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Removal of Hexavalent Chromium from Electroplating Industrial Effluents by Using Hydrothermally Treated Fly Ash

S. Ram Mohan Rao and V.V. Basava Rao
Faculty of Chemical Engineering, University College of Technology,
Osmania University, Hyderabad-500 007, India

Abstract: Chromium in the wastewater coming out from tanneries and electroplating industries is to be treated because of exposure to it may produce effects on the liver, kidney, gastrointestinal and immune systems. On the other hand, fly ash produced from coal fired power plants is having disposal problem and it has to be properly utilized. In this study, the fly ash, subjected to hydrothermal treatment is used as adsorbent to remove Cr (VI) from synthetic samples. The effect of initial stock solution, contact time, adsorbent dose and pH were studied in a batch experiment. Results are compared with powdered activated carbon, granular activated carbon and untreated fly ash. The capacity of adsorption was found to be increased in the case of treated fly ash and it follows the order of powdered activated carbon >granular activated carbon >treated fly ash >untreated fly ash. The adsorption isotherms of Langmuir constants and Freundlich constants for all the adsorbents were determined. The Langmuir adsorption isotherm was recommended.

Key words: Chromium, waste waters, fly ash, activated carbon, batch adsorption, Freundlich and Langmuir, isotherms

INTRODUCTION

Many industrial processes, mainly those carried out in tanneries and galvanic industries, discharge effluents containing high concentrations of chromium, which represents a major environmental and health concern. Chromium occurs in the environment predominantly in one of two valence states: trivalent chromium, Cr (III), which occurs naturally and is an essential nutrient and hexavalent chromium, Cr (VI), which, along with the less common metallic chromium, Cr (0), is mostly produced by industrial processes. Cr (III) is an essential dietary element. The body has several systems for reducing Cr (VI) to Cr (III). Chronic human exposure to high levels of Cr (VI) by inhalation or oral exposure may produce effects on the liver, kidney, gastrointestinal and immune systems and possibly the blood. Additionally, epidemiological studies have clearly established that Cr (VI) should be classified as a human carcinogen. It causes serious disorders and diseases and it can ultimately become lethal (Rai *et al.*, 1999). WHO has fixed considering the toxicity, the maximum tolerance limit for total chromium for public water supply and for bathing ghats at 0.05 mg L^{-1} (Chand *et al.*, 1994). Exposure of human beings to these chrome bearing waters for longer time will cause skin irritation and corrosion of skin, ulcer formation, liver damage, respiratory tract infection, nausea, vomiting, severe diarrhea, epigastric pain and hemorrhage (Bandopadhyay and Biswas, 1998).

The most commonly methods of removing chromium are by chemical precipitation, electrochemical reduction, ion-exchange, evaporation and concentration, electrolysis and electroplating, ion-flotation, reverse osmosis, etc. The high capital cost and recurring expenses of most of these methods do not suit the small scale industries. Removal of chromium from waste water by adsorption on activated carbon is most widely process in small to medium industries (Ouki and Neufeld, 1997; Selomulya *et al.*, 1997; Vinay and Prem, 1997). But high cost of activated carbon prohibits its usage in the waste water treatment. Although it can be regenerated by chemical and thermal treatment, regeneration cost it self is very high and may not be economically feasible for the waste water treatment in general. Therefore, it is important to identify low cost adsorbent materials for the removal of chromium from waste water. On the other hand, in India every year about 70-80 million tonnes of fly ash is produced as the by-product from thermal power stations. It is posing a great problem of its disposal and environmental pollution. The adsorption of chrome dyes on to fly ash is reported by few investigators (Vinod *et al.*, 1998; Tiwari *et al.*, 1989). In the present study includes the removal of chromium (VI) on to fly ash and treated fly ash.

Corresponding Author: V.V. Basava Rao, Faculty of Chemical Engineering, University College of Technology,
Osmania University, Hyderabad-500 007, India Tel: +91-40-27098901 Ext: 244 Fax: +91-40-27098472

MATERIALS AND METHODS

Chromium (VI) solution: Synthetic samples of various chromium (VI) concentrations were prepared by dissolving potassium dichromate (AR grade) in double distilled water such that each ml of solution contains 1 mg of hexavalent chromium. Four solutions having initial concentrations of 1, 5, 10 and 20 mg L^{-1} were prepared.

