Study of Potentiality of Coal Fly ash for the Removal of Cr(VI) from Industrial Wastewater: Equilibrium and Kinetic Studies

Pankaj Kumar Tyagi

Leather Technology Section, Faculty of Engg. & Technology

Aligarh Muslim University, Aligarh, India

ABSTRACT

The present study explore the potentiality of Coal Fly Ash (CFA) as an effective and alternative adsorbent for the removal of Cr(VI) from industrial wastewater. Batch studies has been conducted to determine the potential of CFA as an adsorbent for the removal of Cr(VI) at variable pH, initial metal ion concentration and contact time. The maximum adsorption (81.66%) was found at pH 3 with initial metal ion concentration 50 mg/L. The high value of R^2 0.9694 for Freundlich model suggested that adsorption of Cr(VI) by CFA obey Freundlich model more closely. Kinetic models plotted for the obtained results showed that the adsorption of Cr(VI) by CFA obeyed second order kinetic model. FTIR and SEM analysis had been carried out to study the functional group and surface morphology of the adsorbent. The adsorption capacity of coal fly ash was found to be greater and can be employed in wastewater treatment processes.

KEYWORDS: Adsorption, Chromium, coal fly ash, FTIR, SEM, Morphology, Functional group.

1. INTRODUCTION

Chromium is one of the major heavy metal pollutants in the environment. Chromium is an essential nutrient for plants and animal metabolism. Chromium species mainly exists in two different oxidation states in aqueous solution. Cr(III) is considered as an essential trace element for the maintenance of effective glucose, lipid and protein metabolism in mammals (Kaotash et a., 2000). On the other hand, Cr(VI) which is present as either dichromate ($Cr_2O_7^{2-}$) in acidic environment or chromate (CrO_4^{2-}) in alkaline environments can be toxic for biological systems (Shanker et.al., 2005) and carcinogenic for both humans and animals (Mungasvali et. al.2007), . Therefore, the toxicity and biological activity of Chromium not only depends on the total amount but also on its chemical form (Kot et. al., 2000; Dehirham et. al., 2010). Chromium in its hexavalent formbeing toxic is introduced into the water bodies from different industrial processes such as tanning, electroplating, metal processing, paint manufacturing, steel fabrication and agricultural runoff (Shrivastava et. al., 2008). According to USEPA the maximum permissible limits in waste water and portable water forchromium is 1.0 mg/L and 0.05 mg/L, respectively (Doughee et. al., 2005). The toxic effects of chromium on both lower and higher plants and microbial activities (Nwuche et. al.,2008) have been reported. Hence in order to reduce pollution, it must be removed before discharging into the natural environment.

The common methods for the removal of heavy metals from waste waters are chemical precipitation, ion exchange, electro-dialysis, membrane filtration and sorption of metal oxides. These methods have certain drawbacks namely, high cost, low efficiency, generation of toxic sludge or other waste that requires disposal treatment and imply operational complexity (Dada et. al., 2013). Adsorption has advantages over the other methods due to its simple design with sludge free environment involving low investment (Crini, 2005). In recent years, numerous low cost natural materials such as rice husk (Ajmal et. al., 2003), tea waste (Amir et. al., 2005), ground nut shell (Idris et. al., 2012), local landfill clay (Ghorbel et. al., 2015) , chitosan coated ceramic membrane (Wanida et. al., 2015), treated old paper (Ossman et. al., 2013) and tourmaline mineral (Kan et. al., 2006), ceramic water purifiers made of Iraqi Betonite type (Bp11) (Jassim et. al., 2014), dried activated sludge biomass (Ashfaq 2011), terminalia arjuna (Rao et. al., 2014), flyash (Ashfaq, 2012), have been used to remove chromium and other heavy metals from water and waste waters.

