

# Removal of Cr(VI) from Wastewater using Fly ash as an Adsorbent

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## **Abstract**

*Cr(VI) is a highly toxic metal ion and considered a priority pollutant released from various chemical industries. Treatment methods to remove Cr(VI) from water and wastewater include chemical precipitation, ion exchange, membrane separation, electro-coagulation and reduction. These methods are not economically viable for large scale treatment of wastewater that is rich in Cr(VI). Adsorption is a most popular treatment method for the removal of Cr(VI) from industrial effluents. In the present study, fly ash is used as an adsorbent for Cr(VI) removal from aqueous solutions. Fly ash is activated by giving heat treatment and with the use of concentrated sulfuric acid (98% w/w). There is no significant increase in the percentage removal of Cr(VI) with activated fly ash. Batch adsorption studies exhibited that the fly ash has a significant capacity for adsorption of Cr(VI) from aqueous solution. The effect of important parameters such as pH, contact time, initial Cr(VI) concentration and adsorbent dosage is studied. Results indicate that the maximum adsorption of Cr(VI) is found to be 21 mg/g at low values of pH in the range of 1-3. The obtained equilibrium data is tested with Langmuir, Freundlich and Koble-Corrigan isotherms. The experimental equilibrium data fits well with the Langmuir-Freundlich model. The adsorption process follows second order kinetics. Flyash shows a higher desorption efficiency by more than 95% for the removal of Cr(VI).*

## 1. INTRODUCTION

Chromium and its compounds are widely used in many industries such as metal finishing, dyes, pigments, inks, glass, ceramics, chromium tanning, textile, dyeing and wood preserving industries and certain glues [1]. The effluent from these industries contain hexavalent chromium, Cr(VI), at concentrations ranging from tens to hundreds of mg/L. Cr(VI) is considered by the IARC (International Agency for Research on Cancer in 1982 as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomal aberrations [2]. The U. S. Environmental Protection Agency recommends that the levels of Cr(VI) in drinking water should be 0.1 mg/L. Consequently, the removal of Cr(VI) from industrial wastewater has become a research topic of great interest.

Several methods such as chemical precipitation, ions exchange, electrochemical precipitation, solvent extraction, reverse osmosis [3]. These methods are cost intensive and are unaffordable for large scale treatment of wastewater that is rich in Cr(VI). Adsorption using the activated carbon is an effective method for the treatment of industrial effluents contaminated with Cr(VI) and quite popular as compared to other methods [4]. The cost associated with the commercial activated carbon is very high which make the adsorption process expensive. This indicates that the cost effective alternate adsorbents for treatment of Cr(VI) contaminated waste streams are needed [5-7].

In the present study, a power plant waste product, flyash is used as an adsorbent for the removal of Cr(VI) from wastewater. Batch experiments are carried out for kinetic studies on the removal of Cr(VI) from aqueous solution. The effect of various influencing parameters such as initial pH, contact time, adsorbent amount and initial Cr(VI) concentration are studied. The equilibrium isotherm data and kinetic data are tested with various isotherm models and kinetic models. The used fly ash, after adsorption, are regenerated with the application of acid and base treatment.

## 2. EXPERIMENTAL METHODS

### 2.1. Preparation of adsorbent

The flyash used in this study is collected from National Thermal Power Corporation (NTPC), Tanda. The flyash is washed with distilled water and dried at 110°C for 5 h. The activation of flyash is carried out by treating it with concentrated sulphuric acid (98% w/w) in 1:1 weight ratio and is kept in an oven maintained at a temperature range of 150°C for 24 h. Again it is washed with distilled water to remove the free acid.

### 2.2. Batch experiments

A stock solution of Cr(VI) is prepared by dissolving 2.8287 g of 99.9% potassium dichromate ( $K_2Cr_2O_7$ ) in distilled water and solution made up to 1000 mL. This solution is diluted as required to obtain the standard solutions containing 20-400 mg/L of Cr(VI). The solution pH is adjusted in the range of 1 - 13 by adding 0.5 N HCl and 0.5 N NaOH solutions and measured by a pH meter.

