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Synthesis and Application of Mesoporous Adsorbent for the Removal of Hexavalent Chromium from Water

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Abstract :- Hexavalent chromium is one of the toxic heavy metal, which acts as a pollutant. The objective of the present study is to investigate cost effective adsorbent with high removal capacity for Cr (VI) metal from water. The impact of chromium on environment, sources of chromium pollution and toxicological/health effects is also studied in brief. The adsorption works carried on various adsorbents for Cr (VI) removal are reviewed. Batch adsorption experiments were carried out to examine the removal of Cr (VI) under various parameters such as effects of initial concentration, adsorbent dose, pH, and contact time. The adsorbent capacity was studied by using the Langmuir and Freundlich adsorption isotherm models. The values of constant parameters and correlation coefficients were found out. From the isotherm study it was found that adsorption equilibrium is well-fitted to the Freundlich isotherm. Kinetic data was studied with the help of Pseudo first order and second order kinetic models. From the kinetic study it was found that second-order kinetic model fits the best. According to the result it was found that chemically activated alumina by FeO has higher removal efficiency for hexavalent chromium as compared to bare alumina.

Keywords: - Adsorption isotherm, FeO coated Activated Alumina, Hexavalent chromium, kinetic Study.

I. INTRODUCTION

Chromium (VI) is one of the 16th most toxic elements in the environment and also the most critical and highly soluble metal pollutants that have a wide range of uses in the industries such as metals and chemical industries. When chromium is released in the air, water, and soil it can be leached to the different environmental medium through different processes. Trivalent chromium can be accepted to some extent by plants and animals in low doses but not hexavalent chromium.

Cr enters into water bodies through industries such as paint, leather tanning, ink, dyes, electroplating, cement, steel, aluminium and textiles. When chromium is used in excess quantities it results in large amount of effluents containing chromium which needs treatment for the removal of chromium. Chromium can be used to manufacture explosives, ceramics and photography. Chromium can be found in the aquatic environment in both Cr (III) and Cr (VI) forms. The primary form of chromate CrO_4 and dichromate Cr_2O_7 of Cr (VI) have higher levels of toxicity compared to the other valence states. Therefore, the removal of Cr (VI) from water and wastewater is important to protect the environment.

Direct exposure to Cr (VI) causes dermatitis, internal haemorrhage, nausea, diarrhoea, liver and kidney damage, and respiratory problems. Inhalation causes acute toxicity, irritation and ulceration of the nasal septum and asthma. Ingestion affects kidney and liver functions. Skin contact results in systemic poisoning damage or even severe burns, and interference with the healing of cuts. If it is not treated properly, this can go ahead to ulceration and severe chronic allergic contact dermatitis. Eye exposure causes permanent damage.

The methods available for the removal of Cr (VI) from water consist of reduction, precipitation, ion-exchange and solvent extraction. These treatment methods have demerits such as high cost and low feasibility for small-scale industries, incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. Therefore, these methods are discarded and adsorption method is used as adsorption is the most effective and widely used technique for the removal of toxic heavy metals from water due to its efficiency and low cost. Activated carbon showed the best results but as it is a costly material and cannot be regenerated and reused so chemically activated alumina by FeO has been used for the present study for getting better removal of Cr (VI).

The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard. In addition, National Iranian standard for Cr (VI) concentration in drinking water is 0.05 mg/L (ISIRI number

1053, 1991). The main objective of this work is to evaluate the adsorption capacity of chemically activated fine alumina beads by FeO, for the removal of Cr (VI) from solution by varying the adsorbent dose and Langmuir and Freundlich adsorption isotherm models and kinetic models.

