

**ADSORPTION OF HEXA VALENT CHROMIUM
ONTO GOETHITE**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

**BACHELOR OF TECHNOLOGY
IN
MINING ENGINEERING**

**BY
BHAVNA MISHRA
108MN035**



Department of Mining Engineering

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Under the guidance of

PROF. SK.MD.EQUEENUDDIN

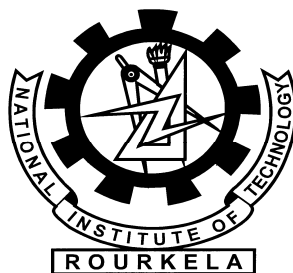


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National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled “**ADSORPTION OF HEXAVALENT CHROMIUM ONTO GOETHITE**” submitted by **Bhavna Mishra** in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT:

Hexavalent chromium being a potent carcinogen need to be treated before its disposal. The adsorption of hexavalent chromium onto goethite was carried out by considering the influence contact time and the initial concentration in solution. The adsorption of hexavalent chromium increased with an increase in the concentration of this metal in solution. Goethite with a positively charged surface played a significant role in chromate ion removal. The Langmuir and Freundlich adsorption isotherms were employed to observe as to how closely the function fits to the experimental data obtained.

Chapter-1

INTRODUCTION

1.1 INTRODUCTION:

Among several toxic heavy metals discharged into the environment and several water bodies thus causing pollution, chromium has become a serious health concern. Chromium exists in several oxidation states ranging from -2 to +6 thus exhibiting contrasting characteristics. The most common oxidation states are +2, +3 and +6 of which hexavalent chromium is a priority metal pollutant, and a potent carcinogen. Hexavalent Cr is known to be 100–1000 times more toxic than the trivalent form (Gauglhofer and Bianchi, 1991). Hexavalent chromium, Cr (VI), is present in the effluents produced during electroplating, leather tanning, mining, metallurgy, dyeing, fertilizer and photography industries (Barnhart, 1997).

According to Indian standards the permissible limit for Cr(VI) for potable water is 0.05 ppm and for industrial discharge water is 0.1 ppm. Concentration of Cr (VI) in industrial wastewaters and mine discharges are much higher than the tolerance limit as shown in Table 1.1. So it is essential that industries treat their effluents to reduce Cr(VI) concentration to below maximum permissible limit.

A wide variety of conventional treatment methods for the removal of toxic metal ions from wastewater involves various chemical, biological, electrolytic and adsorption methods which includes chemical reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation, coagulation, complexation and adsorption on activated charcoal (Rawat and Singh, 1992). To compete with conventional methods, several new methods have come up of which adsorption of metal ions present in low levels on to solid proved to be a cost-effective method for treating industrial effluents.

Many researchers have investigated the use of activated carbon, granular activated carbon and various oxides for heavy metal removal from aqueous solution. Many

investigators have studied the feasibility of less expensive materials such as goethite which is the most widespread iron oxide (Manceau et al., 2000) that can be used as low cost adsorbent, agricultural waste (Orhan and Buyukgunor 1993), zeolites (Ouki et al., 1994), fly ash (Apak et al., 1998), red mud (Lopez et al.,1998) etc. for removal of heavy metals from wastewater.

Table 1.1: Cr(VI) pollution Scenario in Water

Location	Type	Concentration of Cr(VI) (in mg/l)	References
Sukinda, Odisha	Surface Water	BDL-52	Dubey et al., 2001
Sukinda, Odisha	Ground water	BDL-0.48	Dubey et al., 2001
Kanpur	Groundwater	0.01-16.3	Singh et al., 2009
Ranipet, Tamil Nadu	Tannery Industries	2.1-214	Gowd and Govil, 2008
Ludhiana, Punjab	Chromium industries	3.15	Chandra and Kulshrestha, 2004
Southern Switzerland	Production of chromic acid	0.03-3.2	Wanner et al., 2012

BDL: Below Detection Limit

1.2 OBJECTIVE

The present work has the following objectives:

1. To understand the effect of initial concentration and contact time on adsorption of chromate onto goethite.
2. Adsorption kinetic study using Langmuir and Freundlich isotherm

Chapter-2

LITERATURE REVIEW

2.1 CHEMISTRY OF CHROMIUM

Within a specified Eh and pH range Eh-pH diagrams gives the equilibrium data and shows the different oxidation states and chemical species of the chemical substances. At a particular pH and Eh conditions in presence of reducing or oxidising agents one form of chromium is transformed into another which is represented by Figure 2.1.

