Effect of Size of Iron Oxide Coated Sand (IOCS) on Removal of Cr (VI) from Water.

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Abstract—In the present study, influence of iron oxide coated sand (IOCS) on adsorption of Cr(VI) was determined. Batch analysis was done to determine the removal efficiency of Cr(VI) from chromium contaminated water. The effect of pH and dosage on adsorption was studied. Further batch analysis was carried out for kinetic and equilibrium studies which was described using pseudo first order, pseudo second order and were compared using different size fraction of IOCS. Adsorption isotherm was found to fit best in Freundlich isotherm. Intra-particle diffusion model suggested complex adsorption i.e. surface sorption as dominant initial adsorption and transport processes as rate controlling steps. All the above studies were conducted for IOCS of two different size fractions and effect of size on Cr(VI) adsorption was determined.

Keywords— Adsorption, Kinetics, Pseudo second order, Size Fraction.

I. INTRODUCTION

HEAVY metals including lead, chromium, cobalt, mercury are discharged as aqueous waste from mining, leather, tanning industries and nuclear power plants. Most of these heavy metals have ill-effects towards health and some of them are carcinogenic [1][2]. On the other hand, these metals are not easily degradable and require special techniques to decompose them. Chromium exists in two states which are Cr(III) and Cr(VI). Cr(III) is found to have lesser adverse effects on health as compared to Cr(VI). Cr(VI) on the contrary, gets deposited in different parts of body and becomes cancerous if taken in excess amount. Large number of methods have been used to remove Cr(VI) like ion-exchange, filtration, reverse-osmosis and electro-dialysis [6]. The present Cr removal technologies mentioned are not sustainable for rural community in developing countries because of high capital cost and maintenance by skilled labors, thereby making adsorption the most economical and easy to implement for Cr(VI) removal. Therefore, IOCS was used to adsorb Cr(VI) on active sites of sand particles coated with iron oxides. Since, these materials are easily available and economical; it is used as an adsorbent to remove Cr(VI). IOCS has been found to be effective use for treatment of water and wastewater containing variety of heavy metal over a wide range of concentrations [2]. The surface characteristics of IOCS are physically and chemically heterogeneous and are expected to change with time viz. porosity, specific surface area etc. Adsorption of Cr(VI) onto the sand coated with iron oxide from ferric chloride solution gave better results and the media have longer life time when less alkaline solution is employed for the regeneration.

The objective of the present study was to find the potential adsorption of Cr(VI) from the aqueous solution by IOCS under various kinetics and equilibrium conditions at optimum dosage and pH conditions. Apart from these, different size fractions were used to determine the optimum particle size of sand so as to increase adsorption and eventually the removal efficiency of Cr from the water.

II. MATERIALS AND METHODS

A. Preparation of iron oxide coated sand (IOCS)

Sand of a particular size was washed with 0.1N HNO₃ and kept undisturbed for 24 hrs. After acid washing, sand sample was washed with distilled water and dried at 105°C for 5-6 hrs. 1M sample of Fe(III) was prepared by adding FeCl₃ in distilled water. Oven dried sand was added into Fe solution and pH was brought in the range of 8-9 by adding 6M NaOH into it, thereby allowing iron to precipitate onto sand particles. Solution was kept for 24 hrs after which it was washed with distilled water and oven dried at 105°C for 5-6 hrs. In these experimental graphs IOCS-1 (fine) corresponds to IOCS of particle size ranging from 0.3-0.6mm and IOCS-2 (coarse) corresponds to IOCS of particle size ranging from 0.6-1.2mm.

B. Effect of pH

The effect of pH was determined by taking samples of Cr(VI) solution of different pH. 10mg/l of Cr(VI) solution was taken in 4 different containers and sand was added in each container in the ratio of 1:50 (1gm: 50ml). pH of these samples was regulated to 4.5, 5.5, 7, 8.5 by using NaOH solution and H₂SO₄ solution. These samples with different pH were placed in mechanical shaker for 90 minutes. After shaking, amount of Cr(VI) adsorbed was determined using UV spectrophotometer.

C. Dosage study

To each sample of 50 ml of 10mg/l of Cr(VI) solution different amounts of iron oxide coated sand were added viz. 0.25 gm, 0.5 gm, 0.75gm, 1gm and 1.25gm. These samples were adjusted to an optimum pH obtained from pH study and were placed in a mechanical shaker for 90 minutes. After
shaking, amount of Cr(VI) adsorbed was determined using UV spectrophotometer.

