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#### ADSORPTION FOR THE REMOVAL OF CHROMIUM USING FLY ASH Pooia Soni <sup>a</sup> and Shweta Saxena<sup>b</sup>

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Abstract: Among various organic and inorganic pollutants, heavy metal ions are very toxic and carcinogenic in nature. The presence of heavy metals in the aquatic environment has been of great concern because of their toxicity at lower concentrations. In India, several other industrial effluents contribute to contamination of river and groundwater by Cr. Chromium in excess amounts can be toxic especially the hexavalent form. Fly ash is one of the most abundant industrial waste materials and it can be used for the removal of toxic metal ions. In this study, adsorption of Chromium (VI) was investigated by fly ash from aqueous solutions. Fly ash samples were collected from Shri Ram Fertilizers and Chemicals Ltd. (SRFC) Kota, Rajasthan. Physico – chemical analysis was performed of collected fly ash samples. The sorption of Cr (VI) ions by batch method is carried out. U.V. Visible spectrophotometric method was used for Chromium (VI) determination. The study investigates the effect of initial metal ion concentration, adsorbent doses and pH of solution. The result indicate that the adsorption increases with increasing amount of fly ash and initial chromium concentration. Adsorption is maximum on pH 2 and decreases with increasing pH. Various adsorption kinetic models were tested in understanding the adsorption kinetics and it was found that the adsorption was controlled by intra-particle diffusion model.

Keywords: Adsorption; Batch method; Chromium; Fly ash.

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#### INTRODUCTION

Environmental pollution particularly from heavy metals and minerals in the waste water is the most serious problem in India. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal pharmaceuticals. processing. tanneries. pesticides, organic chemicals, rubber and plastics, lumber and wood products (Lakherwal, 2014). The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. Most of the heavy metals discharged into the wastewater are found toxic and

carcinogenic and cause a serious threat to the human health. (Srivastava et al., 2006). Chromium is essential to animals and human. Chromium in excess amounts can be toxic especially the hexavalent form. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials (Sankhla et al., 2016). Chromium (Cr) besides lead, cadmium and copper is widely used for the production of colour pigments of textile dyes and is thus a common contaminant in textile factory effluents (Ugoji et al., 2004; Manzoor et al., 2006; Deepali et al., 2010). Soil contaminated by textile factory effluents has also been found to contain high concentration of Cr (Deepali et al., 2010; Malarkodi et al., 2007). In India, several other industrial effluents contribute to contamination of river and groundwater by Cr (Sanyal et al., 2015).

Electroplating can release chromic acid spray and air-borne Cr-trioxide, both can result in direct damage to skin and lungs as well as chromium dust has been considered as a potential cause of lung cancer (Sankhla, et al., 2016). Sub chronic and chronic exposure to chromic acid can cause dermatitis and ulceration of the skin (USEPA, 1999). Longterm exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding also to the danger eating fish that may have been exposed to high levels of chromium (Sankhla et al., 2016). Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L (Venkateswarlu et al., 2007). The chromium concentration in Hadoti region ranges from a minimum 0.03 mg/L to a maximum 0.29 mg/L (Gupta et al., 2011). At some places most of values were higher than the permissible limit. It is urgent to control chromium in potable water and discharge into inland surface water and to develop effective methods for removal of Cr (VI) (Dong et al., 2011). Adsorption separation has been widely used in environmental chemistry, owing to its relatively low cost, simplicity of design/ operation and pollutant removal to low concentrations (Hsu et al., 2009).

Fly Ash: Coal/Lignite based Thermal Power Generation has been the backbone of power capacity addition in the country (Surabhi, 2017). Flyash is the term defined for the finely divided residues those results from the combustion of the ground coal. Primarily the flyash particles consist of Silica and Alumina; and oxides carbon of iron. calcium. magnesium, sulfur, titanium etc. being the secondary ingredients (Kumar et al., 2008). The chemical compositions of fly ash are high percentage of silica (61.1%), alumina (21.8%), Fe<sub>2</sub>O<sub>3</sub> (4.69%), CaO (3.51%), SO<sub>3</sub> (1.62%) (Ahmaruzzaman, 2011; Rahel et al., 2017). The location of the energy source, nature of fuel and size of the furnace determine the exact nature and quantity of these compounds (Kumar et al., 2008). Fly ash is one of the most abundant industrial waste materials and its major components make it as a potential material for the adsorption of heavy metal contaminants in water and wastewater (Hosseini et al., 2013). The surface of fly ash is porous structure and it has a large specific surface area. Hence it can be used for the toxic metal ions, inorganic anions, organic compounds, and so on (Wang and Wu 2006). As Shri Ram Fertilizers and Chemicals Ltd., Kota (SRFC) is located in Kota (Rajasthan). So, we used fly ash as an adsorbent for removal of Chromium.

## EXPERIMENTAL

The Batch test were carried out in 250 ml flask using fly ash as a sorbent. The fly ash samples were collected from the Shri Ram fertilizers & Chemicals Ltd., Kota (DCM). Chromium samples were prepared by dissolving a known quantity of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in double-distilled water and used as a stock solution and diluted to the required initial concentration. A 1g fly ash was mixed with 100 ml of the aqueous solutions of various initial concentration (0.5mg/L, 1mg/L, 2mg/L, 3mg/L) of chromium (VI) in each flask. The stirring speed was kept constant at 120 rpm. The pH of the solution was measured with a HACH - pH meter. The effects of various parameters on the rate of adsorption process were observed by varying adsorbent concentration, initial Cr Concentration and pH of the solution. The solution volume (V) was kept constant. The measurements were made at the wavelength  $\lambda$ = 540nm, which corresponds to maximum absorbance (Karaca et al., 2004). Using a mass balance, the concentrations of chromium (VI) at different time adsorbed in fly ash was calculated.

$$q_t = \frac{(C_o - C_t) V}{M}$$

Where  $q_t$  is the amount of chromium (VI) adsorbed onto the fly ash at time t,  $C_o$  is the initial concentration of chromium (VI),  $C_t$  is aqueous phase concentration of chromium (VI) at time t, V is the volume of the aqueous phase, M is the weight of fly ash.

