, achromate factory (Tamil Nadu Chromates & Chemicals Ltd (TCCL)), which is not functioning at present, produced sodium chromate, chromium salts and basic chromium sulfate. Solid waste dump (150,000 tons) rich in chromium with other pollutant, accumulated over two decades (Rao et al., 2011). Though the factory is closed, the leachate from the improper disposal has been polluting the ground water in the downstream areas of TCCL premises and levels of Cr (VI) in ground water are exceeding the permissible levels (Sankaran et al., 2010; Rao et al., 2011). The chromium level in the ground water was reported to be 275 mg/l (Rao et al., 2011) in the same TCCL area. The concentration of total chromium in the wells near to TCCL varies between 3.1 to 246 mg/l whereas the concentration of hexavalent chromium varies between 2.1 to 214 mg/l which exceed the concentration of 0.05 mg/l prescribed under Indian Standards Specification for Drinking water quality (CPCB, 2008). The ground

water in these areas, is therefore, severely contaminated with hexavalent chromium. Notably there are several other contaminated sites due to tanneries are located in other parts of Tamil Nadu like Chrompet in Chennai, Ambur and Vaniampadi on the banks of the Palar river (apart from Ranipet) and few in Dindigul and Erode. A study conducted by Brinda and Elango (2012) on ground water pollution caused by tanning industries in Chromepet area revealed that the concentration of chromium was above the permissible limit (0.05mg/l) in 86% of the ground water samples. Kumar and Riyazuddin (2011) reported chromium speciation in ground water around tanneries in chromepet. Cr (VI) concentration ranged from 32.50 and 200.30 $\mu\text{g/l}$ with a mean value of 55.27 $\mu\text{g/l}$. Mondal et al (2005) indicated that ground water in Dindigul area is heavily polluted due to tannery effluent. Distribution of chromium in soil, surface water and ground water (Ramasamy et al., 2000) in vicinity of Ambur and Vaniampadi were also reported to be higher than the permissible limit. Apart from chromium pollution, the tannery effluents confer specific characteristics to the environment (soil, ground and surface water). The general characteristics of tannery waste is distinguished by its high NaCl and other heavy metals like Cd, Pb, Cu, Fe, Mn, Ni and Zn (Ramteke et al., 2010). Gowd and Govil (2008) reported that the surface water in the area of Ranipet leather industrial area is highly contaminated with high concentrations of toxic metals like Cadmium ranging from 0.2 to 401.4 $\mu\text{g/l}$ (average of 51.1 $\mu\text{g/l}$), Chromium 2.4–1,308.6 (average of 247.2 $\mu\text{g/l}$), Copper 2.1–535.5 $\mu\text{g/l}$ (average of 95.5 $\mu\text{g/l}$), Nickel 1.6–147.0 $\mu\text{g/l}$ (average of 36.7 $\mu\text{g/l}$), Lead 6.4–2,034.4 $\mu\text{g/l}$ (average of 467.8 $\mu\text{g/l}$) and Zinc 20.8–12,718.0 $\mu\text{g/l}$ (average of 3,760.4 $\mu\text{g/l}$). High levels of chromium, manganese, nickel and zinc in the post treated tannery effluent at CETP reported by Ramteke et al (2010) shows the contribution of other heavy metal pollution by untreated or less efficiently treated tannery effluents. The same reports by Ramteke et al (2010) shows that sodium salts are added to the environment without removal (sodium ion in untreated effluent = 4090 mg/l and Treated effluent = 4190 mg/l). Sodium chloride is one of the major chemical used in the tanning industry for preserving the raw materials apart from sodium sulphide which is used during liming process (Brinda and Elango, 2012). Studies on the impact of tanning industries on ground water of chrome pet revealed that the concentration of sodium salts was found to be between 91 mg/l and 499 mg/l exceeds the World Health Organization (WHO) permissible limit of 200 mg/l (Brinda and Elango, 2012). The chloride ion in the same vicinity was above the desirable limit of 250 mg/l with alkaline pH revealing the same characteristics of treated effluents (Brinda and Elango, 2012). Mondal and Singh (2011) reports on geophysical survey on the industrial belt (with 80 functional leather factories in southern India on shallow ground water) showed ranges of Na^+ and Cl^- ions that were from 46 to 4,850 mg/l (mean, 348 mg/l) and 25 to 10,390 mg/l (mean, 1,079 mg/l), respectively. The total dissolved solids (TDS) and chloride contents in the open wells in the tannery cluster varied from 27,686 to 39,100 and 12,000 to 13,652 mg/l, respectively (Mondal and Singh, 2012). Thus in addition to Cr(VI) pollution, tannery effluents affected area showed increase in the level of TDS, sodium and chloride ions and other toxic heavy metals. In addition to chromium pollution contributed by tannery industries, textile industries in Tirupur and textile and electroplating industry in Coimbatore have been reported to contribute to metal pollution in Tamil Nadu (Govindarajalu, 2003). Open wells and bore wells in and around Tirupur and downstream of Noyyal exhibited high levels of TDS,