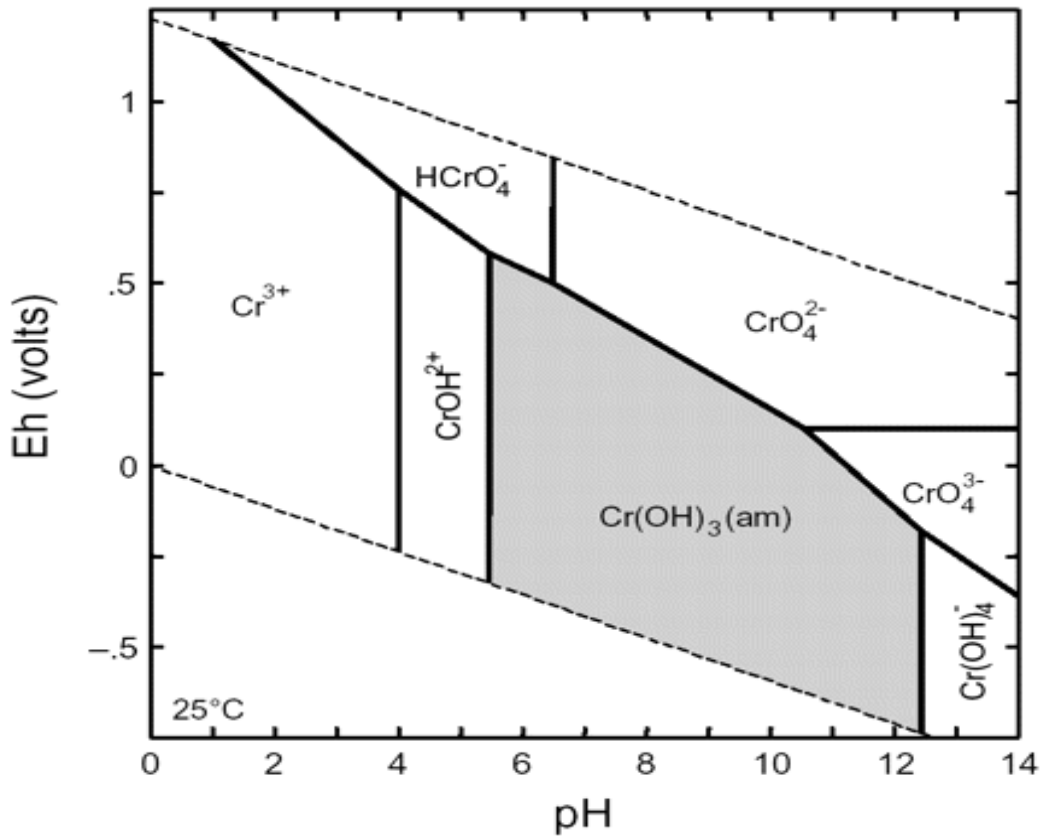
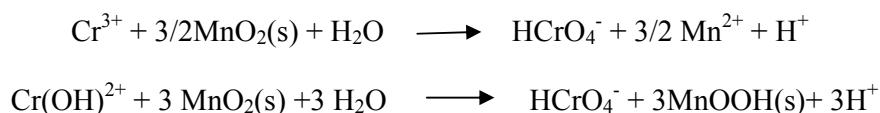


FIG 2.1: Eh-pH diagram for Chromium (Brookins D.G. 1988)

Chromate ion (CrO_4^{2-}) is stable in the more oxidising environment with Eh higher than 0.6 V and pH above 6.0 (Pao-Kuo F. Chin, 1994. At pH values less than 3.0, Cr (III) predominates. At pH values above 3.5, hydrolysis of Cr (III) yields trivalent chromium hydroxy species [CrOH^{2+} , $\text{Cr}(\text{OH})_3$ and $\text{Cr}(\text{OH})_4^-$] (Brookins D.G. 1988).

