Removal of Cr (VI) in aqueous solution using iron oxide coated sand (IOCS)

Aditya Dhagat, Bhushan Goyal, Lalsangzela Sailo

Abstract— In the present study, Iron Oxide Coated Sand (IOCS) was applied to treat water contaminated with chromium. The effect of adsorbent dosage and pH on the removal of chromium (Cr) from aqueous solution using IOCS has been investigated. Batch mode experiment was carried out to assess the adsorption kinetics and equilibrium studies. The kinetics study was best described by pseudo second order. Moderate fitting of Elovich model and intra-particle diffusion model suggested complex adsorption i.e. surface sorption and intra-particle diffusion as rate controlling steps. The adsorption isotherm data fitted well to Freundlich isotherm.

Index Terms— Adsorption isotherm, Chromium,Dosage, Effect of pH , Elovich, Intra-particle diffusion model, Iron oxide coated sand, Kinetics, Pseudo second order.

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1 INTRODUCTION

POLLUTION of water by chromium is of considerable concern; as this metal is widely used in leather tanning industries and chromate manufacturing located in the industrial development area of Ranipet, Tamil Nadu, which is situated only 20 km from Vellore. Extensive efforts and works have been directed towards the water chemistry, environmental mobility, and toxicity of chromium. Since, the Ranipet has numbers of tanneries which discharge high concentration of chromium, so there is a potential risk for ecology and environmental pollution. Tamil Nadu Pollution Control Board (TNPCB, 1996) reported that 150,000 tons approx. of solid waste (sodium, chromium, chromate salt, basic chromium sulfate tanning powder) accumulated over two decades of plant operation has been stacked in the open yard on 3.5 ha of land within Tamil Nadu Chromate and Chemical Limited (TCCL) [1]. The leachate from this stack infiltrates into the soil and pollutes the groundwater due to rain. Rao et al. (2011) reported groundwater Cr concentration in Ranipet as high as 220 mg/l suggesting the extensiveness of the pollution in the area. For the removal of chromium from water, various water treatment technologies like adsorption, ion-exchange, filtration, reverse-osmosis and electro-dialysis have been used. However, the existing technologies are not tailored fit for rural community in developing countries because of high capital cost and maintenance by skilled labors. Consequently, adsorption processes has been found to be most effective and economical treatment for the removal of Cr from the aqueous solution for household as well as small communities. Therefore, in order to remove chromium effectively from the water iron oxide coated sand (IOCS) was used. It is used to remove both soluble and particulate fraction from water through a column packed with IOCS filter media [2, 3]. IOCS has be effective use for treatment of water and wastewater containing variety of heavy metal over a wide range of concentrations [3].

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 result and the media have longer life time when less alkaline solution is employed for the regeneration [3].

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.

2. Materials and Methods

2.1 Preparation of Iron Oxide Coated Sand (IOCS):

Sand passing through 1.2 mm and retaining on 0.6mm sieve was taken and washed with 0.1N HNO3 and kept for 24 hr. Then the sand sample was washed with distilled water and oven dried at 105∘C for 5-6 hrs. Then a 1M sample of Fe(III) was prepared by dissolving FeCl3 in distilled water and the sample of sand was added to it. Then the pH was reduced to 8-9 by adding 6M NaOH into it and allowed to remain undisturbed for 24 hrs. On reducing pH, iron molecules settle on sand thereby enhancing adsorption phenomena. After keeping it for 24 hrs, the sample was washed with distilled water and oven dried at 105°C for 5-6 hrs.

2.2 Effect of pH

The effect of pH on the adsorption processes was studied by taking initial Cr(VI) concentration of 10 mg/l. A soil solution ratio of 1:50 (1gm: 50ml) was taken and the pH was regulated by using NaOH solution and H_2SO_4 solution to have a pH of 4 different set to 4.5, 5.5, 7, 8.5 respectively. These samples with different pH were placed in a mechanical shaker for 90 minutes. After shaking, amount of Cr(VI) adsorbed was determined using UV spectrophotometer.