**D. Kinetic Study**

Kinetic studies were conducted by shaking the samples of Cr(VI) solution for different periods of time. A sample of 10 mg/l of Cr(VI) solution was prepared from K₂Cr₂O₇ (Merck). To 50 ml this solution 1 gm of IOCS was added and sample was rotated in a mechanical shaker for 5 mins, 10 mins, 15 mins, 20 mins, 30 mins, 45 mins, 60 mins, 90 mins, 120 mins and 180 minutes. After shaking the samples were filtered to remove particulate matter and tested for concentration of Cr(VI) removed using UV spectrophotometer. For the study of adsorption isotherm and removal efficiencies, various concentrations of Cr(VI) were shaken in horizontal shaker (Neolab Orbit Shaker Incubator) at 120 rpm till the equilibrium and the isotherm data was fitted into the model. The concentration of Cr(VI) present in different solutions was determined by UV spectrophotometer (CyberLab) using Diphenyl Carbazide method-3500 CR (APHA, 1998).

III. RESULTS AND DISCUSSIONS

**A. Effect of dosage on IOCS of different sizes**

Dosage studies determined the optimum amount of adsorbent (IOCS) required for further batch experiments [6]. The comparison of dosage of IOCS for different sizes (IOCS 2 ~ 0.6-1.2mm and IOCS 1 ~ 0.3-0.6mm) were made. The optimum dosage study in both the cases was almost similar in nature. As per the experiment 1 gm was observed to be the optimum amount of IOCS as specific surface area decreases with increase in dosage. From the curve it was inferred that the removal efficiency with particle size of IOCS-1 (fine) was more as compared to IOCS-2 (coarse) as shown in Fig. 1. As the mass of the adsorbent is increased, the total surface area and in turn the number of active adsorption sites increases. However the amount of Cr(VI) adsorbed per unit mass/area of adsorbent decreases after the optimum dose, due to the increase in available surface area, resulting in reduction of the adsorption capacity (qe).

![Fig. 1 Values for Dosage study](image)

**B. Effect of pH on IOCS of different sizes:**

pH studies conducted determined optimum pH at which maximum adsorption should take place in case of sand with different particle sizes. The experiment results showed that removal efficiency increased with pH till pH range of 5-6 (Fig. 2) in both the cases and then reduced. The basic medium was

not found to be suitable as Cr(VI) is in an oxy-anionic form and gets repelled from the OH⁻ ions. These OH⁻ ions have more affinity towards electropositive Fe coated sand thereby preventing oxy-anion Cr(VI) to get adsorbed onto it. Although reports say that Cr₂O₃ formation takes place at higher pH, finally allowing Cr(VI) to settle down [6], but the rate of formation is less than the desorption rate at basic medium.

![Fig. 2 Values for pH analysis](image)

**C. Kinetic and Equilibrium studies**

To determine the mechanism and rate of adsorption processes of Cr(VI) removal, kinetic studies had been done. These determine the adsorption and diffusion of Cr(VI) in mg/g of IOCS. To determine the amount of Cr(VI) adsorbed different models are used like pseudo first order model, pseudo second order model and elovich model [2][4]. The reaction rates depend on the concentrations of both adsorbate and adsorbent which is given by the equation:

\[ R = k q' \]  

The trend of Cr(VI) adsorption on different particle sizes was obtained from the plot of qₜ vs t which depicts that the adsorption increases with decrease in particle size from size fraction of 0.6-1.2mm to 0.3-0.6mm. The adsorption value of IOCS at equilibrium with particle sizes IOCS-1 (~ 0.3-0.6mm) and IOCS-2 (~ 0.6-1.2mm) are 0.259 mg/g and 0.225 mg/g respectively (Fig. 3). The attainment of equilibrium is found to be 90 mins in both the cases, yet adsorption of IOCS with smaller size was more than adsorption with larger particle sizes. This value of equilibrium time was further used in determining the adsorption isotherm.
D. Pseudo First order model

Sorption Kinetics can be determined by chemosorption characteristics differential equation:

$$\frac{dq_t}{dt} = k_1(q_e-q_t)$$  \hspace{1cm} (3)

This equation on integration becomes:

$$\log(q_e/(q_e-q_t)) = \frac{k_1t}{2.303}$$  \hspace{1cm} (4)

where $q_e$ is the amount of Cr(VI) adsorbed at equilibrium in (mg/g), $q_t$ is the amount of Cr(VI) adsorbed at time $t$ in (mg/g) and $k_1$ is the equilibrium rate constant of pseudo first order kinetics [2]. From the curve (Fig. 4) low $r^2$ values i.e. 0.887 and 0.857 for IOCS-1 and IOCS-2 respectively were observed. These showed that the kinetics of adsorption is much more complex than that of pseudo first order kinetics.

E. Pseudo second order model

Pseudo second order model determines $k_{ad}$ and $q_e$ values both, unlike pseudo first order model. Pseudo second order is based on the assumption that chemosorption of the adsorbate predominates during process of adsorption. This depicted by an eq:

$$\frac{dq_t}{dt} = k_2(q_e-q_t)^2$$  \hspace{1cm} (2)

Where, $K_2$ is the second order rate coefficient (g/mg min) and depends on the applied operating conditions namely, initial metal concentration, pH of solution, temperature and agitation rate, etc [2]. The functional relationship is determined by the linearity of $t/q_t$ vs $t$ curve obtained by the equation:

$$t/q_t = 1/(k_2q_e^2) + (1/q_e).t$$  \hspace{1cm} (3)

The initial adsorption rate, $h$, adsorption capacity $q_e$, and rate constant $k_2$, can be determined experimentally from the slope and intercept of a plot of $t/q_t$ against $t$ as shown in Fig. 5.