2.2 FORMATION OF HEXAVALENT CHROMIUM:

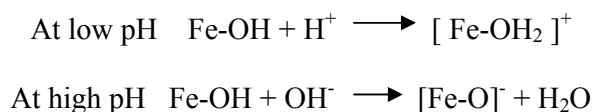
In aquatic environment, manganese oxides are responsible for oxidation of trivalent chromium which is accomplished in three steps of adsorption of Cr(III) onto MnO_2 surface sites followed by oxidation of trivalent to hexavalent chromium by surface Mn(IV) and then the desorption of reaction products, Cr(VI) and Mn(II) as mentioned by Amacher and Baker, (1982) and Eary and Rai (1987).



Chromium and manganese forms a pair of chemical elements with contrasting characteristics. Under oxidizing condition Cr(VI) is soluble as CrO_4^{2-} and Mn(IV) is scavenged as MnO_2 whereas under reducing condition Cr(III) is removed as $\text{Cr}(\text{OH})_3$ and Mn(II) is soluble as Mn^{2+} (Murray et al.,1983). Magnesium release during deuteric alteration of ultramafic rocks leads to the generation of Cr(VI) from inert chromites (Godgul and Sahu, 1995).

2.3 REMOVAL OF Cr(VI) BY GOETHITE

Goethite (FeOOH) is one of the common minerals of soil, particularly in laterite zone. It also occurs as colloids. The Fe-OH group in the colloidal size fraction at the interface between mineral and water shows a pH dependent surface charge.



In between these pH there is a pH_{ZPC} which is defined as the pH at which adsorbent has a net zero surface charge. When pH is less than the pH_{ZPC} the adsorbent surface has a positive charge and when pH is greater than the pH_{ZPC} the adsorbent surface has a negative charge. Goethite has a pH_{ZPC} value of 7.3-9.5 which is higher than the pH value which makes it positively charged thus making the situation favourable for the quantitative adsorption of chromate (CrO_4^{2-}) (Raymahashay, 1998)

2.4 EFFECT OF Cr(VI)

Hexavalent chromium at 10 mg/kg of body weight can cause liver necrosis, nephritis and finally death. Lower doses will cause irritation of the gastrointestinal mucosa. Cr(VI) cause irritation to nasal membranes, resulting in a runny nose, sneezing, itching, and perforation of the nasal septum. It may also cause chronic ulceration of skin surfaces (Goyer, 1991; ATSDR, 1993). Handling liquids or solids containing hexavalent chromium causes allergic contact dermatitis (an allergic skin reaction). Direct skin contact with hexavalent chromium

causes a non-allergic skin irritation. Cr(VI) can also cause damage to kidney and liver, weakened immune system, alteration in genetic material etc. High levels of Cr (VI) ($>2 \mu\text{g}/\text{m}^3$) through inhalation is associated with lung cancer and also affects the respiratory system (Goyer, 1991; ATSDR, 1993).

2.5 ADSORPTION ISOTHERMS

Adsorption equilibrium is described by adsorption isotherm which is defined as a constant temperature equilibrium relation between the equilibrium concentration of the adsorbate and the quantity of the adsorbate adsorbed per unit mass of the adsorbent. Adsorption isotherms are used to know the adsorption phenomenon and it help us to determine the adsorption parameters. Two widely used adsorption isotherms are Langmuir isotherm and Freundlich isotherm.

Langmuir model is applicable for monolayer sorption onto a surface with similar active sites (Ho et al., 2002) which is given by the following expression

$$C_e/q_e = (1/Qb) + (C_e/Q)$$

Where C_e = concentration of adsorbate left in solution at equilibrium in mg/l

b = Langmuir bonding energy coefficient (energy of adsorption)

Q = adsorption maximum in mg/g (adsorption capacity)

q_e = adsorbate adsorbed per unit mass of adsorbent in mg/g

A plot of $1/q_e$ in the Y-axis and $1/C_e$ in the x-axis is drawn. The values of Q and b are determined from the slopes and intercept of the straight line plot.

Langmuir Isotherm is based on the assumption that all the adsorption sites are identical with the retention of a single molecule in each site. All sites are energetically independent of adsorbed quantity (Limousin et al., 2007).