Activated carbon: Powdered activated carbon (activated carbon 1) of AR grade and Granular activated carbon (activated carbon 2) of AR grade obtained from M/S R.K. carbons, Hyderabad were directly used as adsorbents. The Activated Carbon 1 is in the form of powder with surface area of 530 $m^2 g^{-1}$ and Activated Carbon 2 is in the form of 3 mm diameter granules with surface area of 460.3 $m^2 g^{-1}$.

Fly ash: The fly ash was obtained from Vijayawada Thermal Power Plant (VTPS), Vijayawada and National Thermal Power Corporation (NTPC), Ramagundam. Initially, the fly ash has been washed several times with hot (60°C) distilled water, filtered and dried. The sample has been then treated with dilute sulfuric acid and washed with distilled water to remove the excess sulfuric acid. Then it is heated at 120°C in an oven for 12 h to activate and, cooled to room temperature and finally sieved. Screen analysis of the fly ash (untreated) is given in Table 1.

The fly ash was, further, pre-activated with water (the ratio of water- fly ash was 1:1 v/v) in an autoclave for 4 h, then removed and dried at 110°C for 2 h. This is called hydrothermal treatment. The samples obtained were then oxidized with H_2O_2 to modify the pore structure. Treatment by H_2O_2 was done by immersing the samples in H_2O_2 of concentration 10% and boiling in a reflux condenser until no H_2O_2 could be detected, followed by washing with distilled water to neutrally and drying at 110°C for 4 h. This termed as treated fly ash. The Surface area of Fly Ash enhanced, in case of VTPS Fly Ash, to 365 $m^2 g^{-1}$ and whereas in case of NTPC Fly Ash to 348 $m^2 g^{-1}$, after hydro thermal treatment. The chemical compositions of Fly Ash obtained from VTPS and NTPC were tabulated in Table 2.

Batch experiments: The batch experiments were carried out in 250 mL capacity glass flasks with initially prepared stock solutions. 10 g L^{-1} of adsorbent was added to each of four stock solutions and 100 mL of the metal solution was added to each flask. The flasks were shaken in a orbital shaker at room temperature for half an hour. Then the contents were centrifuged at 3000 rpm for 15 min and the supernatant liquid was filtered using Whatman filter

Table 1: Screen analysis of fly ash

Mesh size	Percentage
+250	0.08
-250+150	1.12
-150+75	5.35
-75	93.45

Table 2: Chemical analysis of untreated fly ash

	Fly Ash	
Chemical	VTPS	NTPC
Density (g cc^{-1})	2.40	2.55
SiO_2 (%)	63.14	60.10
Al_2O_3 (%)	24.50	26.50
CaO (%)	2.15	4.80
Fe_2O_3 (%)	3.00	5.47
MgO (%)	1.65	1.20
SO_3 (%)	2.25	0.35
Alkalies (%)	2.11	0.95
Loss of ignition (%)	1.20	0.63
Surface area ($m^2 g^{-1}$)	280.00	268.00

paper (No. 42). The filtrate was used for the determination of metal with the help of UV-Vis spectrophotometer (Shimadzu UV-160A) and metals were determined in duplicate with respect to each initial concentration. The uptake of metal ions on the adsorbent at different initial concentrations of feed solutions was thus calculated. To study the effects of adsorbent dose 1, 5, 10 and 20 g L^{-1} of metal solution and the effects of pH on adsorption pH values 2, 4, 6 and 8 of the medium were taken. The pH of the solution was measured with a digital pH meter (MK VI Systronics).

RESULTS AND DISCUSSIONS

Effect of contact time: The effect of contact time on the adsorbed percent of chromium (VI) metal removal is plotted in Fig. 1. It can be observed that the adsorption rate is very rapid during initial period of contact and later it is slow. However equilibrium is attained within in 170 to 190 min. The equilibrium concentrations are following the order Activated Carbon 1 > Activated Carbon 2 > Treated Fly Ash > Untreated Fly Ash. The benefit of hydrothermal treatment of Fly Ash could be seen clearly. Fly Ash (untreated) found to remove 77.4% Cr (VI) at pH 6.0, temperature 25°C and adsorbent dose 10 g L^{-1}. Where as the hydro thermal treated Fly Ash is found to remove 85.4%. Therefore, the enhancement in the percent removal of Cr (VI) is 10%.