![Fig. 5 Values for Pseudo Second Order Model](image)

This graph best fits in pseudo second order Type-1 model which is evident from the $r^2$ of IOCS-1 and IOCS-2 which are 0.9989 and 0.9994 respectively. The initial adsorption rates ($h$) of both are 0.06 and 0.19 respectively whereas $q_e$ values are 0.27 and 0.23 (mg/g) and $K_2$ has value of 0.92 and 3.68 (g/mg min) respectively. This shows that chemosorption is dominant in both the cases with higher $q_e$ value for IOCS with smaller size and higher surface area.

![TABLE I](image)

<table>
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<th>Linear form</th>
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<th>Parameter OCS2</th>
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This table shows the comparison of pseudo first order and pseudo second order parameters for IOCS-1 and IOCS-2. The results indicate that pseudo second order model provides a better fit compared to pseudo first order model.
Intraparticle diffusion model:

Intraparticle diffusion model has been commonly used to describe the transport mechanism of Cr(VI) particles onto the heterogeneous iron oxide coated sand (IOCS) [3]. The diffusion of Cr(VI) on soil was determined by the obtaining a functional relationship between the adsorbed amount and half-power of t (t^0.5). This theory suggests the diffusion on ions into pore spaces of adsorbent using suitable kinetic model. The most-widely applied intra-particle diffusion equation is given:

\[ q_t = K_{id} t^{0.5} + C \]  \hspace{1cm} (6)

Where \( K_{id} \) is the intra-particle diffusion rate constant (mg/(mg min^0.5)) and the intercept C, obtained by extrapolation of the linear portion of the plot of \( q_t \) versus \( t^{0.5} \), back to the axis is taken to be proportional to the extent of the boundary layer thickness as shown in Fig. 6. As per experiment, the \( r^2 \) value IOCS-1 is 0.94, thereby exhibiting better linearity than particle size of IOCS-2 ranging from 0.6mm-1.2mm which has an \( r^2 \) of 0.645. This result confirms that finer particles with a smaller size as well as pores have more surface area i.e. active adsorption sites and pores where diffusion/transport are dominant factors which results in more adsorption than particles with bigger size.

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  \hspace{1cm} (7)

Where, \( q_e \) is the adsorption of Cr(VI) in mg/g and \( C_e \) is the equilibrium concentration (mg/l).

For particles with smaller size fraction between 0.3-0.6mm the plot of \( \log q_e \) versus \( \log C_e \) (Fig. 7) has a slope with the value of \( 1/n \) and an intercept magnitude of \( \log K_f \). Freundlich parameters \( \log K_f \) and \( 1/n \) were found to be 1.72 and 1.3748 respectively. The \( r^2 \) obtained from freundlich adsorption isotherm model was found to be 0.8689.

Whereas, for particles with larger size fraction between 0.6-1.2mm the plot of \( \log q_e \) versus \( \log C_e \) (Fig. 7) has a slope with the value of \( 1/n \) and an intercept magnitude of \( \log K_f \). Freundlich parameters \( \log K_f \) and \( 1/n \) were found to be 1.92 and 0.89 respectively. The \( r^2 \) obtained from Freundlich adsorption isotherm modal was found to be 0.803.

IV. CONCLUSION

The effect different sizes of IOCS on removal of Cr(VI) has been investigated using different parameters like pH, dosage, kinetic studies, equilibrium studies and adsorption isotherm. It was found that IOCS-1 with smaller size fraction was having a higher Cr(VI) removal efficiency as compared to IOCS-2 with larger size. Maximum percentage removal was found to be 53.6% within 90 minutes with an optimum pH range of 5-6 and dosage of 1gm per 50 ml of solution. The mechanism of Cr(VI) adsorption was found to follow pseudo second order model as compared to pseudo first order model. The removal of Cr(VI) was found to be rapid with about 85% removal.
taking place in 50 mins. The satisfactory fitting of intraparticle diffusion model for both sizes of IOCS suggested transport processes may be the limiting factor in the adsorption. Thus, the kinetics of adsorption is dominated by surface sorption and partly by intraparticle diffusion due to the heterogeneity of the sand particles. The adsorption isotherm study showed that Freundlich isotherm was found to fit better than Langmuir isotherm, with higher adsorption capacity for IOCS-1. Therefore, it was concluded that due to higher surface area of smaller size fractions of IOCS-1, they have a higher adsorption of Cr(VI) from the water, and provide a better scope for removal.

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REFERENCES