Langmuir isotherm can also be expressed as a dimensionless constant separation factor R_L (Budinova et al., 1994) which is given by

$$R_L = 1/(1+bC_i)$$

For a favorable adsorption R_L lies between 0 and 1.

Freundlich equation is based on the adsorption onto heterogeneous surface into many layers given by the following equation

$$\log q_e = \log K_f + (1/n) \log C_e$$

where K_f (in mg/g) and n are the Freundlich constants characteristic of the system and are indicators of adsorption capacity and adsorption intensity (Ho et al., 2002). A plot of $\log C_e$ in the x-axis and $\log q_e$ in y-axis is drawn where values of n and K_f are calculated from the slope and the intercept. Value of $1/n$ between 0.1 and 1 represents a good adsorption.

Chapter-3:
MATERIALS AND METHODS

3.1 SAMPLE COLLECTION

Goethite sample was collected from Rungta Iron Mines, Keonjhar, Odisha, which was further confirmed through X-ray diffraction study.

3.2 X-RAY DIFFRACTION TEST

The collected sample was crushed and sieved through 230 mesh and subjected to X-ray diffraction study (XRD) using X-Pert diffractometer from Panalytical for mineralogy study. Copper was used as target with wavelength 1.54 angstrom. As sample and detector were rotated till $2\theta = 70^\circ$, intensity of reflected X-rays are recorded and a graph of 2-theta verses intensity was obtained.

3.3 ADSORPTION EXPERIMENT

Goethite sample of size between 54 μm and 63 μm was used for effective adsorption of Cr(VI). A stock solution of 1000 mg/L was prepared which is followed by preparation of various concentration of solutions. The prepared sample was added to the solution and kept in an orbital shaking incubator for proper mixing. After a stipulated time period they are filtrated using vaccum filter and nylon filter paper.

A stock solution of 1000 ppm Cr(VI) was prepared by dissolving 2.83 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 ml of distilled water. By diluting the stock solution, standard solutions of 0.01 ppm, 0.02 ppm, 0.04 ppm, 0.08 ppm and 0.10 ppm Cr (VI) was prepared for calibration purpose. It was prepared by pipetting 100 μl , 200 μl , 400 μl , 800 μl , 1000 μl of standard solution into five different 100 ml volumetric flask and diluting it to 100 ml with distilled water.

A 10 ppm solution was then prepared by diluting 100 ml of 1000 ppm standard solution prepared earlier to 1000 ml. The pH of the solution was measured using ORION pH electrode, and found to be 5.4. About 2 gm of goethite sample was taken in conical flask and

50 ml of the prepared 10 ppm solution was added and kept in an orbital shaking incubator at 150 rpm and 25 °C at variable time. The solutions were then filtered using vacuum filter and membrane filter paper. The filtrate was subsequently used for analysis of Cr(VI) by the colorimetric method.

Another set of experiments was carried out by changing the initial concentration from 5 ppm to 20 ppm for the period of 240 minutes by keeping all other parameters constant. The filtrate were analysed through Double beam UV-Visible spectrophotometer for Cr(VI) concentration.

3.4 ANALYSIS OF Cr(VI)

Concentration of Cr(VI) was carried out using colorimetric method followed by APHA (1995). 0.2 N sulphuric acid was added to the filtrate solution obtained and 0.25 ml of orthophosphoric acid was added. Then, 2 ml of diphenylcarbazide solution, which was prepared by dissolving 250 mg 1,5 diphenyl carbazide in 50ml of acetone, was added and mixed thoroughly. The solution was kept for 5 to 10 minutes after which a violet colour was developed. The absorbance at 540 nm wavelength was measured by Double beam UV-Visible spectrophotometer. A calibration curve was constructed by plotting absorbance value against concentration which is given in Figure 3.4. The calibration curve is used as a reference to find the unknown concentration at a particular adsorption in the subsequent experiments.