2.3 Dosage study

To each 50 ml Cr(VI) solution different amount of IOCS viz. 0.25 gm, 0.5 gm, 0.75gm, 1gm and 1.25gm were added respectively. These samples with optimum pH of 7.5 were placed in a mechanical

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shaker for 90 minutes. After shaking, amount of Cr(VI) adsorbed was determined using UV spectrophotometer.

2.4   Kinetics study

A sample of Cr(VI) contaminated water was prepared from K2Cr2O7 (Merck) and initial solution for the kinetic study was taken as 10 mg/l Cr(VI). Samples were prepared by adding 1 gm of iron oxide coated sand (IOCS) to 50 ml of 10 mg/l Cr(VI) sample and each sample was rotated in a mechanical shaker for 5mins, 10mins, 15mins, 20mins, 30mins, 45min, 60mins, 90mins, 120mins and 180 minutes. After shaking for predefined interval, the samples were filtered to remove sand particles and tested for concentration of Cr(VI) removed using UV spectrophotometer.

For the study of adsorption isotherm, various concentrations of Cr(VI) was 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).

3.   Results and Discussions:
3.1   Effect of pH on adsorption of Cr(VI)

According to the experiment conducted, amount of Cr(VI) adsorbed is found to be higher at a lower pH than higher pH; similar trend has been reported in various studies. The adsorption takes place till 5.5 and then desroption takes place as we increase pH which indicates that acidic medium is optimum for reduction of maximum amount of Cr(VI) from the solution ranging from pH 5-6. Since, Cr(VI) solution is in oxy-anionic form, therefore, the increase in pH of the solution will induce repulsion due to higher electro negativity at greater pH [2] as shown in Fig 1.
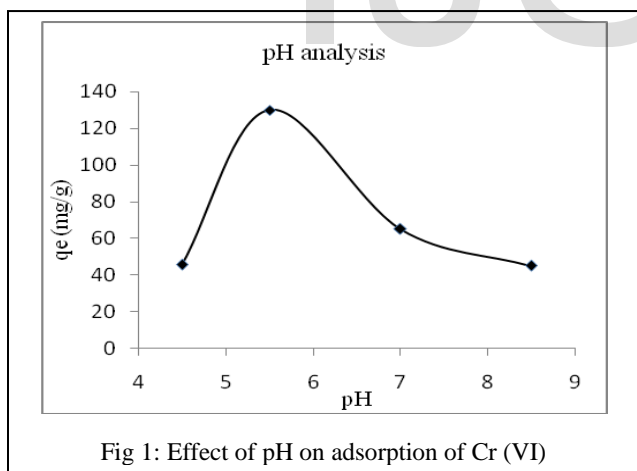

Fig 1: Effect of pH on adsorption of Cr (VI)

3.2   Impact of dosage on adsorption of Cr(VI)

Dosage studies determined the optimum quantity of IOCS to be used as an adsorbent. Large number of particles might hinder the adsorption process. According to the experiment, 1 g IOCS comes out to be optimum dosage for maximum removal of Cr(VI) which has been used in subsequent batch analysis. Initially, Cr(VI) concentration reduces till 1gm and becomes which then increases till 1.25g as shown in Fig 2. Cr(VI) reduces by 40% after adding 1 g of IOCS. Increase in IOCS might reduce the available active sites of adsorption or increase desorption rate because of which there is a sudden reduction in Cr(VI) removal.
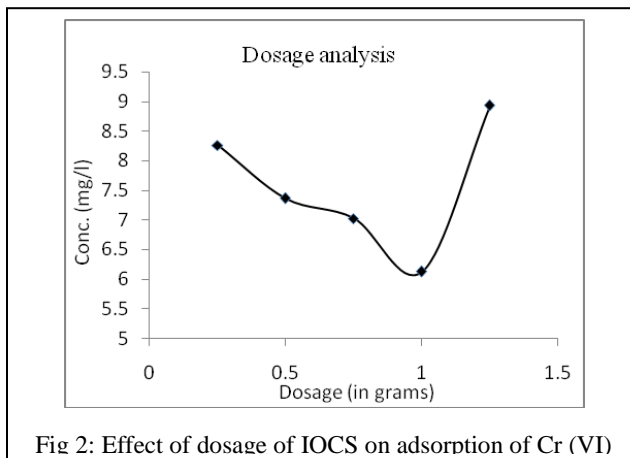