II. MATERIALS AND METHODS

2.1 Preparation of FeO Coated Activated Alumina

Activated Alumina was purchased from a German company named Sasol that produces alumina of versatile shapes like extrudates, spheres/beads, and coarse or fine powder. The fine alumina beads were chemically activated by impregnating (0.01M & 0.001M) of ferrous sulphate onto 10 gm of Activated Alumina and then the mixtures were kept in orbital shaking incubator for 24 hours at 150 rpm and 27℃ temperatures. Then samples were taken out and filtered by using whatmann filter paper and the residue remaining over the filter paper was washed thoroughly using distilled water and then the collected samples were dried in the oven at 65℃ for 10 hours until it gets completely dried. Then the dried samples were kept in the muffle furnace to get the samples calcined at 500℃ for 4 hours. The calcined materials were used for the adsorption study for Cr (VI) removal.

2.2 Preparation of standard Cr (VI) Stock solution

A standard stock solution of hexavalent chromium was prepared in deionised water, from potassium dichromate in different concentrations. The other standards were prepared by diluting the stock solution with doubled distilled water.

2.3 Batch Adsorption Experiments

Batch adsorption Study was performed to understand the mechanism for the removal of Cr (VI) by using Activated Alumina and FeO activated fine alumina beads(0.01m & 0.001M) by constantly shaking 50 ml of Cr (VI) water with these adsorbents in different doses (0.05gm, 0.1gm, 0.2gm, 0.3gm, 0.4gm, 0.5gm) in a 250-ml conical flask. Then the conical flask was kept in the orbital shaking incubator for 24 hours at 150 rpm and 27℃ temperatures. The samples were taken out after 24 hours time interval and filtered through Whatman No. 42 filter paper. The filtrates were analysed for removal of Cr (VI) and the concentration of solution was measured by using UV visible spectrophotometer.

III. RESULTS AND DISCUSSIONS

3.1Adsorption studies

The adsorption capacity increased with increase in Activated Alumina and chemically activated fine alumina beads by FeO dosage for the concentrations studied. The percentage removal increases from 1.53 to 46.36 with the increase in activated alumina dosage and 26.31 to 67.73 with the increase in the dosage of chemically activated fine alumina beads by FeO (0.01M) and 37.53 to 85 with the increase in the dosage of chemically activated fine alumina beads by FeO (0.001M). The maximum removal among the doses studied is observed at 0.5gm. The readings are shown in TABLE 1 & Fig.1.

Table 1. Batch Adsorption study

Dose (gm/50 ml)	% Removal		
	Activated Alumina	FeO Coated Activated Alumina (0.01M)	FeO Coated Activated Alumina (0.001M)
0.05	1.53	26.31	37.53
0.1	9.09	37.354	60.66
0.2	16.37	50.32	72.30
0.3	29.55	57.36	79.17
0.4	36.81	63.478	81.75

0.5	**46.36**	**67.73**	**85**

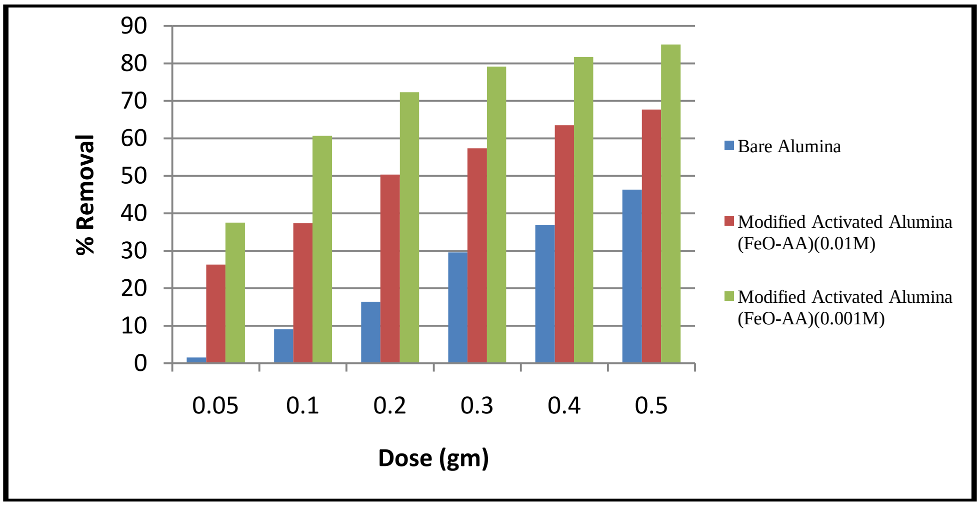

Figure.-1 Comparison of Activated Alumina and its modified Samples

3.2 Adsorption Isotherm

Adsorption isotherm parameters describe the behaviour between solutes and adsorbent that tells us the surface properties and attraction of the adsorbent. The Langmuir and Freundlich models are used to explain the equilibrium adsorption isotherms. The Langmuir equation that is based on the assumption that there is no reaction between molecules adsorbed on nearby sites is given by:

$$C_{eq} /C_{ads} = [1/Q_b] + [C_{eq}/Q]$$

Where,

Q is the maximum adsorption at monolayer (mg/ g),

C_{eq} is the equilibrium concentration of Cr (VI) (ppm),

C_{ads} is the amount of Cr (VI) adsorbed per unit weight of adsorbent at equilibrium concentration (mg/ g)

b is the Langmuir constant related to the affinity of binding sites (ml/mg) and is a measure of the energy of adsorption. A linear plot of C_{eq} /C_{ads} against C_{eq} gives Q and b.

The Freundlich equation based on sorption on a heterogeneous surface is given by:

$$C_{ads}=K\ C_{eq}\ l/n$$

The linear form of this equation is expressed as

$$\log C_{ads}=1/n \log C_{eq} + \log K$$

Where, *K* and *n* are Freundlich constants indicating adsorption capacity (mg/g) and intensity respectively. *K* and *n* can be determined from a linear plot of log C_{ads} against log C_e.

The results of the Langmuir and Freundlich isotherm constants are given in Table 2. It is found that the adsorption of Cr (VI) on chemically activated fine alumina beads by FeO (0.001M) correlates well (R > 0.984) with the Freundlich equation as compared to Langmuir equation under the concentration range
Studied

Table 2. Adsorption isotherm Constants

Langmuir Isotherm Constants			Freundlich Isotherm Constants		
Q_{max} (mg/g)	k (l/mg)	R^2	k_f (mg/g)	1/n	R^2
2.087	0.1207	0.978	0.5723	1.274	0.984