chloride, heavy metals (zinc, chromium, copper and cadmium) in ground water (Govindarajalu, 2003). Noyyal River flowing in Coimbatore, Erode and Karur districts are also heavily polluted with metal ions and NaCl salts. The metal and salt pollution is due to high levels of NaCl and metal based dyes used in textile processing units (Govindarajalu, 2003).

TOXICITY OF CHROMIUM

Hexavalent chromium is highly toxic than other chromium species and is regarded as the possible human carcinogen (US EPA, 1998). The route of exposure of any chromium species includes (a) Inhalation (b) Ingestion and (c) Dermal contact (US EPA, 1998). On oral inhalation, insoluble forms of chromium enter lungs and linger for several years and it occurs due to the occupational exposure by breathing contaminated air. Dermal entry of Cr (III)/Cr(VI) can occur only when skin is damaged leading to minor exposure to general population. Oral ingestion is the predominant route of exposure to general population (US EPA, 1998). The kinetics of orally ingested chromium compound depends on its valence state and its ligand. Hexavalent chromium species is absorbed more readily than the trivalent chromium species in insoluble (CrCO_3) as well as in soluble form (CrCl_3). As a natural mechanism, certain percentage of ingested Cr(VI) enters into the body through digestive tract and gets converted in stomach into insoluble Cr (III) which in turn reduces the absorbance level of toxic chromium (ATSDR, 2012). The other absorbed chromium distributes itself into various regions of body like tissues, kidney, liver and bone. When exposed to higher level of chromium, as an alarming act high level of chromium is articulated in blood, urine, expired air, hair and nails and are considered as biomarkers for chromium contact (ATSDR, 2012). On health aspects, the vulnerable targets of Cr(VI) include respiratory tract, gastrointestinal and the reproductive system (US EPA, 1998). The high level of respiratory inhalation leads to nasal irritation and breathing problems like asthma and wheezing. The stomach and intestine exposed to Cr (VI) showed high level of irritation and abrasion leading to ulcer development, internal bleeding, necrosis and bloody diarrhea. The male reproductive system is affected by decrease in sperm count and damage. Accidental/deliberate oral consumption of Cr(VI) has confirmed hematological effect leading to anemia followed by hemorrhage (US EPA, 1998). Extreme consumption affects the respiratory, cardiovascular, gastro intestinal, hematological, renal, neuron system and might ultimately lead to death (ATSDR, 2012). Cr(VI) is also considered as mutagenic as they are demonstrated to produce genotoxic adducts in the presence of glutathione causing inhibition to DNA replication (US EPA, 1998). Industrial exposure and animal studies specify that breathing and oral exposures to chromium (VI) compounds are coupled with respiratory and gastrointestinal system cancers, respectively. Hence Cr(VI) is classified to be human carcinogen compound by the International Agency for Research on Cancer (IARC) (ATSDR, 2012). With exception of occupational exposure, general population living in the vicinity of contaminated site also experience drastic health effect due to consumption of chromium contaminated agricultural products and water Gowd and Govil (2008).

METHOD/PROCEDURE

SAMPLING

The river sediment was collected from a portion of a river course in Kashere ward in Akko Local government area of Gombe state, Eastern Nigeria using Ekman dredge at 20cm down the river.