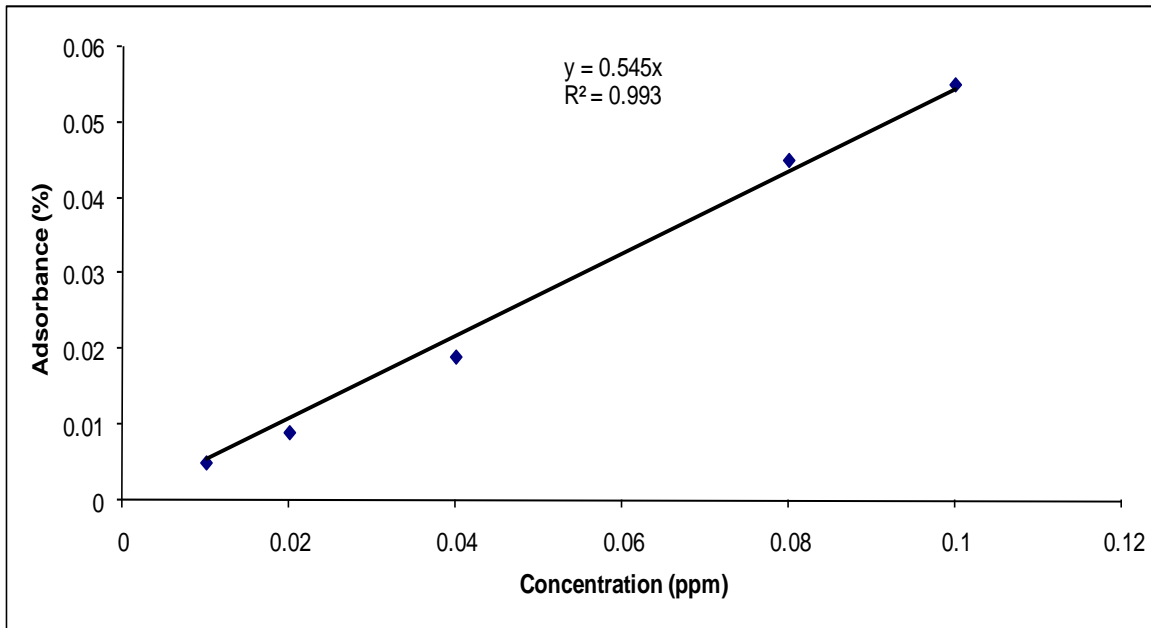


FIG 3.1: Calibration curve for Cr (VI)

Chapter-4:
RESULTS AND
DISCUSSIONS

4.1 MINERALOGY STUDY

By keeping a track of the d value calculated using Bragg's equation, mineral identification of the sample was performed. It was observed that sample contains goethite only. This data helped to use the goethite sample in the entire experiment for the adsorption of hexavalent chromium.

