Adsorptive Removal of Hexavalent Chromium using Synthetic Goethite Nanoparticles

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ABSTRACT

This study investigated the adsorptive removal of hexavalent chromium from aqueous solution using synthetic goethite nanoparticle. The goethite particle (α-FeOOH) was synthesized and characterized usingFourier Transform Infrared, Scanning Electron Microscopy, Transmission Electron microscopy and Malvern nanosizer.Broad peaks around 3142 and 3404 cm^{-1}were attributed to O-H stretching vibration of the hydroxyl group and the strong intensities at 634 cm^{-1}, 796 cm^{-1} and 893cm^{-1}were attributed to Fe-OHstretching frequencies. The physico-chemical parameters including pH, colour, point of zero charge (pzc) and surface area were determined. Batch adsorptionexperiments were carried out on hexavalent chromium Cr (VI)as a function of pH, contact time, initial concentration of the adsorbateand temperature of the solution. The maximum concentration adsorbed was 20 mg/l at a maximum pH of 2. The maximum adsorption was achieved within 120 minutes and adsorption was observed to increase with increase in temperature. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model. Thermodynamic parameters showed that adsorption was spontaneous in nature, and endothermic. The equilibrium data better fitted the Freundlich isotherm model.

Keywords: Adsorption, Goethite, Hexavalent Chromium, Kinetics, Thermodynamic

INTRODUCTION

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of these heavy metals are dangerous to health and to the environment. Heavy metals from industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel.The removal of these wastes cannot be achievedusing secondary methods, therefore tertiary or advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption can be used to remove these wastes[1].

The metal, chromium (Cr) is a steel-gray solid with a high melting point and an atomic weight of 51.996g/mol[2]. Chromium can exist in several chemical forms displaying oxidation numbers from 0 to 6. They form many compounds in both the chromium (III) and chromium (VI) forms. The Cr (III) compounds are sparingly soluble in water and they are bio-element while Cr (VI) compounds are readily soluble in water and they are mutagenic[3].Hexavalent chromium, Cr (VI) in discharged wastewater typically comes from industries. As its contamination is a widespread environmental problem, the technologies to remove Cr (VI) have been developed, including cyanide treatment, electrochemical precipitation, reverse osmosis (RO), ion exchange, and adsorption. Currently, adsorption of Cr (VI) onto different adsorbents is considered as one of the most promising treatment approaches for Cr (VI) polluted wastewater, because this method has many advantages such as low-cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, and avoidance of the formation of secondary pollutants[4].

This present work revealed the adsorption of hexavalent chromium from aqueous solution on the surface of synthetic goethite nanoparticle as the adsorbent. Goethite (α-FeOOH) is the most abundant and most stable of all forms of iron-oxides in soil and its surface chemistry affects the distribution of soluble species in soil[5].Synthetic goethite has been extensively studied and applied for the removal of heavy metals contaminants from industrial solutions, radionuclides from nuclear reactor plants and for municipal water treatment.

EXPERIMENTAL METHODS

Materials

Iron nitrate, potassium hydroxide, hydrochloric acid, nitric acid, potassium dichromate and sodium hydroxide were used and were all analytical grade including de-ionized water.

Synthesis of Goethite nanoparticle

The goethite (α-FeOOH) was prepared by using modified method ofSchwertmann and Cornell (1991). The preparation was carried out under nitrogen atmosphere. A 50ml of 1M $Fe(NO_3)_3$ solution (freshly prepared by dissolving un-hydrolysed Fe $(NO_3)_3.9H_2O$ in deionized water) was added rapidly to 90ml of 5M KOH solution, reddish brown ferrihydrite was precipitated at once. The suspension was diluted to 1 litre with doubly deionized water and held in a closed polyethylene flask at 70°C for 60hours in the oven. The vessel was removed from the oven, centrifuged and the precipitate was washed by dialysis, filtered by Millipore glass membrane vacuum filtration system and oven dried[6].

Characterization techniques

The synthesized goethite nanoparticle was characterized by using Fourier Transform Infrared, x-ray diffraction, scanning electron microscopy, transmission electron microscopy and Malvern nanosizer, Brunauer-Emmet-Teller (BET).

Preparation of stock solution of hexavalent chromium

An aqueous solution of Cr (VI) was prepared by dissolving 283mg of potassium dichromate in 100ml of deionized water to obtain a solution of 1000 mg/l of the stock solution. Standard solutions between 0 to 500 mg/l were thenprepared from the stock solution by serial dilution.1.0 to 5.0ml of 0.1M trioxonitrate acid (HNO_3) was used to adjust the pH to 3. An initial Cr (VI) concentration of 1 to 1000mg/l at pH 3 was contacted with 20mg of each iron oxide on a mechanical shaker for 120minutes at 298K. The mixture was filtered and analyzed on a UV-Visible spectrometer at a wavelength of 340 nm[7]. The adsorption capacity of Cr (VI) was measured and calculated from the difference between initial and final concentration of chromium. The amount adsorbed (mg/g) was calculated using the formula:

$$Q = \frac{V(c_i - c_f)}{W} \qquad \text{(i)}$$

Where Q = Quantity of solute adsorbed from solution of volume, V cm^3

C_I = initial concentration before adsorption (mg/dm^3)

C_f = Concentration after adsorption (mg/dm^3)

V = Volume of the adsorbate used in litres

W = mass of the adsorbent in gram

Influence of Some Physicochemical parameters on Sorption

Effect of pH

The effect of pH was carried out for Cr (VI) on goethite sample at 20mg/l equilibrium concentration of Cr (VI). 20mg of the goethite nanoparticle was contacted with 20ml of the equilibrium concentration of pH ranging between 1 and 10. The mixture was agitated on a mechanical shaker for 120minutes. After shaking, the samples were withdrawn and filtered[4]. The filtrates were analyzed by UV-Visible spectrometer at wavelength 340nm.

Effect of Adsorption Time

The kinetics study was carried out at pH 2 for Cr (VI) on goethite nanoparticles. 20mg of the sample was contacted with 20ml of 20mg/l concentration. The mixtures were agitated on an orbital shaker at different time intervals (15, 30, 70, 120, 150, 180, 220, 240 minutes). After shaking, the samples were withdrawn at time intervals and filtered. The filtrates were analyzed by UV-Visible spectrophotometer at wavelength 340nm. The equilibrium time was determined from the graph of amount of solute adsorbed per gram of goethite versus time of contact[7].