# RESULTS AND DISCUSSION

# Effect of initial Cr (VI) concentration

The effect of variation of initial Chromium (VI) concentration was studied on Fly ash.

Chromium solutions at different initial concentrations from 0.5 to 3 mg/L were treated with 1 g of adsorbent at constant temperature 30°C. (Figure 1) shows the effect of the varying concentration of Cr (VI) on the removal efficiency of the chromium (Hosseini et al., 2011). It can be seen that the adsorption increases with increase in initial Cr concentration, which may be due to the availability of a greater number of Cr (VI) ions in solution for sorption (Baral et al., 2006). Whereas percent adsorption decreases with increase in initial concentration of Cr (VI). 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 (Gupta et al., 2008). Earlier studies (Hosseini et al., 2011), (Baral et al., 2006) and (Devi et al., 2010) showed similar results with type of zeolite synthesized from coal fly ash, treated sawdust and Eco-friendly activated carbon respectively.

### Effect of Fly ash Amount

Chromium (VI) batch adsorption were carried out for amount of fly ash in the range of 1 g to 3 g fly ash. The initial Chromium (VI) concentration was taken 2 mg and temperature was kept constant at 30°C. This is evident from Figure 2, where percentage adsorption was plotted against adsorbent dose that the percentage adsorption increased from at lower adsorbent dose to higher adsorbent dose. The phenomenon of increase in percent chromium removal with increase in adsorbent dose was due to the availability of more and more adsorbent surfaces for the solutes to adsorb (Bishnoi et al., 2004). This is because at the higher dosage of sorbent due to increased surface area, more adsorption sites are available causing higher removal of Cr (VI) (Malkoc et al., 2007). The similar results were obtained by activated rice husk carbon and activated alumina (Bishnoi et al., 2004), tea factory waste (Malkoc et al., 2007), guar gum (Khan et al., 2017), bagasse fly ash (Gupta et al., 1999), wheat straw and eupatorium adenophorum (Song et al., 2016).

#### Effect of pH

The pH value of solution has a significant impact on the adsorption of Cr (VI). The effect of pH on adsorption of Cr onto fly ash was studied at pH 2, 4, 6, 8 and 10. The maximum adsorption capacity of fly ash was found to be at pH 2. Figure 3 shows the adsorption of chromium with pH, and it was found that chromium adsorption decreased with increasing pH value in the range of 2-10. And very slightly changes change between pH 4-10. Adsorption of hexavalent chromium varies as a function of pH with HCrO<sub>4</sub> -, Cr<sub>2</sub>O<sub>7</sub> <sup>2-</sup> and CrO<sub>4</sub> <sup>2-</sup> ions appear as dominant species. At pH of 2, HCrO<sub>4</sub> <sup>-</sup> is the dominant species. The surface charge of adsorbent is positive at low pH, and this may promote the binding of the negatively charged HCrO<sub>4</sub> - ions (Panda et al., 2017). A significant reduction in the adsorption of Cr (VI) at higher pH is possibly due to the abundance of hydroxy ions resulting in an increased hindrance to the diffusion species (Gupta et al., 1999). A similar trend of result has been observed for the removal of Chromium (VI) by using an eco-friendly activated carbon (N. Devi et al., 2010), a low-cost fertilizer industry waste material (Gupta et al., 2009), fly ash (Gupta et al., 2008) and poly-acrylonitrial-based porous carbon (Feng et al., 2018).







Figure 2: Effect of fly ash amount on adsorption of Cr (VI)



#### **Kinetics**

There are several adsorption kinetic models like zero order, first order, second order, pseudo-first order, pseudo-second order, intraparticle diffusion and elovich equation model that can be helpful in understanding the adsorption kinetics, particularly the limits imposed on the adsorption rate (Dizadji et al., 2011). The possibility of intra-particular diffusion is explored by using the following equation, already applied by Furusawa and Smith (Furusawa et al., 1974):

$$q_t = K_{dif} (t)^{1/2} + C$$

Where C is the intercept and  $K_{dif}$  is the intraparticle diffusion rate constant.

Consistent with Eq. (1), the values of  $q_t$  correlated linearly with values of t1/2, as shown by Figure 4 and the rate constant K<sub>dif</sub> directly evaluated from the slope of the regression line. The values of intercept *C* provide an

information about the thickness of the boundary layer, *i.e.* the resistance to the external mass transfer (Khezami, 2005). In applying all the kinetic models, the value of R<sup>2</sup> was obtained maximum and the standard error of estimation (SEE) value was minimum for the intra-particle diffusion model. So, it can be seen, the adsorption process was controlled by the intraparticle diffusion model.





### CONCLUSION

The present study highlighted the ability of fly ash to adsorb Cr (VI) from aqueous solutions. It was observed that using fly ash 80% of the Cr (VI) was removed. The removal efficiency was found to be dependent on the adsorbent dose, initial metal ion concentration and pH of the solution. The result indicate that the adsorption increases with increasing amount of fly ash and initial chromium concentration. Adsorption is maximum on pH 2 and decreases with increasing pH. Kinetic model was successfully applied to the experimental data. confirming that adsorption was controlled by intra-particle diffusion model.

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