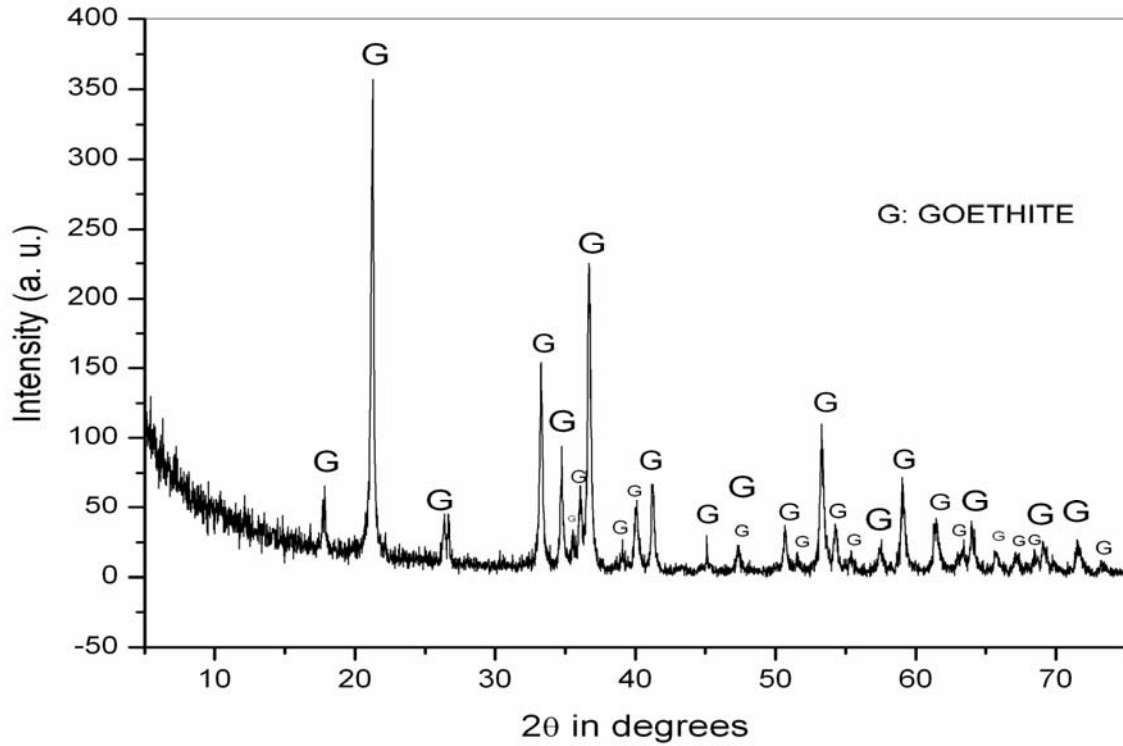


FIG 4.1: XRD Pattern of Goethite Sample

4.2 EFFECT OF TIME ON REMOVAL OF Cr(VI)

As the adsorption experiment was carried out by varying the time of adsorption from 10 minutes to 330 minutes, the absorbance value obtained by analysis and their respective calculated final concentration are shown in Table 4.1 and given in Figure 4.2.

TABLE 4.1: Effect of time on removal of Cr(VI)

Time (in minutes)	Absorbance	Final concentration (in ppm)	Percent Removal
10	0.09	8.251	17.49
20	0.086	7.884	21.16
40	0.079	7.242	27.58
60	0.071	6.509	34.91
70	0.069	6.326	36.74
120	0.032	2.934	70.66
150	0.0265	2.429	75.71
180	0.02	1.834	81.66
210	0.017	1.558	84.42
240	0.01	1.145	88.54
270	0.009	0.825	91.75
300	0.0075	0.688	93.12
330	0.007	0.642	93.58

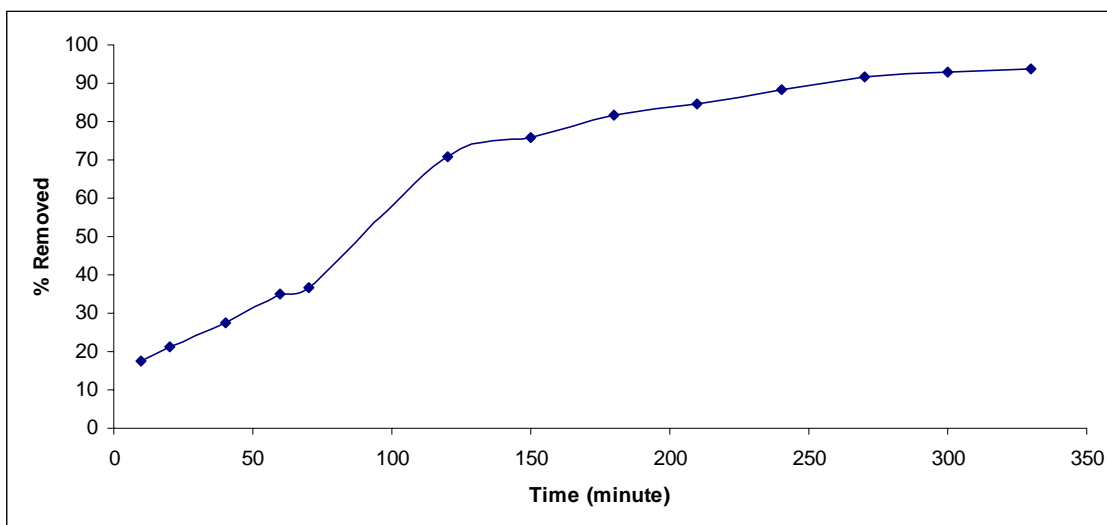


FIG 4.2 Effect of time on adsorption

It was observed that with an increase in the contact time, the percent removal of Cr(VI) also increases rapidly upto 120 minutes after which it increases gradually till it attains the saturation at nearly 240 minutes.