2.   MATERIALS AND METHODS

2.1 Preparation of adsorbent

Raw sample of coal fly ash was collected from Kasimpur Thermal Power Plant, Aligarh in powder form. The sample was primarily washed with double distilled water repeatedly three to four times to remove any adhering impurities. The cleaned sample was kept in sunlight for drying. The sample was than sieved to obtain particles of uniform diameter of 150 micron. This sample was than stored in an air tight container to be used for analysis related to adsorbent characterization and batch studies.

2.2 Characterization of adsorbent

To observed the surface morphology of the adsorbent before and after adsorption of Cr(VI), SEM analysis was employed by using Scanning Tunneling Microscope, JEOL-JSM 6510 LV at USIF (University Sophisticated Instrumentation Facility) Aligarh Muslim University, Aligarh.

The types of binding groups present on the adsorbent (CFA) were identified by using Perkin-Elmer Fourier Transformer Spectrophotometer (FTIR) Version 10.03.08 by using KBr pellet technique in the wavelength range 450-4000 cm^{-1} at Instrumentation Lab, Department of Chemistry, AMU, Aligarh.

2.3 Adsorbate Solution

A stock solution of 500 mg/L of Cr(VI) was prepared by dissolving required amount of potassium chromate, K_2CrO_4 in DDW in a 1L standard flask. This stock solution was used to prepare the working solutions of desired concentrations for all experiments. The pH values of the solutions were adjusted by adding 0.1 mol/L NaOH or 0.1 mol/L HCl. The concentrations of Cr(VI) in the solution before and after adsorption were measured by using GBC-902 Atomic Absorption Spectrophotometer (AAS).

2.4 Adsorption studies

Batch process were conducted at room temperature to study the adsorption of Cr(VI) ions by coal fly ash. An accurately weighed 0.5g of CFA was placed in 100 ml stopper conical flask containing 50 ml of Cr(VI) ions solution of concentration 50 mg/L. These solutions were shaken in a rotary shaker for required time to attain equilibrium. All the experiments such as effect of pH, adsorbent, contact time were conducted at room temperature with 50 ml Cr(VI) ions solutions of 50 mg/L except during the study of effect of concentration where 10 to 200 mg/L Cr(VI) ions concentration solutions were used. The final concentration of metal ions in the solution was analysed by Atomic Absorption Spectrophotometer (AAS). The amount of metal ion adsorbed was calculated by subtracting final concentration from initial concentration. The removal percentage (R%) of Cr(VI) ions and adsorption capacity, q_e(mg/g) of CFA were calculated for each run by the following expression

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100$$

$$q_e = \frac{(C_i - C_e)}{m} \times V$$

where, C_i is the initial concentration of metal ions in the solution (mg/L), C_e is the equilibrium concentration of metal ions (mg/L), V is the volume of the solution (L) taken, m is the mass of the adsorbent (g) used.