Fig 2: Effect of dosage of IOCS on adsorption of Cr (VI)

3.3   Kinetics of Cr(VI) adsorption

In order to determine the rate of different processes and factors which influence them, kinetics studies have been conducted. Through these studies possible mechanism of adsorption and the different transition states on the way to the formation of the final adsorbate–adsorbent complex have been evaluated. These reaction rates are dependent on the respective concentrations of adsorbate and adsorbent which is given by the equation:

$$R = [A]^a[B]^b \ldots\ldots\ldots \quad (1)$$

where k is the rate coefficient and a, b represent the order with respect to the species A and B [4].

The type of soil component can drastically affect the rate of metal sorption. Sorption reaction can involve physical sorption, outer-sphere complexation (electrostatic attraction), inner-sphere complexation (ligand exchange), and surface precipitation. Various kinetic models namely pseudo-second-order, Elovich model and intra-particle diffusion models have been used to test their validity with the experimental adsorption data. From the kinetic study experiment the adsorption of Cr(VI) on the IOCS was found to be rapid as 90% adsorption took place within the initial 30 minutes as shown in Fig 3. A maximum of 47% of Cr(VI) was found to be removed after shaking for 60 minutes after which equilibrium was attained.
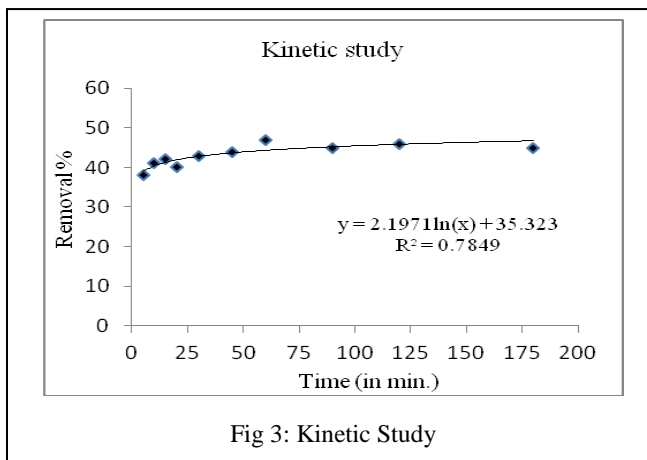

Fig 3: Kinetic Study

3.3.1 Pseudo-Second-Order kinetic model

Pseudo second-order kinetic model determines the values of k_{ad} and q_e which pseudo first order kinetic model doesn't. The pseudo-second-order model is based on the assumption of chemosorption of the adsorbate on the adsorbents. This model can be represented in the following form:

$$dq_t/dt = k_2(q_e-q_t)^2 \qquad (2)$$

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. The validity of pseudo second order kinetics depends on the linearity of the curve plotted between time/adsorbed amount versus time which is shown in eq(3).

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e).t \qquad (3)$$

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. The various linearized forms of pseudo second order are given in Table 1.

TABLE 1
PARAMETERS OF PSEUDO-SECOND ORDER KINETICS

Type	Linear form	Plot	Parameter
Type 1	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t$	$\frac{t}{q_t} \; vs. \, t$	$q_e = 0.23$ $K_2 = 3.68$ $h = 0.19$
Type 2	$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	$\frac{1}{q_t} \; vs. \, \frac{1}{t}$	$q_e = 1.38$ $K_2 = 3.16$ $h = 5.99$
Type 3	$q_t = q_e + \left(\frac{1}{K_2 q_e}\right)\frac{q_t}{t}$	$q_t \; vs. \, \frac{q_t}{t}$	$q_e = 0.16$ $K_2 = 9.1$ $h = 0.23$
Type 4	$\frac{q_t}{t} = K_2 q_e^2 - K_2 q_e q_t$	$\frac{q_t}{t} \; vs. \, q_t$	$q_e = 0.21$ $K_2 = 5.03$ $h = -0.22$