Effect of Adsorbent Dosage

The effect of adsorbent dosage was carried out pH 2 for Cr (VI). This was contacted with 10mg to 250mg (10, 20, 50, 100, 200, 250mg) of goethite nanoparticles. The samples were withdrawn and filtered. The filtrates were analyzed by UV – Visible spectrometer at wavelength 340nm[4].

Effect of Temperature

The effect of temperature was carried out at pH 2 for Cr (VI) on the goethite sample at 20 mg/l equilibrium concentration of Cr (VI). This was contacted at different temperatures of 283, 303 and 323K. The samples were withdrawn and filtered. The filtrateswere analyzed by UV-Visible at wavelength 340nm.

Desorption analysis of hexavalent chromium

The study was carried out on samples of Cr (VI) loaded goethite with 0.1 M HNO_3 and 0.1 M HCl as the desorption solutions. To determine the most effective desorption solution, goethite nanoparticle containing Cr (VI) was contacted with 20 ml of the desorption solutions for 120 minutes. The mixtures were filtered after desorption and filtrates were analyzed for residual concentration of Cr (VI) by UV-Visible spectrometer. The desorption efficiency is the ratio of the desorbed amount to the initial adsorbed amount[7].

Adsorption Isotherm

The data obtained in this study by varying the initial concentration of Cr (VI) solution was fitted with Langmuir and Freundlich adsorption isotherms.

Langmuir Adsorption Isotherm

The Langmuir isotherm takes an assumption that adsorption occurs at specific homogeneous sites within the adsorbent. The equation is as follows:

$$Q_e = \frac{Q_m K C_e}{1 + K C_e} \qquad \text{(ii)}$$

Where: Q_e (mg of adsorbate per g of adsorbent) is the adsorption density at the equilibrium solute concentration C_e.

C_e is the equilibrium concentration of adsorbate in solution(mg/L).

Q_m (mgofsoluteadsorbedper g of adsorbent) is the maximum adsorption capacity corresponding to complete monolayer coverage.

K is the Langmuir constant related to energy of the adsorption (L of adsorbate per mg of adsorbent).

The previous equation can be rearranged to the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \qquad \text{(iii)}$$

The linear form can be used for linearization of experimental data by plotting $\frac{C_e}{Q_e}$against C_e. The Langmuir constantsQ_m and k can be evaluated from the slope and intercept of the linear equation:

$$Q_e = \frac{Q_m K C_e}{1+KC_e} \qquad \text{(iv)}$$

Freundlich Adsorption Isotherm

TheFreundlich isotherm is an empirical equation employed to describe the heterogeneous system. The equation is given below:

$$Q_e = K_f {C_e}^{1/n} \qquad \text{(v)}$$

Where:

Q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent).

C_e is the concentration ofadsorbate at equilibrium

$K_f$and 1/n are empirical constants dependent on the natureof sorbent and sorbate and the temperature.

Both values (K_f and 1/n) are important in selecting an adsorbent as a separating medium, in which K_f (mg/g) is the over-all adsorption capacity and1/n is the heterogeneity factor. The heterogeneity factor 1/n indicates the strength of bond energy between adsorbate andadsorbent.Thisequationisconvenientlyusedin linearformbytaking the logarithmic of both sides as:

$$\ln Q_e = \ln K_f + \frac{1}{n} lnC_e \qquad \text{(vi)}$$

A plot of $\ln Q_e$ against lnC_e yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

Adsorption kinetic studies

In order to comprehensively investigate the mechanism of adsorption, two kinetic models i.e. pseudo-first order and pseudo-second order was fitted to experimental data to determine the kinetics of adsorption.

The adsorption kinetics can be described by a pseudo-first order equation as suggested by Lager Gren. $\frac{dq}{dt} = k_1(q_e - q_t)$ (vii)

which on integration becomes

$\ln(q_e - q_t) = lnq_e - k_1 t$ (viii)

Where: k_1(min^{-1}) is the rate constant of the pseudo-first order model, q_t (mg/g) is the amount of adsorption at time t (min), and q_e(mg/g) is the amount of adsorption at equilibrium.

The adsorption rate constant, k_1 will be experimentally determined by the slope of linear plots of $\ln(q_e - q_t)$ vs t

The pseudo-second order equation is written as $\frac{dq}{dt} = k_2(q_e - q_t)^2$ (ix)

which on integration becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad \text{(x)}$$

Where k_2 (g/mg/min) is the rate constant of the pseudo-second order.

K_2 and q_e will be obtained from the intercept and slope of plotting $\frac{t}{q_t}\ vs\ t$

Adsorption thermodynamics studies

Thermodynamic parameters such as free energy (G), enthalpy (H) and entropy (S) changes during adsorption were evaluated from the equation.

$G = -RTlnK_c$ (xi)

$logK_c\left(\frac{S}{2.303R}\right) - \left(\frac{H}{2.303RT}\right)$ (xii)

Where: K_c is the Langmuir constant,

C_e is the adsorbate concentration at the equilibrium in mg/mol

ΔG, ΔH and ΔS are changes in Gibbs free energy, enthalpy and entropy in kJ/mol

R is the gas constant and T is the temperature in Kelvin.

The values of ΔH and ΔS were determined from the slope and the intercept of Van Hoff plots of lnk_cversus 1/T

RESULTS AND DISCUSSION

Physicochemical properties of Goethite nanoparticles

Table 1: Physical properties of goethite nanoparticle

pH	9.3
Pzc	7.9
Colour	Brownish yellow
Texture	Fine
Surface area	130.096 m^2/g
% yield	68%
Bulk density	0.4408

The pH of the goethite nanoparticle on measurement gave pH 9.3. The point of zero charge, pzc, of the synthesized goethite nanoparticle was found to be at pH 7.9.

At pH below the pzc, the goethite surface had a net positive charge.

The adsorption of positive species will be electrically unfavourable. When adsorption takes place below the pzc, then the adsorption may be attributed to either metal adsorption on to the few negatively charged surface sites or an adsorption of anionic species preceding cationic species, which increases the net negative on the goethite surface[8].The value is within the range of values reported for goethite (7.8–8.4)[9,10]. The surface area which is 130.096m^2/g falls within the specified range of 60 – 200 m^2/g which was reported by IITA[11].