The batch experiments are carried out in 100 ml borosil conical flasks by shaking a pre-weighed amount of the flyash with 25 ml of the aqueous Cr(VI) solutions for a predetermined

period (found out from the kinetic studies) at 30<sup>0</sup>C on a water bath shaker. Adsorption isotherm study is carried out with different initial Cr(VI) concentrations ranging from 20 to 400 mg/L while maintaining the adsorbent amount of 10 g/L. The effect of the contact time and the initial pH of solution are studied at 30<sup>0</sup>C with an initial Cr(VI) concentration of 50 mg/L and an adsorbent amount of 10 g/L. The effect of the adsorbent amount is studied by varying it in the range of 4 to 24 g/L with the initial Cr(VI) concentration of 50 mg/L at 30<sup>0</sup>C.

The concentration of free Cr(VI) ions in the effluent is determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as a complexing agent [8]. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min.

Desorption studies are conducted by batch experiments. The 15 g of saturated flyash obtained from adsorption studies is first treated with 150 ml of 1 N NaOH solution for 1 day. After the NaOH treatment, flyash are separated from the solution and washed with distilled water. Washed adsorbent is further regenerated with 150 ml of 1 N HCl. The flyash are washed with distilled water and dried at room temperature (~30<sup>0</sup>C) for 6 h. Desorption experiments are carried out with different initial concentrations of Cr(VI) ranging 20 to 400 mg/L.

### **3. RESULTS AND DISCUSSION**

In the present study, fly ash is used as an adsorbent for Cr(VI) removal from aqueous solutions. Fly ash is activated by giving heat treatment and with the use of concentrated sulfuric acid (98% w/w). There is no significant increase in the percentage removal of Cr(VI) with activated fly ash. Hence, for further batch adsorption studies fly ash without activation is used. The effect of various parameters such as initial pH, contact time, adsorbent amount and initial Cr(VI) concentration are studied and discussed in detail in the following sections.

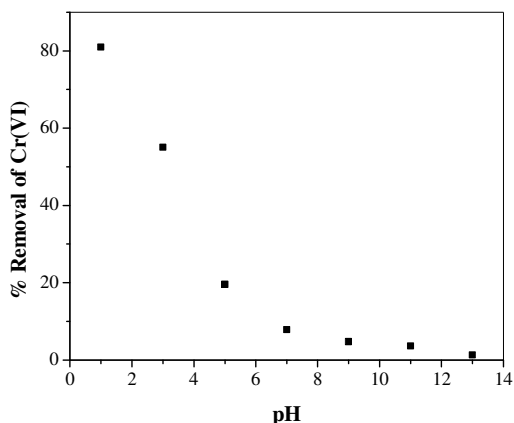
#### **3.1. Effect of initial pH**

The effect of the initial pH of solution on Cr(VI) removal is shown in Fig. 1. Removal efficiency is found decreasing with increase in the initial pH and reached 82% at initial pH value of 1. At lower pH (pH = 1) value, the dominant form of Cr(VI) is  $\text{HCrO}_4^-$  while the surface of adsorbent is charged positively [5, 9]. The stable forms of chromium such as  $\text{H}_2\text{CrO}_4$  and  $\text{CrO}_3$  exist as polynuclear species at a high Cr(VI) concentration and hence the low pH value of 1 results in a higher percentage removal of Cr(VI) using flyash.

#### **3.2. Effect of contact time**

Fig. 2 shows the percentage removal of Cr(VI) for different values of the initial Cr(VI) concentration ranging from 100 to 400 mg/L at pH value of 1. It is apparent from Fig. 2 that till 6 h, the percentage removal of Cr(VI) from aqueous solution increases rapidly and reaches up to 69% to 43% of the Cr(VI) removal for 100 to 400 mg/L of the initial Cr(VI) concentration respectively. After that, the percentage removal of chromium (VI) increases slowly till 25 h and becomes constant. A further increase in the contact time has a negligible effect on the rate of adsorption of Cr(VI). Therefore, the contact time of 22 h could be considered for the adsorption of Cr(VI) on flyash for entire batch studies. The rate of adsorption of Cr(VI) is faster in the initial periods and has a less effect on the rate of adsorption in later half of the process. The rate of adsorption

decreases in the later stages of the Cr(VI) adsorption as intraparticle diffusion becomes predominant and may be due to the slow pore diffusion of the Cr(VI) into the bulk of the adsorbent.