The experiment conducted determines the amount of chemosorbtion on the sorbate. The graph shows to be best fitting with pseudo second order kinetics. The initial sorption rate (h) obtained from the experiment performed was found to be 0.19 whereas, the adsorption capacity q_e and rate constant k_2 were 0.23 (g/mg) and 3.68 (g/mg min) respectively from the Fig 4. The linearity of curve has a good agreement between the amounts of Cr(VI) adsorbed per unit mass (qe) obtained from second order model.
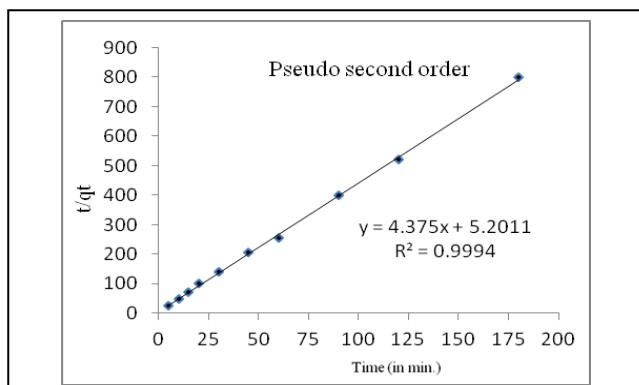

Fig 4: Plot for Pseudo second order adsorption kinetic

3.3.2 Elovich kinetic model

The Elovich equation has been widely used in adsorption kinetics, which described chemical adsorption in nature. This model assumes that neither the inter-particle interaction nor desorption affects adsorption of Cr(VI) on IOCS at lower surface coverage [4]. The rate decreases with time due to an increase in surface coverage. This equation has also been commonly used to describe the sorption of pollutants from aqueous[5]. The Elovich equation can be written in the form:

$$dq_t/dt = a \exp(-b \, q_t) \qquad (4)$$

where a represents the rate of chemisorptions at zero coverage (mg/(g min)) and b is the extent of surface coverage and activation energy for chemisorptions (g/mg), the above Eq. 2.24 can be simplified as

$$q_t = (1/b)*\ln(ab) - (1/b)*\ln(t) \qquad (5)$$

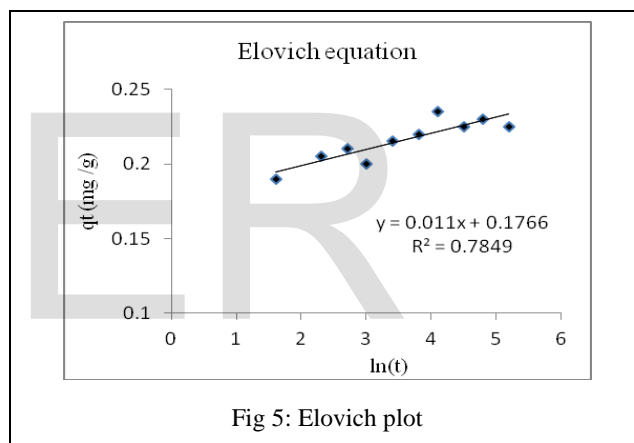where, constant a and b were calculated from the slope and intercept of plot q_t versus $\ln(t)$ as in Fig 5.

Fig 5: Elovich plot

Elovich equation helps determine the values of a and b which from the performed experiment come out to be 103227.4 (mg/(g min)) and 90.90 (g/mg) respectively. From the graph, the value r^2 which is 0.784 which is lower than pseudo second order kinetics. All the above data hereby, support the chemosorption property of the IOCS and Cr(VI) particles.