SAMPLE PRE-TREATMENT

The river sediment was brought to the laboratory and treated with distilled water for about 20 times until the river sediment as completely clean and was allowed to dry at room temperature for a period of four days. The sample was sieved using a 1mm sieve to remove big stones, plants roots, and other large particle that may contaminate the analyte. 200g was washed with 0.5M sodium hydroxide (NaOH) and 0.1M hydrochloric acid solution (HCl) followed by rinsing the sample with a distilled water to remove any metal or oxyanion from the surface of the sample and allowed to dry up for a period of 48 hours in the laboratory at room temperature.

KINETIC ADSORPTION STUDIES

10g of sediment was added into a 400cm³ of 0.1M NaCl solution and left hydrated for 24hours. 0.95g of Cr(NO₃)₂ was added into the suspension all in 500 cm³ conical flask and agitated with a magnetic stirrer for a Period of four hours at 25°C. The solution was allowed to settle for 20minutes after the agitation followed by withdrawing of 20ml and placed in container. The 20ml was withdrawn three times at 20minutes interval and also two times at 30minutes interval for complete two hours and finally the samples was subjected to AAS analysis for absorbance concentration of chromium present in solution. The quantity of chromium absorbed at equilibrium and the removal efficiency of the adsorbent was calculated using equations below:

$$q_e = (c_i - c_e) \frac{V}{w}$$

Where q_e is the Cr concentration in adsorbent at equilibrium, c_i is the initial concentration of lead, c_e is the equilibrium concentrations of lead in liquid phase, V is the volume of lead solution and w is weight of sediment.

$$\text{Removal\%} = \left(\frac{c_i - c_e}{c_i} \right) \times 100$$

PREPARATION OF 2mg/L, 4mg/L, 6mg/L, 8mg/L AND 20mg/L CHROMIUM NITRATE Cr(NO₃)₂

A series of solutions were prepared by weighing 2.278g chromium nitrate Cr(NO₃)₂ and dissolved in 500cm³ of distilled water in 500cm³ volumetric Flask making stock solution. 10cm³ of the stock solution was taken and diluted in 100cm³ of Distilled water making 100mg/L stock solution and then 2cm³, 4cm³, 6cm³, 8cm³ and 20cm³ of each was also diluted in 100cm³ of distilled water making five dilute solutions and which the calibration curve was made using their absorbance.

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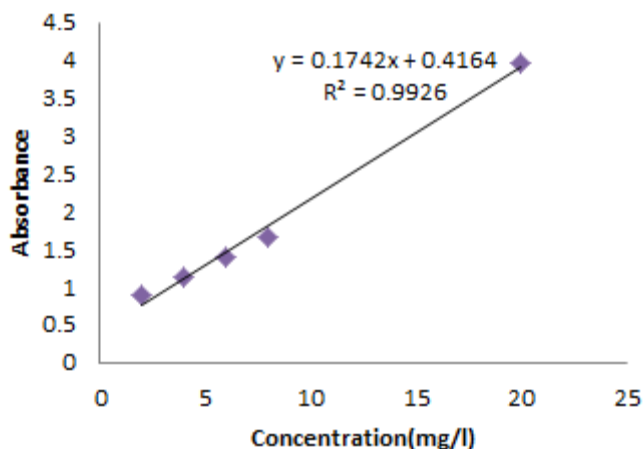


Figure 1: Calibration curve of $\text{Cr}(\text{NO}_3)_2$

RESULTS AND DISCUSSION

EFFECT OF DOSAGE

0.01g, 0.025g and 0.05g of adsorbent were added into three beakers containing 80ml of 0.1M NaCl Solution and were agitated with a magnetic stirrer for two hours and after agitation the absorbance of each was taken for AAS analysis. From the figure below showed that % removal of chromium was optimum at 0.05g and therefore the removal of chromium was higher with increase in dosage.