**Figure 1: Effect of pH on Cr(VI) removal using flyash as an adsorbent**  
( $T = 30^{\circ}\text{C}$ ,  $C_0 = 100 \text{ mg/l}$ ,  $M = 10 \text{ g/l}$ ,  $t_T = 19 \text{ h}$ )

### 3.3. Effect of adsorbent amount

The effect of the flyash amount on the adsorption of Cr(VI) is shown in Fig. 3. The percentage removal increases from 77% to 84.9% by increasing the adsorbent amount from 4 to 24 g/L respectively. The adsorption capacity dropped from 17 to 3 mg/g by increasing the adsorbent amount from 4 to 26 g/L respectively. The increase in Cr(VI) removal with an increase in the flyash amount is due to the increase in surface area and adsorption sites available for adsorption of Cr(VI). However, the decrease in adsorption capacity by increasing the adsorbent amount is basically due to the sites remaining unsaturated during the adsorption process.

### 3.4. Effect of initial Cr(VI) concentration

Fig. 4 predicts the effect of initial Cr(VI) concentration on the percentage removal of Cr(VI) and the adsorption capacity of flyash. The percentage removal decreases from 81% to 53% and the adsorption capacity increases from 1.8 to 22 mg/g with increase in the initial Cr(VI) concentration from 20 to 400 mg/L, respectively. The decrease in the percentage removal of Cr(VI) can be explained with the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain Cr(VI) concentration. The increase in the adsorption capacity with increase in the initial Cr(VI) concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration.

### 3.5. Adsorption mechanism

In the present study, the initial pH of solution is maintained at pH value of 1. At the lower value of pH (1-3), dominant form of Cr(VI) is  $\text{HCrO}_4^-$  while the surface of adsorbent is charged positively. The increase in Cr(VI) adsorption is due to the electrostatic attraction between positively charged groups of adsorbent surface and the  $\text{HCrO}_4^-$  which is dominant at lower value of pH (1-3).

### 3.6. Adsorption isotherm

In the present study, as the new adsorbent is developed, hence it is needed to test the equilibrium data obtained for Cr(VI) removal using activated tamarind seeds with different isotherm models available in the literature. In the present work, Langmuir [10], Freundlich [11] and Koble-Corrigan [12] isotherm models are tested with the experimentally obtained equilibrium data.

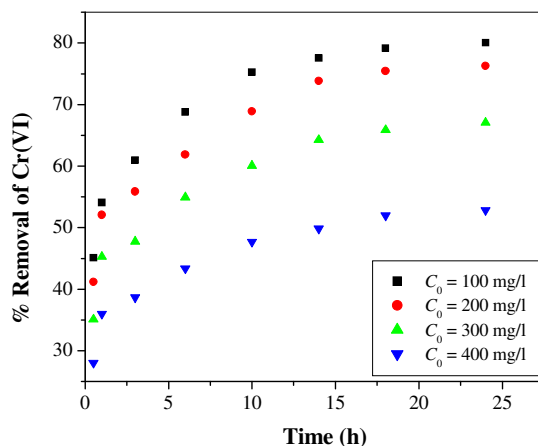


Figure 2: Effect of contact time on Cr(VI) removal using flyash as an adsorbent ( $T = 30^{\circ}\text{C}$ ,  $\text{pH}=1.0$ ,  $M = 10$  g/l)