3.   RESULTS AND DISCUSSION

3.1 Characterization of adsorbent

3.1.1 SEM Analysis

SEM analysis was carried out to examine the surface morphology of CFA before and after adsorption of Cr(VI) ions. The SEM images of raw and chromium loaded CFA are shown in Fig.1 and 2, respectively. The SEM image of raw CFA clearly depicts that the surface is irregular and porous which indicated the presence of adsorption sites on the surface. After adsorption of Cr(VI), the surface morphology of CFA has changed as it becomes dense and regular. The white patches on the surface of CFA could be seen clearly which confirmed adsorption of chromium on the surface of CFA.
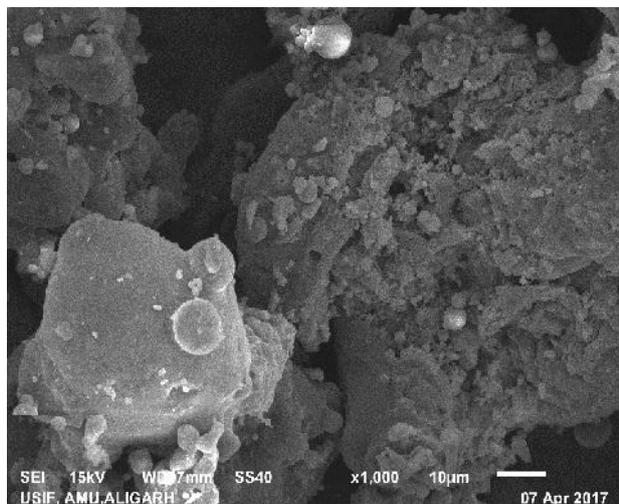
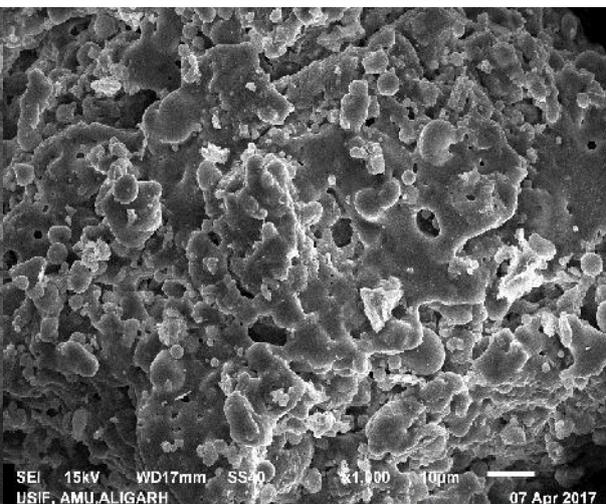Fig. 1 SEM image of untreated CFA

Fig. 2 SEM image of Cr(VI) treated CFA

3.1.2 FTIR Analysis