Infrared Spectroscopy

The spectrum in figure 1showed that the synthesized sample was closely identical to goethite nanoparticles. A broad peak around 3142 and 3404 cm^{-1}were attributed to O-H stretching vibration of the hydroxyl group. The strong intensities at 634 cm^{-1}, 796 cm^{-1} and 893cm^{-1}were attributed to Fe-OH stretching frequencies. The weak intensity at 1384cm^{-1} was attributed to O-H bending frequency, the weak intensities at 1541cm^{-1}, 1647cm^{-1}, and 1791cm^{-1} was assigned to ∂(HOH), H_2O water of crystallization. The weak intensity at 3749cm^{-1} was attributed to the water of crystallization stretching frequencies. The result corresponds to what was obtained by Cambier[12].

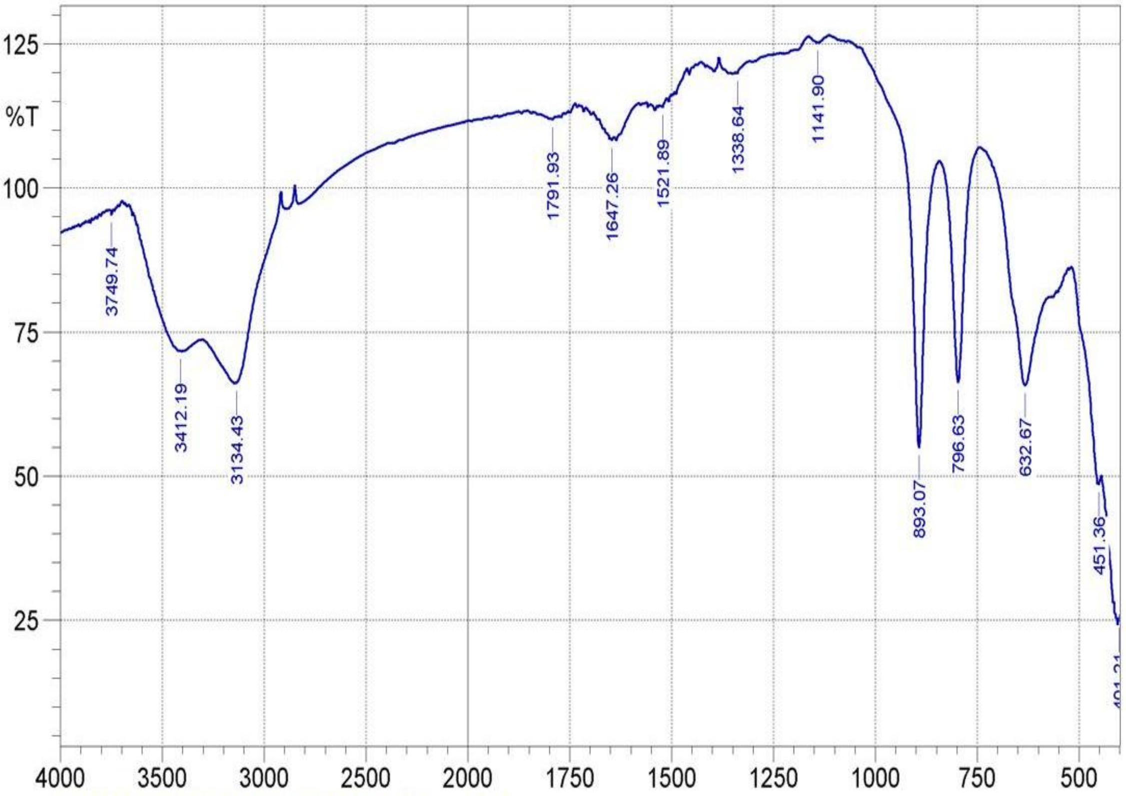


Figure 1:Infrared spectroscopy of goethite nanoparticle

Scanning electron microscopy

The SEM micrograph of goethite product (Fig. 2) showed that the morphology of the synthesizedgoethite at magnification 10 μm. The particles from bright yellow goethite were needle-like in shape and regular. This indicates the quality hiding power that the pigment will show[13].