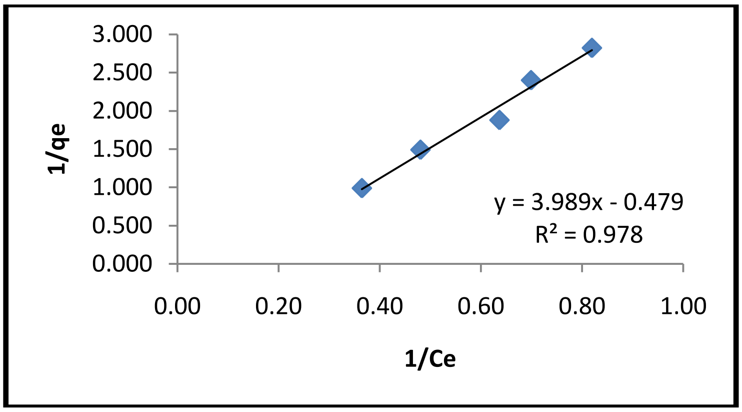

Figure 2. Langmuir Adsorption Isotherm

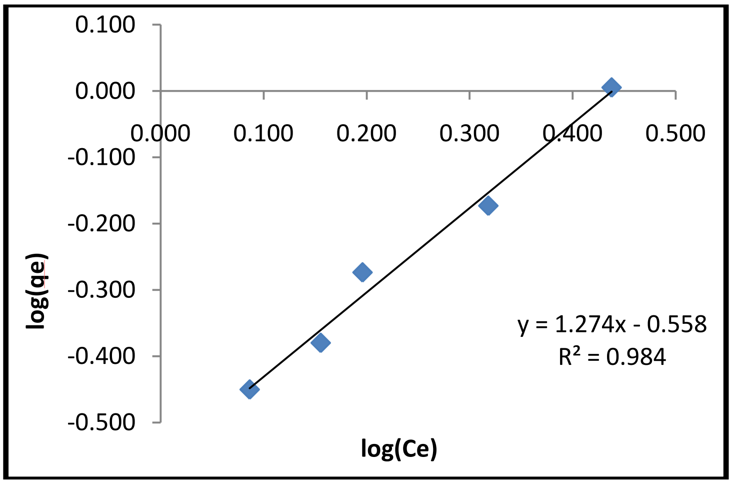

Figure 3. Freundlich Adsorption Isotherm

3.3 Effect of pH

The pH of the initial solution plays an important role in the adsorption of metal ions on various adsorbent. The study is concentrated on the initial solution pH and was varied between 2.0 and 10.0. The (Fig. 3) shows the effect of the initial solution pH on Cr (VI) adsorption onto chemically activated fine alumina beads by FeO (0.001M). At pH 2 removal is maximum and after that at all the pH the removal observes is near about constant which shows that the material is stable and can be regenerated and reused.

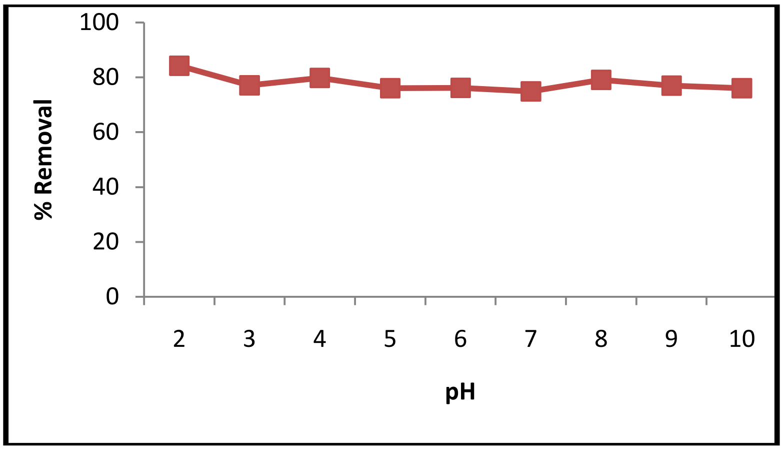

Figure 4. Removal of Cr (VI) due to pH study

3.4 Kinetic study

The power of the contact time on the removal of Cr (VI) from the solution using the FeO coated alumina has been analyzed keeping the initial solution concentration 10 mg Cr (VI)/L, pH 6.5, and adsorbent dosage 0.5gm as constant. The results are shown in Figure 4 that shows a slow increase in the adsorption up to 190 min of the contact time. After that the material gets saturated.

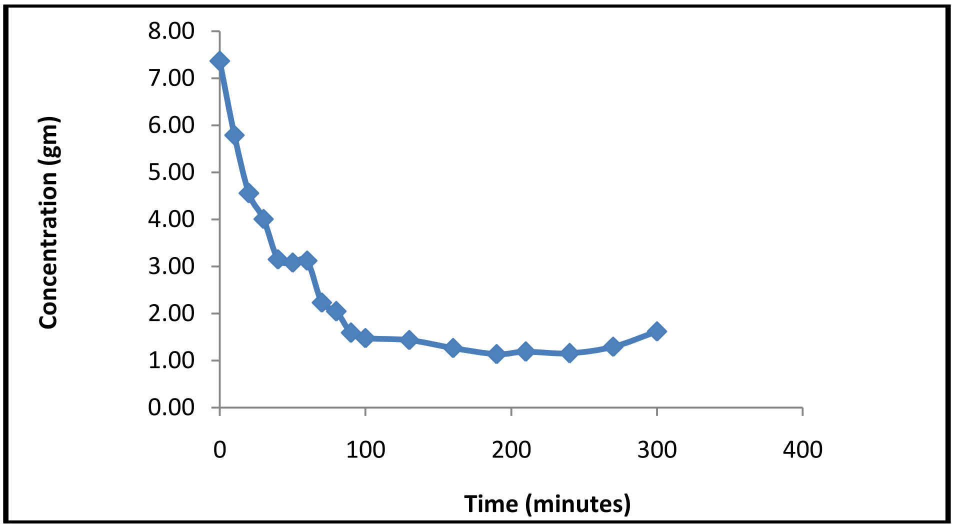

Figure 5. Removal of Cr (VI) due to contact time study

3.5Kinetic Model

The adsorption data for the removal of Cr (VI) by FeO coated Alumina adsorbent was fitted using Lagergren pseudo-first-order model and pseudo-second-order model. The linear form of first order Lagergren equation is given by:

$$\log (q_e - q_t) = \log q_e - K_{1ads} * t/2.303$$

The pseudo-second-order equation:

$$t/q = 1/k_{2ads} * q_e^2 + t/q_t$$

Where, q_e is the mass of metal adsorbed at equilibrium (mg/g),
q_t the mass of metal at time t(min.),
$k_{1,ads}$ the first-order reaction adsorption (per minute),
$k_{2,ads}$ the pseudo-second order rate constant of adsorption mg/g min^{-1}.

The values of constants are shown in TABLE 3

Table 3. Kinetic Data

Pseudo First Order kinetics Constants		Pseudo second order Kinetics Constants		
K_{ad}	R^2	q_e (mg/g)	K (g/mg.min)	h
-1.7894	0.983	6.667	0.0065	0.290

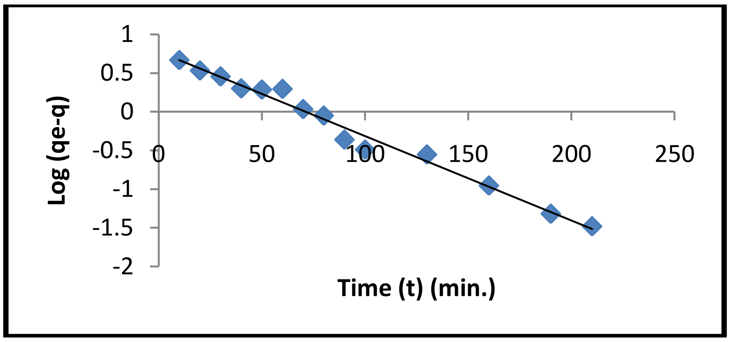

Figure 6. Pseudo First Order kinetics

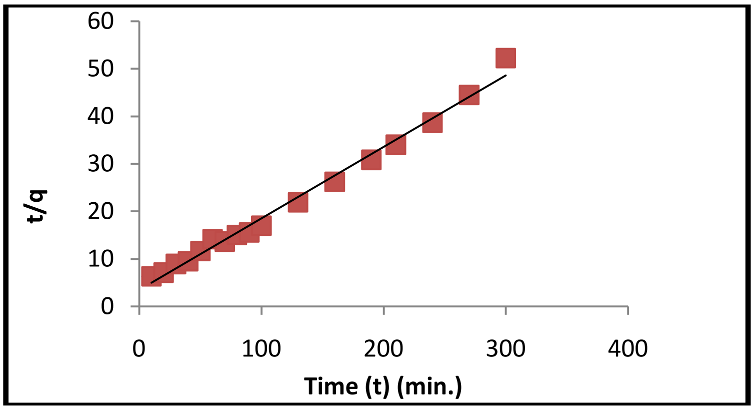

Figure 7. Pseudo Second Order kinetics

IV. CONCLUSION

The study shows that iron oxide impregnated activated alumina beads with 0.001 M concentration can be effectively used for the removal of Cr (VI) from water. From the isotherm study it was found that Freundlich adsorption isotherm is well fitted as compared to Langmuir adsorption isotherm. Kinetic data was studied with the help of Pseudo first order and second order kinetic models. From the kinetic study it was found that second-order reaction fits the best as the R^2 value is 0.99. The ph study shows that the adsorbent is stable at varying pH range. Thus it can be summarised that the Iron oxide coated activated alumina has lot of potential in removal of Cr(VI) and other heavy metal ion water.

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