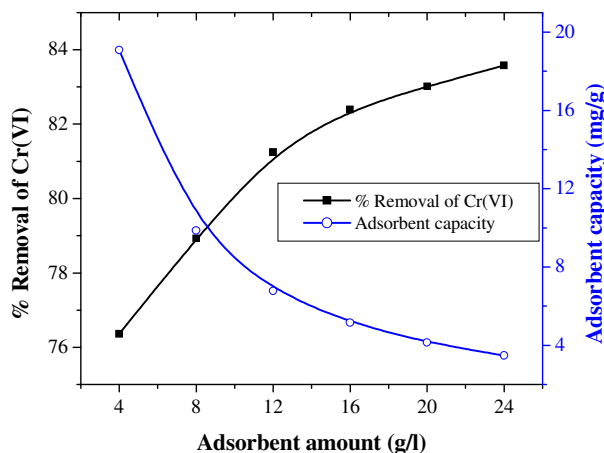
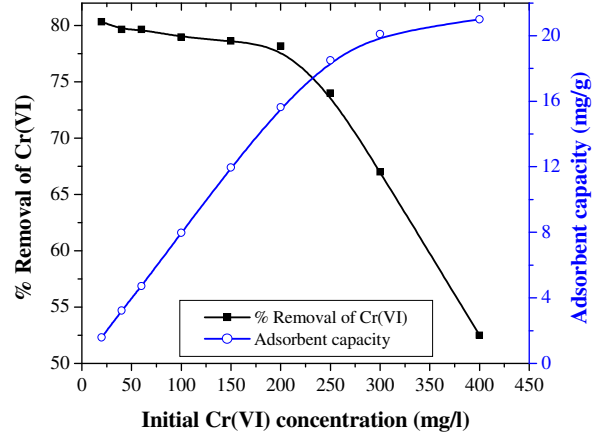


Figure 3: Effect of adsorbent amount on Cr(VI) removal using flyash as an adsorbent ( $T = 30^{\circ}\text{C}$ ,  $C_0 = 100$  mg/l,  $\text{pH}=1.0$ ,  $t_T = 19$  h)



**Figure 5: Effect of initial Cr(VI) concentration using flyash as an adsorbent ( $T = 30^{\circ}\text{C}$ ,  $\text{pH}=1.0$ ,  $M = 10 \text{ g/l}$ ,  $t_T = 19 \text{ h}$ )**

### 3.6.1. Langumir isotherm model

This isotherm equation gives the fractional coverage ( $\theta$ ) in the form of Eq. 1:

$$\theta = \frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (1)$$

where,  $b$  is  $k_a/k_d$  (where  $k_a$  and  $k_d$  are the rate constant for adsorption and desorption, respectively) (L/mg) and  $q_m$  is the quantity of adsorbate required to form a single monolayer on the unit mass of adsorbent (mg/g) and  $q_e$  is the amount adsorbed on the unit mass of the adsorbent (mg/g) when the equilibrium concentration is  $C_e$  (mg/L). A plot of  $(C_e/q_e)$  vs.  $C_e$  should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then yield the constants  $q_m$  and  $b$ , respectively. The Langmuir constant,  $q_m$ , is obtained as 42.3 mg/g in the initial pH value of 1. The Langmuir constant,  $b$ , which denotes adsorption energy, is found to be 0.011 L/mg. The low value of coefficient of determination ( $R^2 = 0.85$ ) obtained indicates that there is not a good agreement between the experimental values and isotherm parameters.

### 3.6.2. Freundlich isotherm

For adsorption from solution, the Freundlich isotherm is expressed by Eq. 2:

$$q_e = K_f C_e^n \quad (2)$$

where,  $K_f$  is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and  $n$  is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The Freundlich coefficients can be determined from the plot of  $\log q_e$  versus  $\log C_e$ . The values of  $K_f$  and  $n$  are

0.5604 and 0.8402 respectively. It is found that the coefficient of determination obtained from the Freundlich isotherm model for flyash is 0.96 which is higher than that for Langmuir isotherm model.