FTIR spectra of raw and chromium treated CFA is shown in Fig. 3 and 4. FTIR spectra of raw CFA displayed a number of peaks pertaining to different functional groups. The wide band observed at 3448 cm^{-1} indicates the free and intermolecular bonded O-H groups. The peak observed at 1079 cm^{-1} was assigned to the stretching vibration of strong C-O group. The peak observed at approximately 911cm^{-1} and 790 cm^{-1} indicated the alkene bonds (=C-H) present in CFA. The peak observed at 574 cm^{-1} showed the presence of alkyl halide (C-Br) group. The peak at 452 cm^{-1} confirmed the presence of metallic oxide attached to the surface. After adsorption of Cr^{6+} shifting of peaks from 3448 cm^{-1}, 1877 cm^{-1}, 1079 cm^{-1}, 911cm^{-1}, 790cm^{-1}, 574 cm^{-1} and 452 cm^{-1} to 3441 cm^{-1}, 1873 cm^{-1}, 1075 cm^{-1}, 905 cm^{-1}, 565 cm^{-1} and 444 cm^{-1} was observed which might be due to the interaction of Cr(VI) ions with the functional groups present on the surface of CFA.
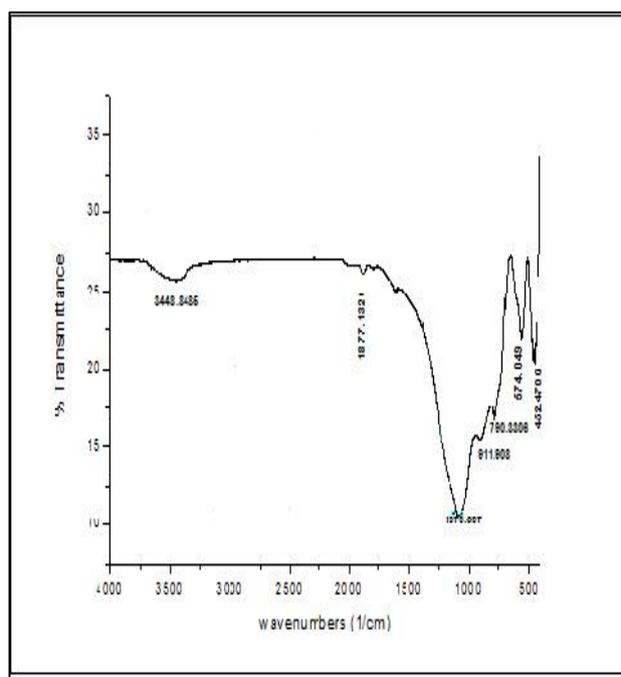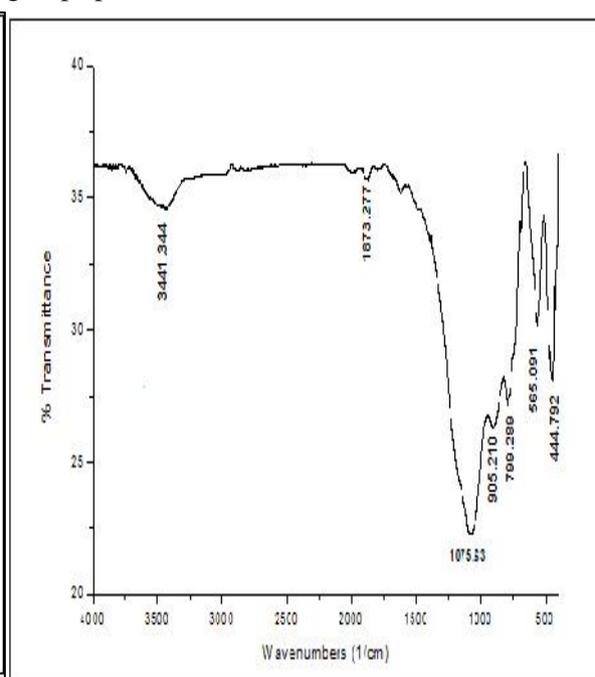