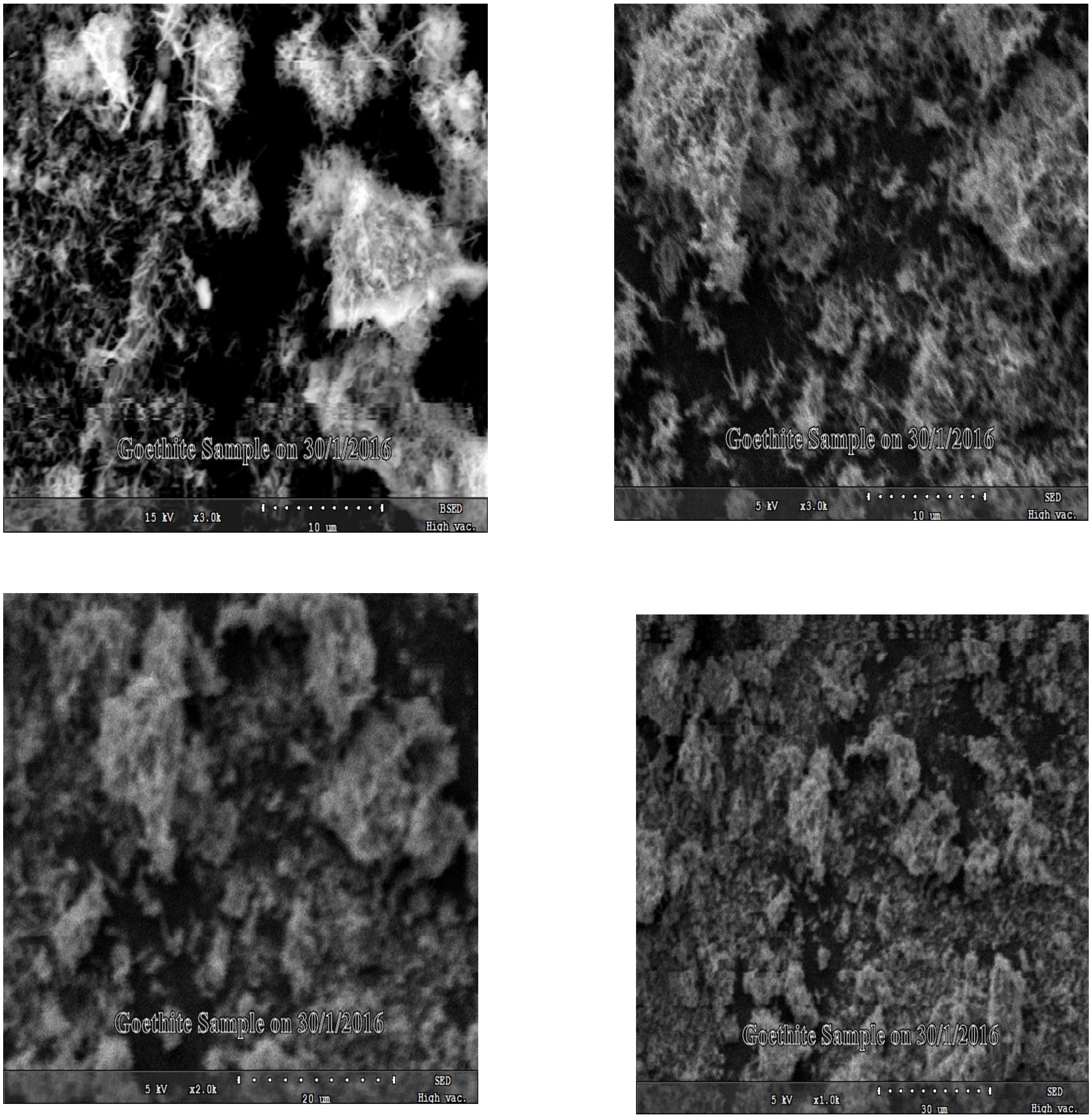
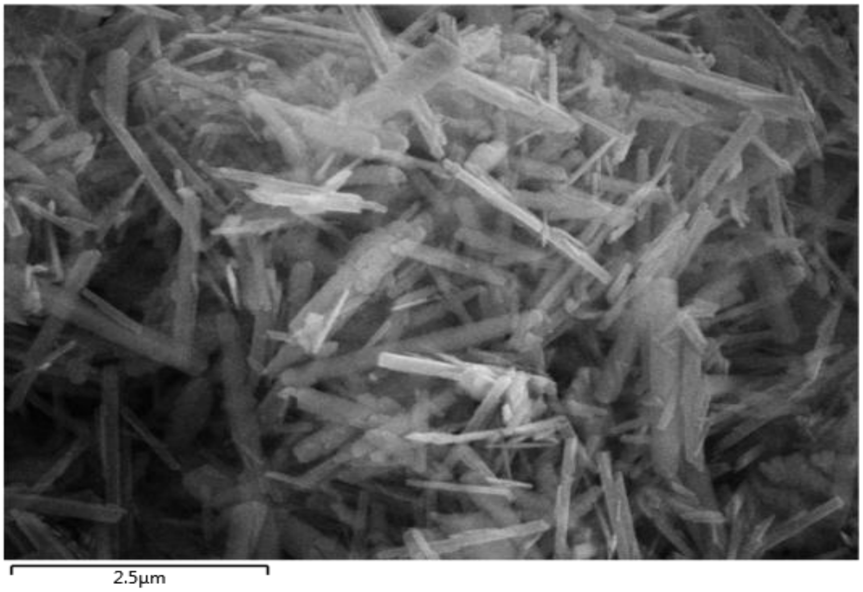


Figure 2: Scanning electron micrographs goethite at different magnification

Transmission electron microcopy (TEM)

The TEM micrographs in fig 3 show the shape and the crystallite sizes of the goethitenanoparticle.

G1



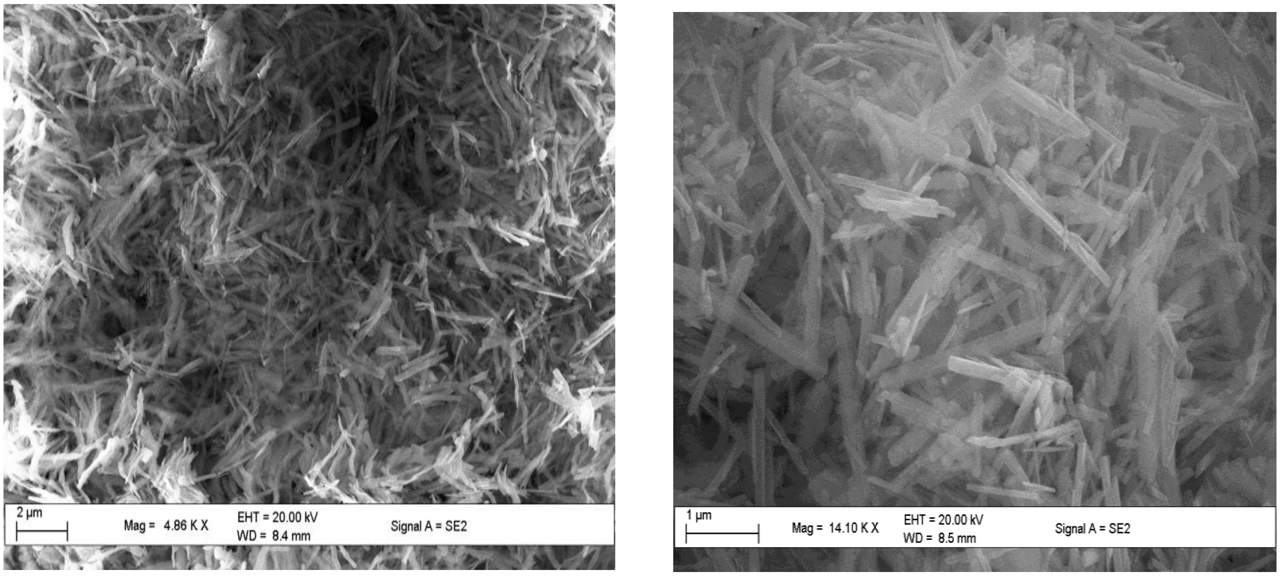


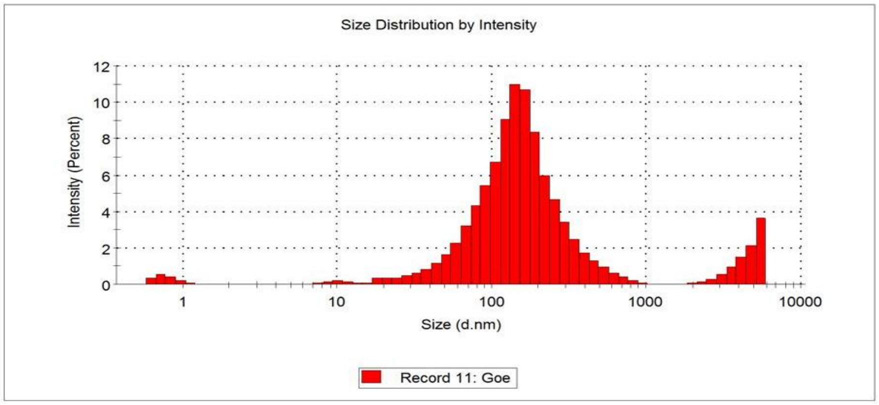
Figure 3: Transmission electron micrographs of goethite at different magnifications

Particle-Size Distribution

The particle size distribution revealed that the goethite nanoparticles are in the nanometer range as revealed by the intensity distribution.