4.3 EFFECT OF CONCENTRATION ON REMOVAL OF Cr(VI)

Effect of concentration on the adsorption of Cr(VI) was also observed by varying the initial concentration. Percentage of removal with change in concentration is given in Table 4.3 and shown in Figure 4.3. It was observed that with increase in concentration, percentage of removal decreases. This is attributed to the saturation of the adsorption sites of goethite.

TABLE 4.2 : Effect of concentration on percent removal of Cr(VI)

Initial concentration(in ppm)	Final concentration (in ppm)	Percent Removed
5	0.53	89.4
10	1.14	88.6
20	2.9	85.5
40	7.9	80.25
80	17.6	78

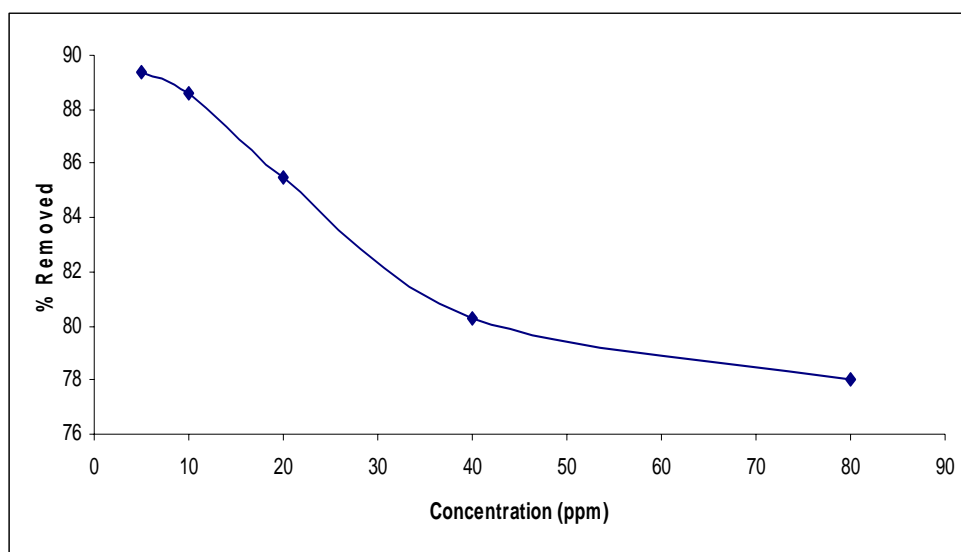


FIG 4.3: Effect of concentration on percent removal of Cr(VI)

4.4 ADSORPTION ISOTHERMS

Adsorption isotherms were studied using the percentage removal with change in initial concentration. They are used to determine the adsorption phenomenon and help us to calculate the adsorption parameters. Langmuir and Freundlich isotherm curves are shown in Figure 4.4 and 4.5.