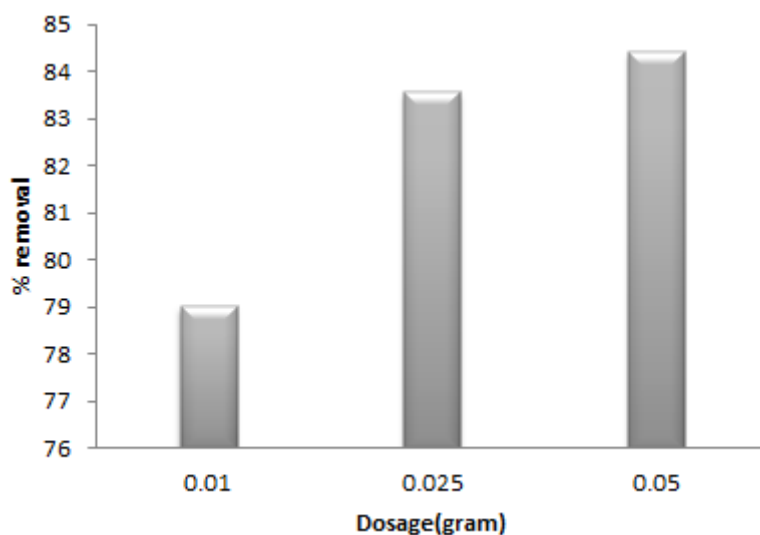


Figure 2: Effect of dosage on the removal efficiency of $\text{Cr}(\text{NO}_3)_2$

EFFECT OF TEMPERATURE

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2g of river sediment was added to each of three beakers with 80ml of 0.1M of sodium chloride and 0.19g of chromium nitrate $\text{Cr}(\text{NO}_3)_2$ was also added to each beaker. These beakers were agitated for a period of two hours while the temperature was varied to 25, 35 and 50°C. The figure below showed that the removal of chromium increase with the decrease in temperature and implies that the efficiency in removal of chromium is optimum at low temperatures (25 and 30°C).

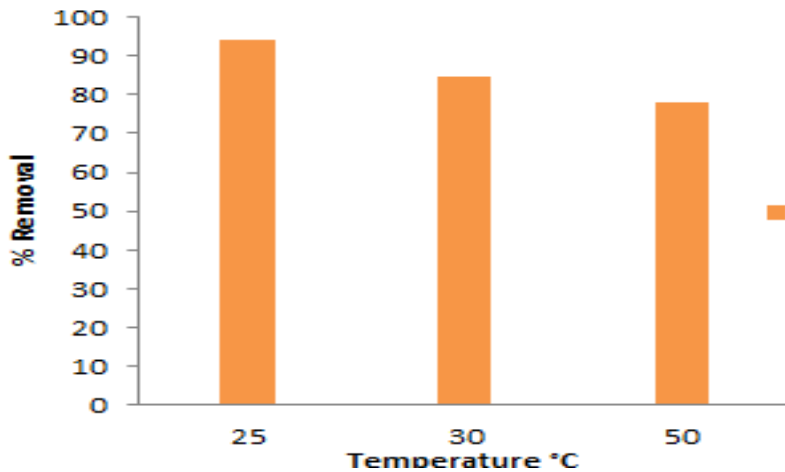


Figure 3: Effect of temperature on adsorption of $\text{Cr}(\text{NO}_3)_2$ by sediment

EFFECT OF CONTACTS TIME

The adsorption study was done by varying the time from 20 to 120 minutes to have vital expression on the adsorption capacity by adsorbent. From the figure below showed that the removal of chromium was higher after increasing the time which started from 40 minutes and drastic increased occurred at 120 minutes.

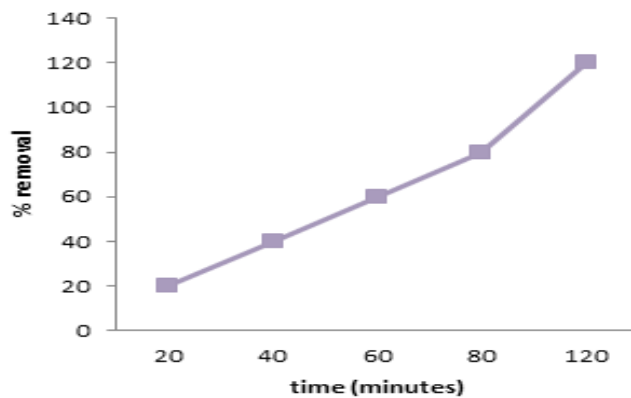


Figure 4: Effect of contact time on the removal of $\text{Cr}(\text{NO}_3)_2$

ADSORPTION ISOTHERM MODELS

The adsorption isotherm of chromium onto kashere river sediment was studied at 25°C and initial solution pH of 7.0. Two commonly used adsorption isotherm models were used in this study to evaluate the adsorption capacity of sediment. Application of the isotherm equation to adsorption data was based on comparison of the correlation coefficients (R^2) values of both models. The Langmuir and Freundlich plots are shown in Figures below while the adsorption parameters obtained from this plots are tabulated in table 2.