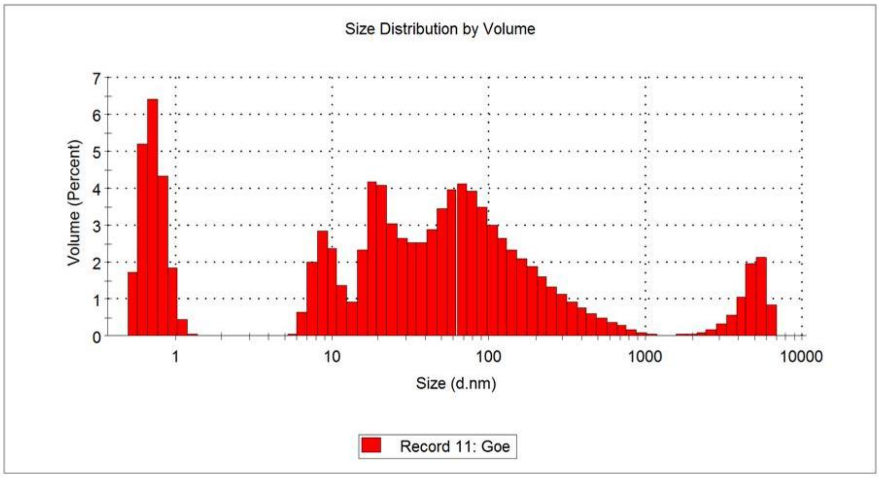
Size distribution report by intensity

			Size (d.n...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	391.0	Peak 1:	172.6	87.6	114.2
PdI:	0.472	Peak 2:	4661	9.2	931.2
Intercept:	0.496	Peak 3:	0.7672	1.5	0.1214
Result quality	Refer to quality report				

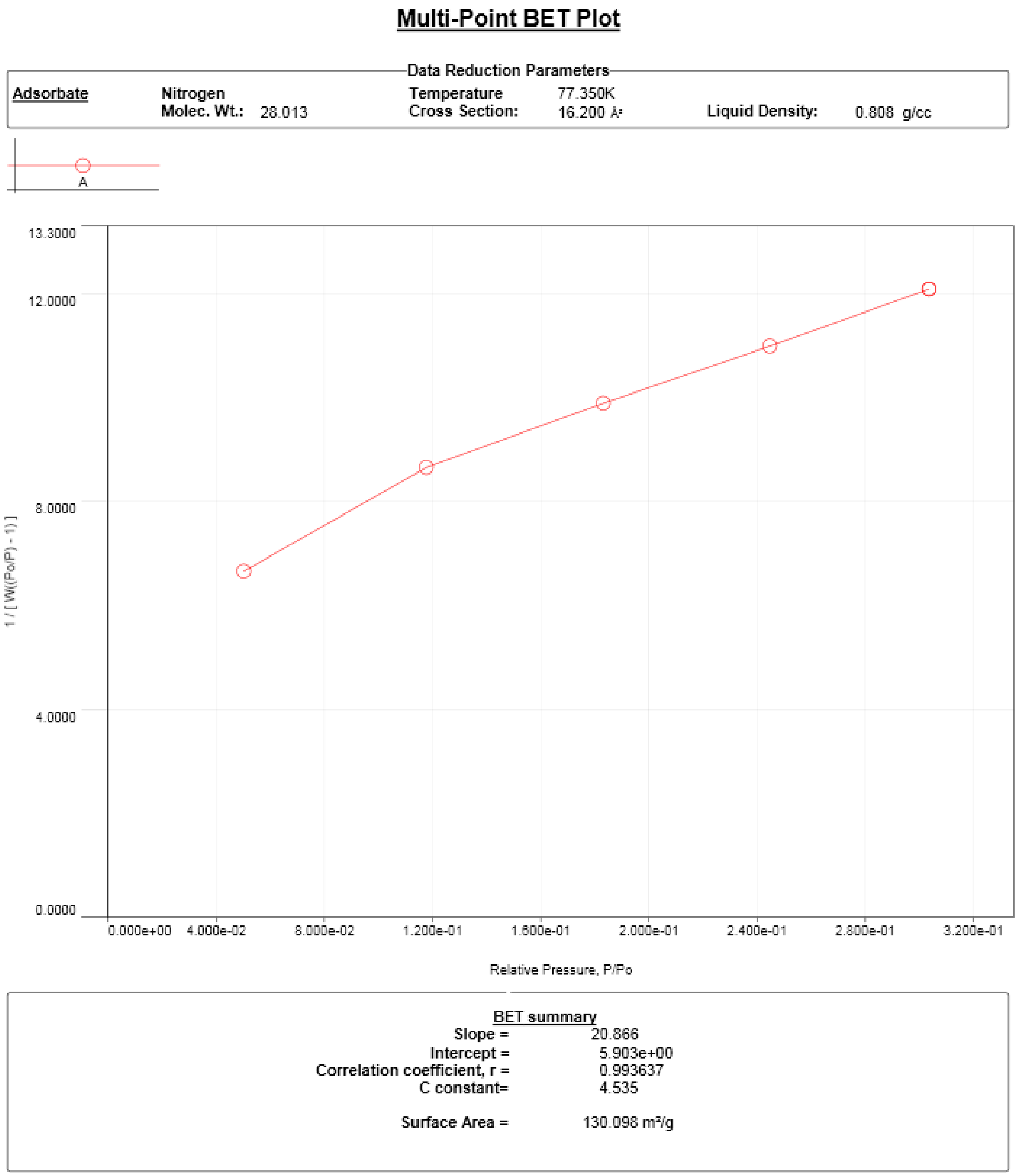


Size distribution report by volume

			Size (d.n...	% Volume:	St Dev (d.n...
Z-Average (d.nm):	391.0	Peak 1:	131.8	44.9	131.3
PdI:	0.472	Peak 2:	4832	6.9	1039
Intercept:	0.496	Peak 3:	0.7359	19.3	0.1335
Result quality	Refer to quality report				



Brunauer-Emmet-Teller (BET)



Multi-Point BET Plot

Data Reduction Parameters

Adsorbate: Nitrogen
Molec. Wt.: 28.013
Temperature: 77.350K
Cross Section: 16.200 Å²
Liquid Density: 0.808 g/cc

BET summary

Slope = 20.866
Intercept = 5.903e+00
Correlation coefficient, r = 0.993637
C constant= 4.535

Surface Area = 130.098 m²/g

Influence of Some Physicochemical parameters on Sorption

Effect of initial concentration of Cr (VI)

The effect of initial hexavalent chromium concentration on the adsorption efficiency of goethite nanoparticle under optimum conditions of pH and contact time is shown in Figure 4. The maximum amount adsorbed was 20 mg/l, this could be due to the surface area of the adsorbent. Since the amount of the goethite used was kept constant for the effect of the initial concentration, the surface of the adsorbent might have been saturated at equilibrium, and therefore, not accommodating more of adsorbate. At this point, equilibrium is reached, thereby resisting the uptake of Cr (VI)[14].