3.3.3 Intra-particle diffusion model

The IOCS being a heterogeneous in terms of its composition as well as sizes therefore surface sorption and diffusion, transport mechanism was suspected. This theory suggests the diffusion on ions into pore spaces of adsorbent using suitable kinetic model[7]. The most-widely applied intra-particle diffusion equation is given:

$$q_t = K_{id}t^{0.5} + C \qquad (6)$$

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.
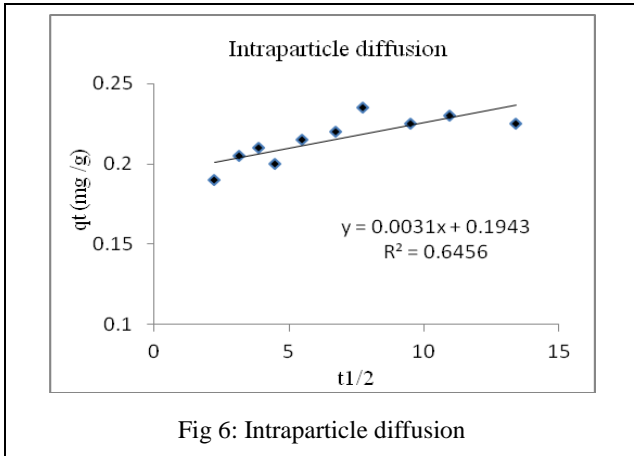
Fig 6: Intraparticle diffusion

The value of r^2 from the curve is 0.65 (Fig 6) which suggested the likelihood of intra-particle diffusion being a minor mechanism of adsorption. Therefore, the rate limiting steps for kinetic study can be attributed to intra-particle diffusion.

3.4   Adsorption Isotherm

The Freundlich adsorption model which is based on multilayer adsorption was found to fit better than the Langmuir isotherm which is based on monolayer adsorption[6]. The Freundlich adsorption isotherm model (adsorbed mass per mass of adsorbent (mg/g)) is expressed by a power law function of the solute concentration:

$$\log q_e = \log K_f + 1/n^* \log C_e \qquad (7)$$

where, q_e is the adsorption of Cr(VI) in mg/g and Ce is the equilibrium concentration (mg/l).

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.
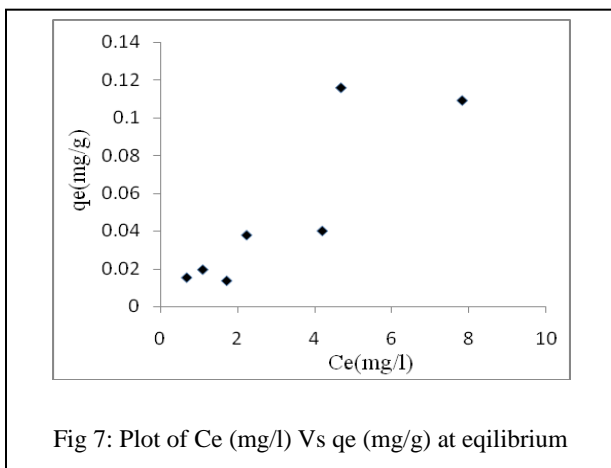

Fig 7: Plot of Ce (mg/l) Vs qe (mg/g) at eqilibrium

Utilization of iron oxide coated sand (IOCS) was investigated for the removal of chromium in batch experiment from water as a low cost adsorbent for use in small community and household unit. The maximum percentage removal of Cr(VI) was found to be 47% with an initial concentration of 10 mg/l. The optimum pH for the removal of Cr(VI) was found to be in the range of 5-6 and the dosage test at this pH suggested 1g in 50 ml of solution (1:50, IOCS: Solution). The adsorption kinetics study revealed that rapid sorption takes place at the initial 30 minutes where 90% of the adsorption occurs. Pseudo-second order kinetics was the best fit model for the study confirming chemosorption as the main adsorption mechanism. The intra-particle diffusion model exhibits moderate relationship in the sorption kinetics model, thus suggesting the rate limiting factor to be transport mechanism. Freundlich adsorption isotherm model was found to be the best fit model for the Adsorption isotherm.

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4   CONCLUSION