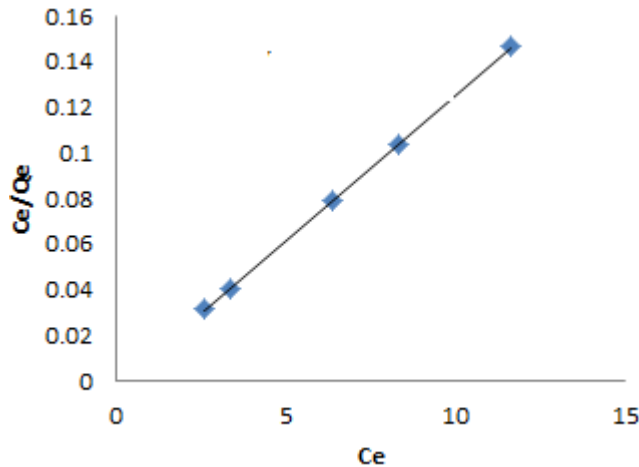


Figure 5: Langmuir plot of $\text{Cr}(\text{NO}_3)_2$ on sediment

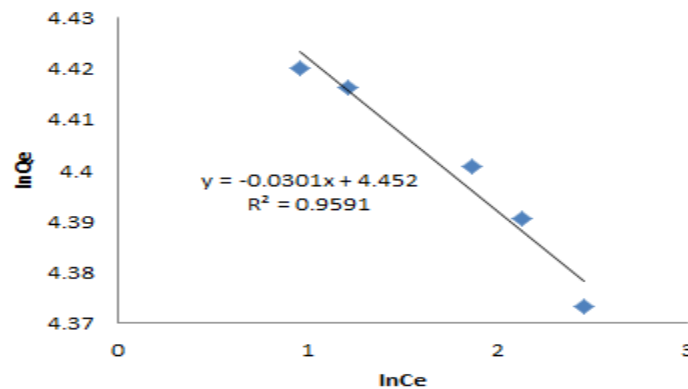


Figure 6: Freundlich plot of $\text{Cr}(\text{NO}_3)_2$ on sediment

From the above figures, the R^2 value of Langmuir was 0.9998 and value of R^2 from Freundlich 0.9591 which was lower than that of Langmuir and so the adsorption process followed Langmuir because it showed monolayer adsorption process due to the high value of R^2 .

Table 2

Isotherm	parameter				
Langmuir	T(K)	q_m (mgg ⁻¹)	KL (Lmg ⁻¹)	R _L	R ²
	298	41.6	7.81	0.0128	0.9998
<hr/>					
Freundlich	T(K)	K_f (mg/l)(L/mg ^{1/n})		1/n	R ²
	298	3.8		0.0301	0.9591

Kinetic models that used in the experiment are pseudo first and pseudo second and from the result obtained showed that the adsorption mechanism and optimum removal capacity and also adsorption efficiency of chromium followed pseudo second order due to highest value of correlative coefficient R² ranging from 0.9998 to 1.000 aproximety. Also adsorption capacity of chromium at equilibrium q_e was high with value of 4.66 to 8.69 in pseudo second order compared with 7.931 of pseudo first order.

Table 3:

model	parameter				
Pseudo first order	T(K)	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)	K ₁ (l/min)	R ²
	298	0.0122	7.931	0.028	0.9815
<hr/>					
Pseudo second order	T(K)	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)	K ₂ (l/min)	R ²
	298	4.66	8.69	0.012	0.9998

CONCLUSION

Our experiment for the removal of chromium from aqueous solution using sediment was achieved an excellent removal because of the adsorption process is the best method for removal of heavy metals due to its initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances. And also sediment is a good adsorbent due its good absorbing properties such as high porosity of particles, large size and attractive surface.

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