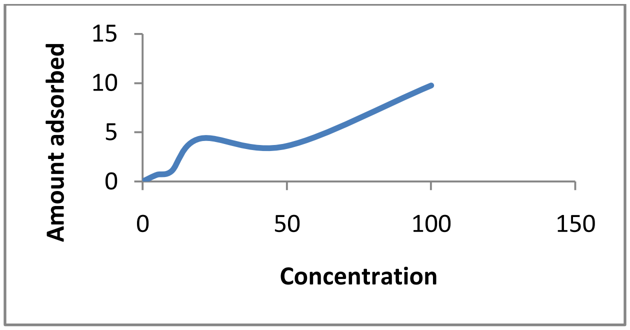


Fig 4: Effect of initial concentration on Adsorptionof Cr (VI)

Effect of pH

The effect of pH on the adsorption of the metal ions was carried out within the range of 1 to 10. It can be seen in the Figure 5 that the maximum of hexavalent chromium adsorption at the lower pH value. The maximum adsorption was observed at pH 2 and the amount adsorbed decreased as the pH increased. The favorable effect of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions ($HCrO_4^-$) and their subsequent adsorption. ($HCrO_4^-$) is the dominant and ionic form of hexavalent chromium between pH 2.0 and 4.0[15]. As shown in the equation below, hydroxyl species are released from the process of Cr (VI) adsorption instead of hydrogen ions.

$$R + H_2O + HCrO_4^- \leftrightarrow R - HO_3Cr^+ + 2OH^-$$

Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes and can also be due to the competition from excess OH^-ions with the anions for the adsorption site. This is similar to what was reported by other investigators[15].

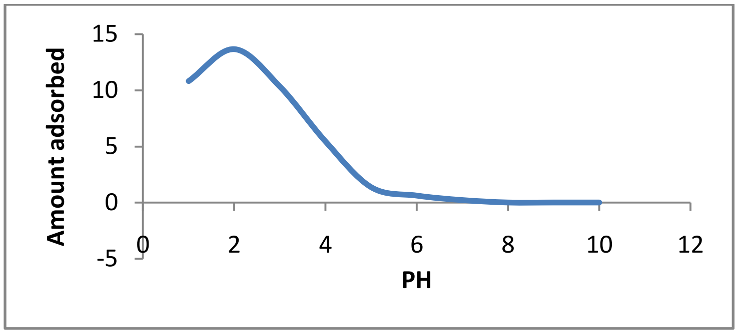


Figure 5: Effect of pH

Effect of Time

The result of the effect of time is shown in the figure 6. The figure shows that adsorption of Cr (VI) increases with time. The maximum adsorption was achieved at 120 minutes, further increase in contact time reduced had no significant effect or can even reduce the adsorption capacity.

Generally, by the time adsorption involves a surface reaction process, the initial adsorption is fast, then, as lower adsorption would follow at the available adsorption site which is gradually decreased. This is sincemany vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. This is also observed in some other reports[16].

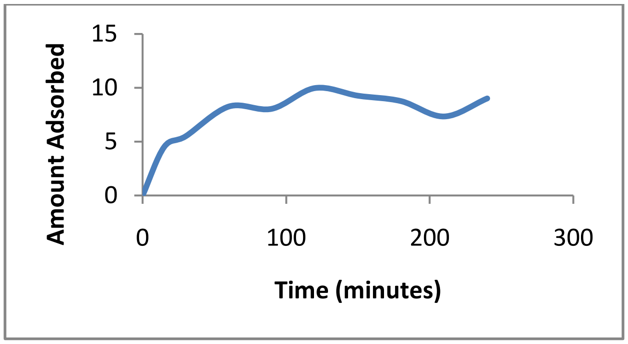


Figure 6: Effect of time

Effect of Temperature

It was observed that the percentage of adsorption increases from 8 to 13 for hexavalent chromium ions with the rise in temperature from 283 to 323K, this is shown in figure 7. The rise of adsorption capacity with temperature was due to the increase in kinetic energy of adsorbent particles. Thus, the collision frequency between adsorbent and adsorbate increases, which results in the enhanced adsorption onto the surface of the adsorbent. Secondly, at high temperature due to bond rupture of functional groups on adsorbent surface increases active adsorption sites, which may also lead to enhanced adsorption[17].Also, the adsorbent shows the endothermic nature of adsorption.

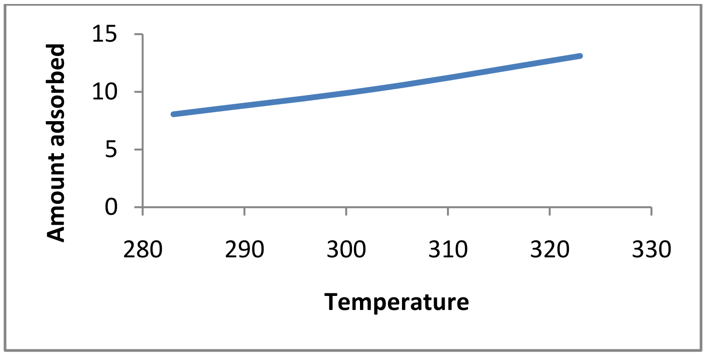


Figure 7: Effect of Temperature on Adsorption of Cr (VI)

Desorption analysis of Cr (VI)

The desorption analysis of Cr (VI) was carried out by using two different acid. This was done to know which of the acid has better desorption capacity. The result is as shown in the Table 2 below. The table shows that trioxonitrate (V) acid (HNO_3) has a higher capacity to recover Chromium (VI) better than hydrochloric acid (HCl).