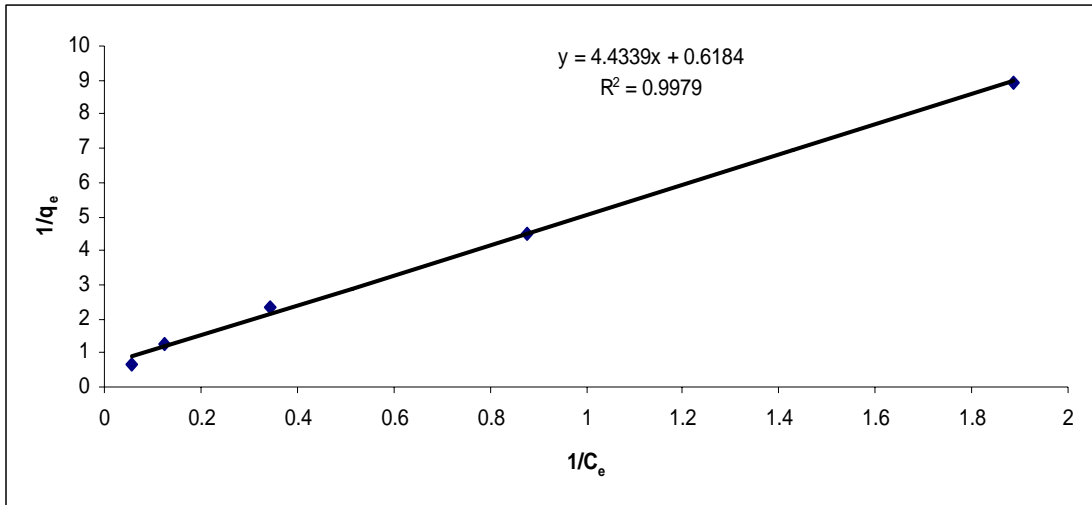


FIG 4.4: Langmuir Isotherm

C_e is the final concentration of the adsorbent and q_e which is the quantity of adsorbate per unit mass of adsorbent is calculated as the ratio of the difference of the final concentration from the initial concentration to dosage. From the curve the value of adsorption capacity and adsorption energy was found to be 1.617 mg/g and 0.139 L/mg respectively. Separation factor R_L was calculated and found to be 0.067, which indicates that adsorption is favorable.

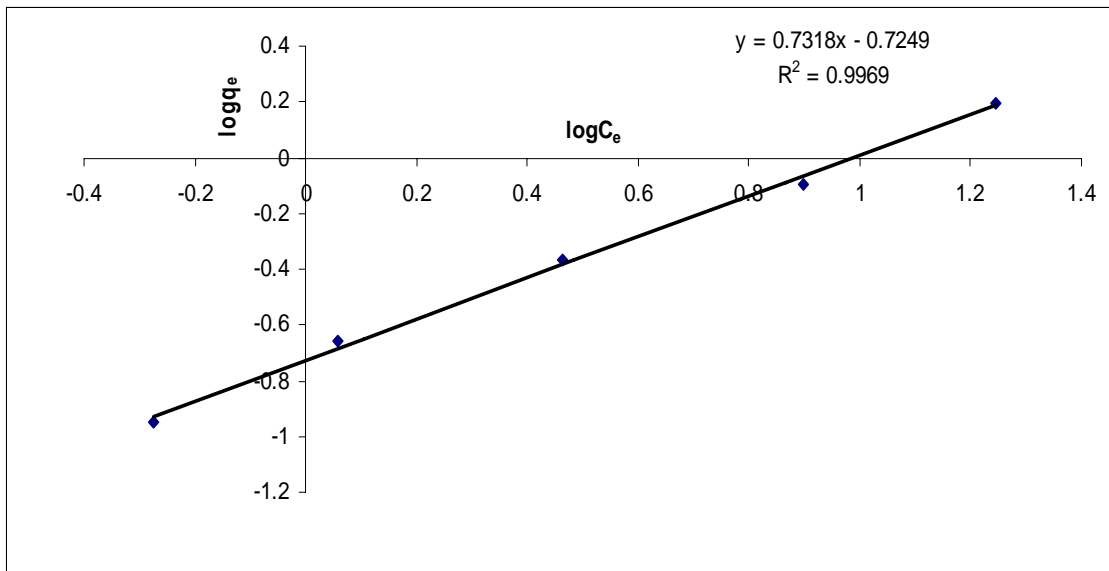


FIG 4.5: Freundlich Isotherm

From the curve the value of the adsorption capacity and adsorption intensity was found out to be 0.484 mg/g and 1.366 L/mg respectively. The value of $1/n$ was calculated as 0.732 which represents good adsorption of Cr(VI) on goethite. It was observed that Langmuir isotherm with a greater correlation coefficient of determination best fits the data.

Chapter-5:

CONCLUSIONS

CONCLUSION

From the experiment conducted following is concluded:

1. With an increase in the time of adsorption the percent removal of hexavalent chromium increases
2. With an increase in the concentration of the solution the removal percent of the metal decreases.
3. Goethite was found to be an effective adsorbent for the removal of hexavalent chromium in a concentration range up to 10 mg/l.
4. The adsorption data show good fit to the Langmuir and Freundlich adsorption isotherm with the Langmuir isotherm giving a best fit to the experimental data obtained.

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