Effect of initial concentration: The effect of initial concentration of stock solutions on the adsorption of Cr (VI) is shown in Fig. 2. Adsorption capacity was found to decrease with increase in metal concentration. The high removal of metal Cr (VI) was obtained for lower initial concentration because the availability of more isolated metal ions.
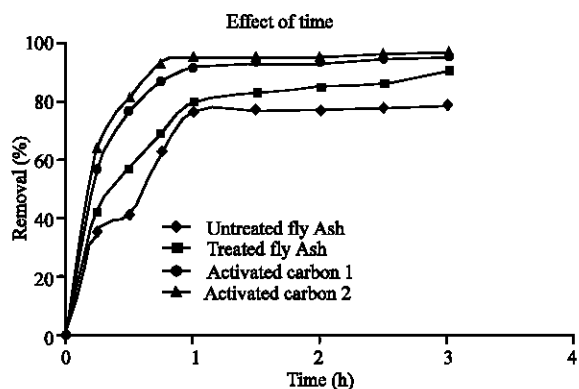
Fig. 1: Effect of contact time on percent removal of metal Cr (VI) (at Initial Concentration 10 mg L^{-1}, pH 6.0, Temperature 25°C and Adsorption Dose 10 g L^{-1})
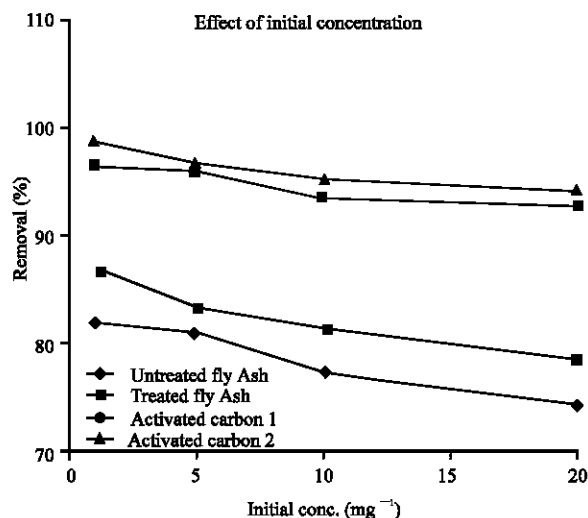

Fig. 2: Effect of initial concentration on percent removal of metal Cr (VI) (at pH 6.0, Temperature 25°C, Adsorbent Dose 10 g L^{-1} and Contact Time 2 h)

Effect of adsorbent dose: The effect of adsorbent dose on the removal Cr (VI) using different adsorbents at pH 6.0 and temperature 25°C is shown in Fig. 3. It clearly indicates that the percent removal of Cr (VI) increases with increase in adsorbent dose. It is obvious from the Fig. 3 that, as the adsorbent dose is increased, percent of metal removal also increases, but after an optimum dose of 15 g adsorbent per liter of metal solution, there is no appreciable change in removal. Further, at lower adsorbent dose the adsorbate is more easily accessible and because of this, removal per unit weight of adsorbent is higher. The initial rise in adsorption with adsorbent or adsorbate concentration is probably due to bigger driving force and lesser surface area. The rate of adsorption is high in the beginning as sites are available and
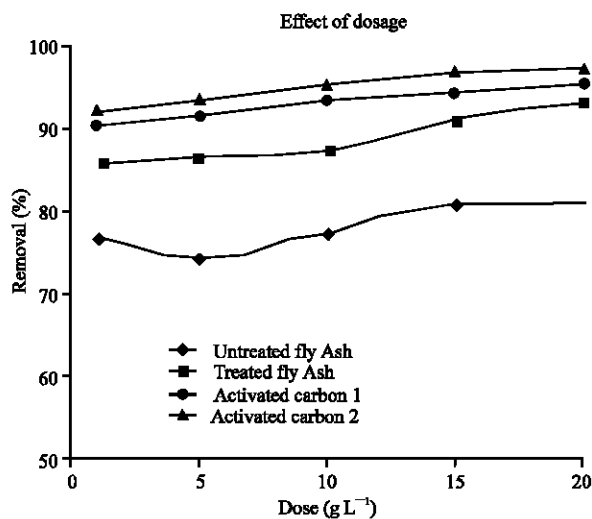