Table 2: Desorption of Cr (VI)

Concentration	Amount recovered	% recovered
0.1 M HNO_3	0.515	51.5%
0.1M HCl	0.120	12%

Adsorption Isotherm

The results clearly showed that the adsorption of hexavalent chromium on goethite fits well with the Langmuir model than the Freundlich model. The value of the dimensionless factor L from the Langmuir isotherm which is between 0 and 1 suggests a favorable adsorption between goethite and hexavalent chromium ion[17]. From the Freundlich isotherm, if the value of n is equal to unity, the adsorption is linear. If the value of constant n is below unity, it implies that the adsorption process is unfavourable[17]. Therefore, the value of n which was above unity suggested a favorable adsorption.

Table 3: Adsorption isotherm constant

Adsorption isotherm constant	values
Langmuir isotherm	
Adsorption capacity Qm (mg/g)	3.6996
Energy of adsorption K	0.3709
Dimensionless factor (L)	0.9886
R^2	0.1188
Freundlich isotherm	
Adsorption capacity K_f (mg/g)	1.096694
Heterogeneity factor 1/n	0.3328
N	3.0048
R^2	0.7459

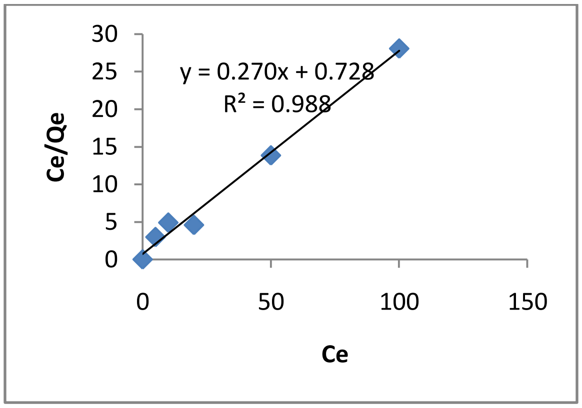


Figure 8:Langmuir isotherm for Cr (VI)

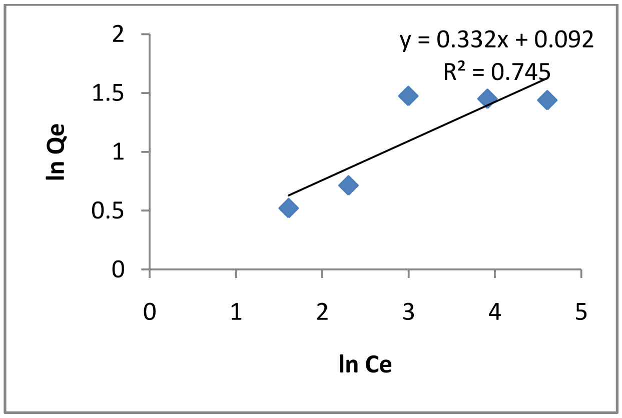


Figure 10: Freundlich isotherm for Cr (VI)

Adsorption Kinetics Result

The adsorption of Cr (VI) fits in well into the pseudo-second order model than the pseudo first order model.The correlation coefficient, R^2, for thesecond-order kinetic model was almost equal to unity signifying the applicability of the model.Moreover, the calculated qe (mg/g) values obtained frompseudo-second-order kinetics were in good agreement withthe experimental (mg/g) values. Thus, it appearedthat the system under study is more suitably describedby pseudo-second-order kinetics which assumed that the rate limiting step may be chemisorption concerning valences forces through sharing and exchange ofelectrons. The pseudo-second-order kinetics model has been successfully applied to several adsorption systems as reported by[17].

Table 4: Kinetics parameters

Adsorption kinetics result	values
Pseudo-first order model	
Slope ($\ln q_e$)	-0.203
Q_e	0.9799
Inteercept (-K1)	2.0595
K_1	-2.0595
R^2	0.9183
Pseudo second order model	
Slope ($1/q_e$)	0.1067
q_e	9.3721
K_2	0.1041
R^2	0.9836

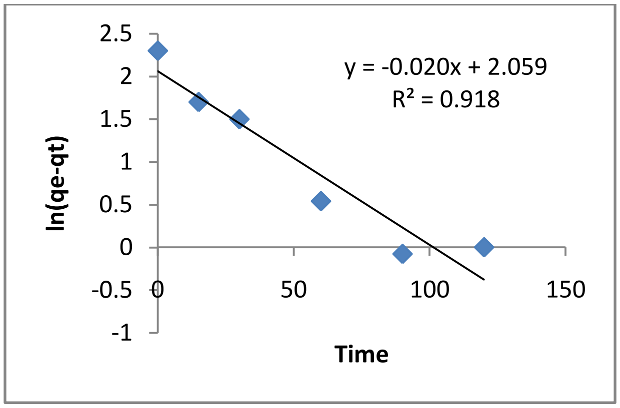


Figure 9: Pseudo first order model of Cr (VI)

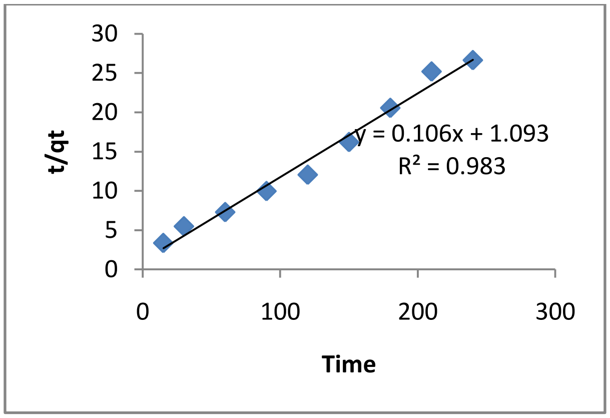


Figure 11: Pseudo-second order model of Cr (VI)

Thermodynamics study of Cr (VI)

The calculated values of thermodynamic parameters for Cr (VI) are listed in the Table 5. The positive value of enthalpy change confirms the endothermic nature of the adsorption process. The low values of ΔH give clear evidence that the interaction of hexavalent chromium and goethite was weak suggesting physical adsorption process. The positive value of entropy, ΔS^o, represents an increase in the degree of freedom of the adsorbed species which indicates that some changes occur in the internal structure of goethite during the adsorption process. The negative values of Gibbs free energy, ΔG^o demonstrates that the adsorption is rapid and spontaneous. The negative value of ΔG^o ensures the feasibility of the process. Generally, ΔG^o values range from 0 to −20 kJ/mol for physical adsorption and −80 to −400 kJ/mol for chemical adsorption[17].