### 3.6.3. Koble-Corrigan isotherm

It is a combination of the Langmuir and Freundlich isotherm models and is given by Eq. 3:

$$q_e = \frac{aC_e^n}{1 + bC_e^n} \quad (3)$$

where,  $a$ ,  $b$  and  $n$  are the Koble-Corrigan parameters, respectively. The three isotherm constants  $a$ ,  $b$  and  $n$  are evaluated using a professional graphics software package ORIGIN (version 6) and found as 0.2901, 0.0082 and 1.337 respectively. The coefficient of determination is obtained as 0.995 which shows that the equilibrium data obtained for the adsorption of Cr(VI) using flyash follows Koble-Corrigan isotherm model.

## 3.7. Adsorption kinetics

In order to understand the kinetics of removal of Cr(VI) using flyash as an adsorbent, pseudo first-order [13] and second-order [14] kinetics are tested with the experimental data.

### 3.7.1. Pseudo first-order kinetics

The non-linear form of the pseudo first-order equation is given by Eq. 4:

$$\frac{dq_t}{dt} = k_{ad}(q_e - q_t) \quad (4)$$

where,  $q_e$  and  $q_t$  are the amounts of Cr(VI) adsorbed (mg/g) at equilibrium time and at any instant of time,  $t$ , respectively, and  $k_{ad}$  (L/min) is the rate constant of the pseudo first-order adsorption process. The values of first-order rate constants,  $k_{ad}$  and  $q_e$  for the initial Cr(VI) concentration ranges of 100-400 mg/L are calculated and listed in Table 1. The true values of  $q_e$  obtained from experiments for different initial Cr(VI) concentrations are not in agreement with the pseudo first-order model predicted values as given in Table 1.

### 3.7.2. Second-order kinetics

The second-order kinetic rate equation is given by Eq. 5:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where,  $k_2$  is the second order rate constant, g/(mg) (min). The application of the second-order kinetics by plotting  $t/q_t$  vs.  $t$ , yielded the second-order rate constant,  $k_2$ , estimated equilibrium capacity  $q_e$ , and the coefficient of determination ( $R^2$ ) for the initial Cr(VI) concentration ranging from 100 - 400 mg/L, which are reported in Table 1.

## 3.8. Desorption studies

In the present study, flyash is regenerated and is used for the removal of Cr(VI) at different initial Cr(VI) concentration in the range of 20 – 400 mg/L. The regenerated flyash is again used for the adsorption of Cr(VI) using the same initial Cr(VI) concentration ranging between 20 mg/L and 400 mg/L as used for fresh activated flyash. The percentage removal of Cr(VI) obtained found to

decrease from 74% to 35% respectively as compared to the corresponding values for fresh adsorbent ranging from 82% to 52%.

**Table 1: Calculated kinetic parameters for different kinetic models for the adsorption of Cr(VI) using flyash as an adsorbent**

S No	$C_0$ (mg/l)	$q_e$ (exp.) (mg/g)	First order kinetic model			Second order kinetic model		
			$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$
1	100	8.0	0.199	3.56	0.994	0.156	8.22	0.999
2	200	15.25	0.201	7.78	0.972	0.066	15.7	0.996
3	300	20.12	0.175	9.76	0.985	0.048	20.7	0.996
4	400	21.13	0.171	9.92	0.970	0.047	21.9	0.996

#### 4. CONCLUSIONS

The following conclusions could be drawn from present study.

- The maximum adsorption of Cr(VI) took place in the initial pH value of 1.
- The equilibrium time for the adsorption of Cr(VI) on the activated tamarind seeds is found to be 22 h.
- The percentage removal of Cr(VI) increases with increase in the adsorbent amount.
- The equilibrium data obtained for the adsorption of Cr(VI) can be well described by Koble-Corrigan isotherm model.
- Adsorption of Cr(VI) on the flyash yielded maximum adsorption capacity of 21 mg/g.
- Adsorption of Cr(VI) obeys second order rate equation.
- Regenerated flyash show the higher desorption efficiency by more than 90% of the fresh activated tamarind seeds for the removal of Cr(VI).

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