Fig. 3: Effect of adsorbent dose on percent of removal (at Cr(VI) Concentration in mg L^{-1}, pH 6.0, Temperature 25°C and Contact Time 2 h)

unimolecular layer increases. Adsorption and desorption occur together and rates become equal at a stage called adsorption equilibrium when isotherm are applied. That is why there is little increase in percent removal on increasing adsorbent dose from 15 to 20 g mL^{-1} of solution. The subsequent slow rise in percent removal may be due to adsorption and intraparticle diffusion taking place simultaneously with dominance of adsorption. With rise in adsorbent dose there is less increase in adsorption resulting from lower adsorptive capacity utilization of adsorbent. This is called solid concentration effect increasing overcrowding of particles.

Effect of pH: Hundred milliliter of solution of 10 mg L^{-1} Cr (VI) was adjusted to pH 2 to 8 with HCl/ NaOH and treated with 1 g of adsorbent and 2 h agitation in Orbital Shaker. The influence of pH of solution on the extent of adsorption of Cr (VI) is plotted in Fig. 4. The Cr (VI) removal is highly dependent on the pH of the surfactant solution, which affects the surface charge of the adsorbent and degree of ionization. The lower pH values were better for the adsorption. The pH effects were found to be slightly different for different adsorbents. The pH, 2 to 6, was found to be good for Cr (VI) removal. The treated fly ash was also showing the similar trend with same range of pH, but the results were better than untreated fly ash.

Adsorption isotherm: The adsorption studies conducted at fixed initial concentration of Cr (VI) and by varying adsorbent dose and the equilibrium data were fitted to the Langmuir and Freundlich isotherms (Hamadi *et al.*, 2001).

Table 3: Values of langmuir and freundlich isotherm constants for adsorption of Cr (VI)

Adsorbent materials	Langmuir constants		Freundlich constants		Recommended isotherms
	a (l mg^{-1})	b (mg mg^{-1})	K	n	
Activated carbon 1	0.0286	3.684	0.1268	1.385	Langmuir
Activated carbon 2	0.0176	5.895	0.1148	1.276	Langmuir
Untreated fly Ash	0.0023	16.876	0.0376	0.875	Langmuir
Treated fly Ash	0.0089	12.854	0.0543	0.954	Langmuir
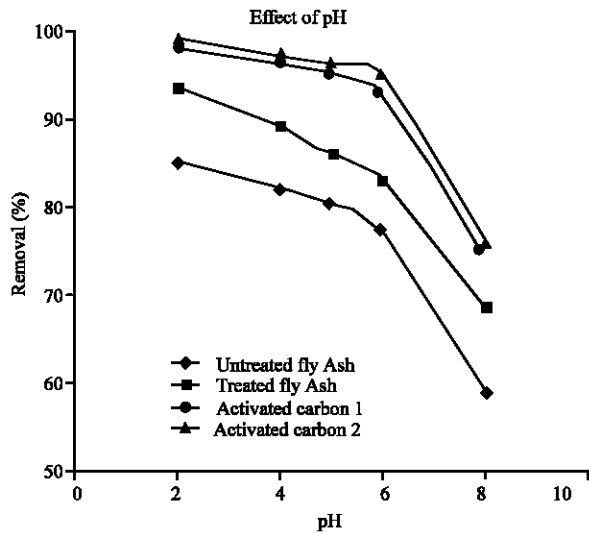
Fig. 4: Effect of pH on percent removal (at Cr (VI) concentration 10 mg^{-1}, temperature 25°C, contact time 2 h and adsorbent dose 10 g L^{-1}