Table 5: Thermodynamics study of Cr (VI)

Temperature (T)	Gibbs energy(ΔG)	Enthalpy (ΔS)	Entropy (ΔS)
283	-3.0781	9.259	0.04359
303	-3.296	9.259	0.04143
323	-3.513	9.259	0.03954

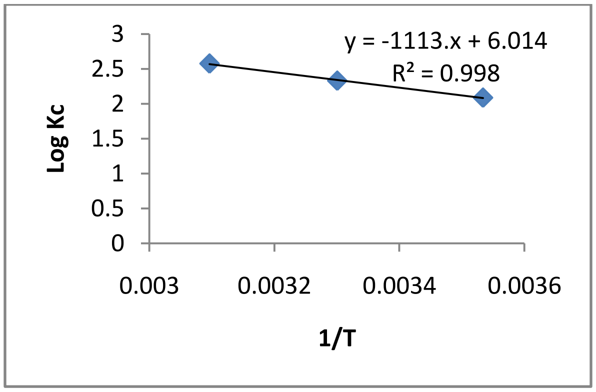


Figure 12:Thermodynamics study of Cr (VI)

CONCLUSION

This work has successfully shown the synthesis of goethite nanoparticle and its application in the adsorption of hexavalent chromium from aqueous solution. The result shows a high adsorption capacity of the goethite nanoparticle, this can be attributed to the hydroxyl group which was identified by the FTIR.

The adsorption was greatly governed by pH and the results of effect of temperature showed significant increase with the increase in temperature, therefore, pH and temperature can be manipulated to enhance adsorption capacity of the goethite. The kinetics studies conducted showed that the adsorption of hexavalent chromium by goethite was best described by the pseudo-second-orderkinetic model. The Langmuir and Freundlich adsorption isotherm models were used to express the adsorption phenomenon of the hexavalent chromium. The value of the dimensionless factor, L indicated that relationship between the goethite/Cr (VI) gives a favorable adsorption. The thermodynamics studies predictthattheadsorptionisfeasible, spontaneous and endothermic in nature with negative value of change in Gibbs free energy (ΔG^{o}) and positive values of enthalpy (ΔH^{o}) andentropy(ΔS^{o}) at temperatures of 298, 303, and 323 K.

Thenegative value of ΔG° confirmed the spontaneous nature of adsorption process. The positive value of ΔS° showed the increased randomness at the solid-solution interface during adsorption and the positive value of ΔH° indicated the adsorption process was endothermic. This suggests that goethite nanoparticle is effective for the removal of hexavalent chromium from waste water especially from textile and tanning industries.

REFERENCES

1. Dimple L, (2014). *Adsorption of Heavy Metals: A Review*, International Journal of Environmental Research and Development. 4(1), 41-48.

2. Mohamed O.A and Youssouf D.S, (2014). *Waste water treatment in chemical industries: the concept and current technologies*, Hydrology Current Research, 5 (1), 1-8,

3. Moreno-Castilla C,(2004).*Adsorption of organic molecules from aqueous solutions on carbon materials*. Journal of Colloid and Interface Science 42, 83–94.

4. Yan W, Hanjin L, Hou W, Can W, Jian Z, Zilong Z,(2013). *Adsorption of hexavalent chromium from aqueous solutions by grapheme modified with cetyltrimethylammonium bromide*. Journal of Colloid and Interface Science 394, 183–191.

5. Cornell R. M and Schwertmann U. (1996). *The Iron Oxides: structure, properties, reactions, occurrence and uses*. VCH VerlagsgesellschaftWeinheim.

6. Schwertmann U. and Cornell R.M, (1991). *Iron oxide in the laboratory: preparation and characterization*. Wiley-VCH Weinhein, Germany, p1 – 132.

7. Adegoke H.I, Adekola F.A, Fatoki O.S and Ximba, B.J. (2014). *Adsorption of Cr (VI) on synthetic hematite (α-Fe_2O_3) nanoparticles of different morphologies*. Korean Journal of Chemical Engineering, 31 (1): 142 – 154.

8. Abdus-Salam, N. and Adekola, F. A. (2005). *The influence of PH and adsorbent concentration on adsorption of lead and zinc on a natural goethite*. African Journal of Science and Technology (AJST).Science and Engineering Series Vol.6, No. 2, pp. 55 – 66.

9. Behera R.K., Rout K., Nayak B. and Das N. N. (2010). *Mineralogical characterization and sorption properties of goethite rich iron ore from daitariorissa*, Proceedings of the XI International Seminar on Mineral Processing Technology (MPT-2010).pp. 16–23.

10. Julius N.N and Joseph K.M. (2013). *The Adsorption Efficiency of Chemically Prepared Activated Carbon from Cola Nut Shells by $ZnCl_2$ on*

Methylene Blue, Journal of Chemistry Volume 2013, Article ID 469170.

11. International Institute of Tropical Agriculture (IITA). 1979). *Selected methods for soil and plant analysis*. Manual series No 1, 3 – 29.

12. Cambier P. (1986). *Infrared study of goethite's of varying crystallinity and particle size: interpretation of OH and lattice vibration frequencies*, Clay Minerals, 21, 191-200.

13. Elodia. and Waal D. (2007). *The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste*. Article in Dyes and Pigments. Impact Factor:3.97· DOI: 10.1016/j.dyepig.2006.01.038.

14. Simonides K, Tresintsi S, Martinez-Boubeta C, Vourilas I, Tsiaoussis G, Stavropoulos G, Mitrakas M and Angelakeris M.(2011). *Magnetic separation of hematite-coated* Fe_3O_4 *particles used as arsenic adsorbents*. Journal of Chemical Engineering, 168(3): 1008-1015.

15. Das B. and Mondal N.K. (2011). *Calcareous soil as a new adsorbent to remove lead from aqueous solution: equilibrium, kinetic and thermodynamic study,* Universal Journal of Environmental Research and Technology, 1 (4): 515–530.

16. Mohan D, Singh K.P. and Singh V. K.(2006). *Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth*, Journal of Hazardous Materials, 135(1–30); 280–295.

17. Tamirat D, Khalid S, and Shimeles A.K. (2014). *Adsorption of hexavalent chromium from aqueous solution using chemically activated carbon prepared from locally available waste of bamboo (Oxytenantheraabyssinica)*, Hindawi Publishing Corporation, ISRN Environmental Chemistry Article ID 438245, 1-9.