$$q_e = \frac{abC_e}{1 + bC_e} \rightarrow (1) \text{ Langmuir equation}$$

and

$$q_e = kC_e^{1/n} \rightarrow (2) \text{ Freundlich equation}$$

where, C_e is equilibrium concentration of Cr (VI) (mg L^{-1}), q_e is the amount of Cr (VI) adsorbed per unit weight of adsorbent (mg mg^{-1}), a and b are the Langmuir isotherm constants and indicate the adsorption capacity and adsorption equilibrium constant. The Langmuir isotherms and Freundlich isotherms for all the adsorbents used in the experiments were plotted in Fig. 5 and 6. The parameters (a and b) were calculated along with k and n which are Freundlich constants.

The estimated values of a, b, k and n are presented in Table 3. On the basis of coefficient of correlation, the applicability of Langmuir and Freundlich isotherms were determined. The adsorption of Cr (VI) for all the 4 adsorbents is favourable for Langmuir isotherm.
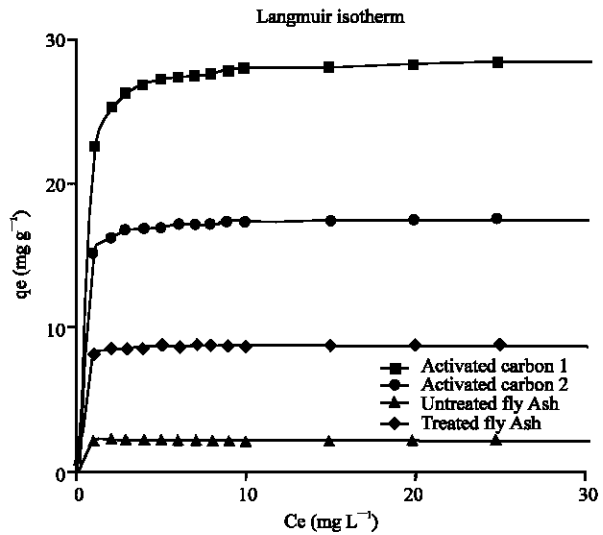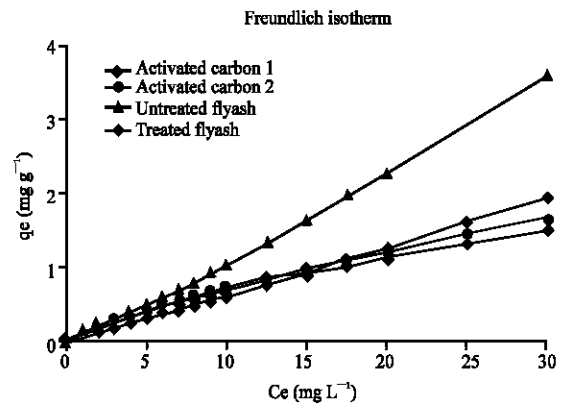

Fig. 5: Langmuir Isotherm for the adsorbents

Fig. 6: Freundlich Isotherm

CONCLUSIONS

The hexavalent chromium is toxic and carcigenic if it presents in waste waters and it is to be treated with low cost adsorbent. On the other hand, fly ash is also solid waste from coal fired power plants and it is to be properly utilized. The fly ash was subjected to hydrothermal treatment and it is found that adsorption capacity was increased. Removal of Cr (VI) is significantly affected by initial stock solution concentration, contact time,

adsorbent dose and pH of the system. In the present investigation the maximum removal of Cr (VI) was found within the range of 2.0 to 6.0 for all the adsorbents.

Further, the treated fly ash found to be better than untreated fly ash. Hence it is always better to use pH of 6.0. for fly ash with hydrothermal treatment for sufficiently good adsorption capacity. Also, the Langmuir isotherm follows affectively than the Freundlich isotherm.

NOMENCLATURE

a : Langmuir constant ($1\,mg^{-1}$)
b : Langmuir constant ($mg\,mg^{-1}$)
C_e : Equilibrium concentration ($mg\,L^{-1}$)
k : Freundlich constant
n : Freundlich index
q_e : Equilibrium adsorbate concentration on adsorbent ($mg\,mg^{-1}$).

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