Fig. 3 FTIR spectra of untreated CFA

Fig. 4 FTIR spectra of Cr(VI) treated CFA

3.2 Batch Studies

3.2.1 Effect of pH

The pH of solution is one of the important controlling parameter in the adsorption process. The percentage removal of Cr(VI) in pH range 1 to 12 is shown in Fig. 5. It has been observed that the percent removal of metal ion decrease as pH value of the solution is increased. CFA showed higher adsorption at pH 3 (81.66%). At a higher pH, Cr(VI) ion gets precipitated as hydroxides which decreases the rate of adsorption and subsequently the percent removal of metal ions also decreased (Pagnaelli et. al., 2003; Lugo et. al., 2010).

3.2.2 Effect of concentration of metal ions

The percentage removal of Cr(VI) by CFA in range of concentration 10 to 200 mg/L is shown in Fig.6. It was observed that the adsorption capacity of Cr(VI) increased from 2.33 mg/g to 14.18 mg/g whereas the adsorption percentage decreased with the increase in concentration of metal ions in the solution from 100 to 70.94 %. This was due to the fact that empty adsorbent sites adsorbed Cr(VI) ions rapidly at lower concentration but at higher concentration the adsorption sites have been occupied and therefore at high concentration Cr(VI) ions occurred by diffusion (slower step) into the inner sites of the adsorbent. The maximum adsorption was observed at 10 mg/L (100%) and minimum adsorption observed at 150 mg/L (69.84%).
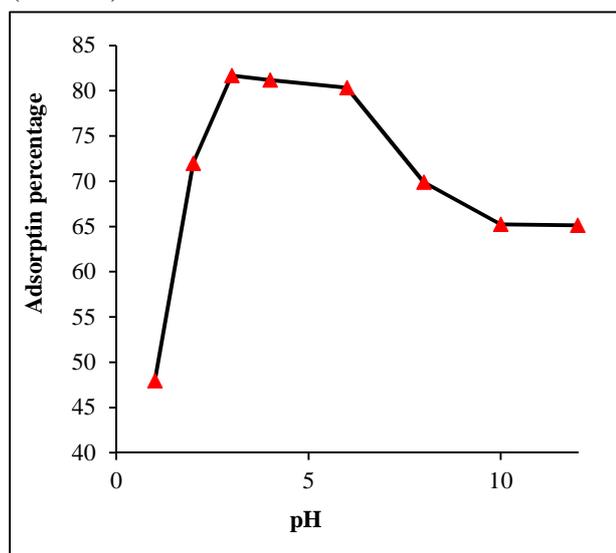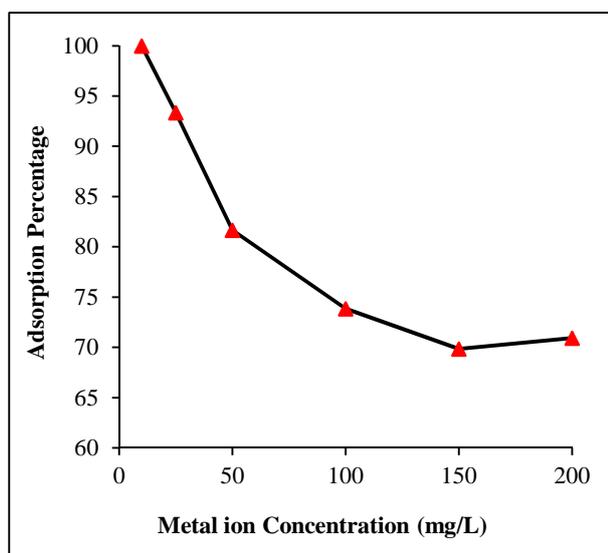

Fig. 5 Effect of pH   Fig. 6 Effect of initial metal ion concentration

3.2.3 Effect of contact time

The adsorption of metal ions on adsorbent generally found to increase with increasing of contact time until equilibrium is attained. The Cr(VI) uptake by CFA versus contact time is shown in Fig. 7, indicates that equilibrium is attained in 30 min, where maximum adsorption percentage was 81.66%. The adsorption percentage of Cr(VI) ions versus time is single and continuous line leading to saturation. The equilibrium time of 30 minutes investigated in the present work was much shorter than other adsorbents reported earlier for Cr(VI) adsorption.

3.2.4 Effect of adsorbent dose

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion in the solution. The adsorption percentage of Cr(VI) at different doses of CFA is shown in Fig. 8. It was observed that increasing the adsorbent dose increased the percentage removal of Cr(VI) upto 96.66% at adsorbent dose of 1.0 g. The adsorption percentage of Cr(VI) increased with the increase of adsorbent dose due to increase in number of vacant sites available due to increase surface area of adsorbent.
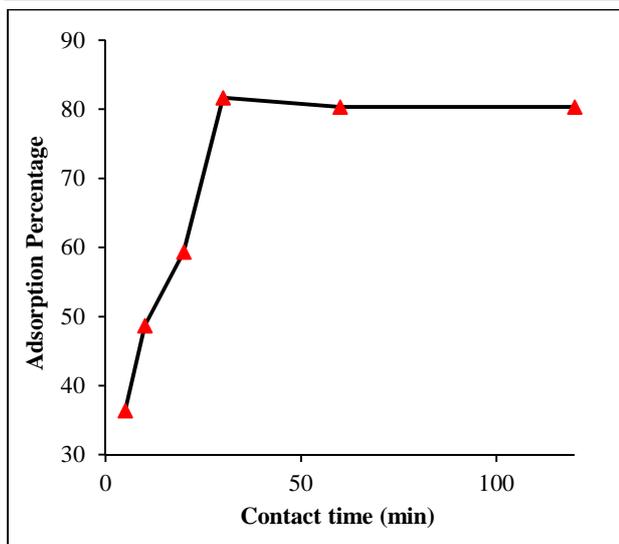
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Fig. 7 Effect of adsorbent dose
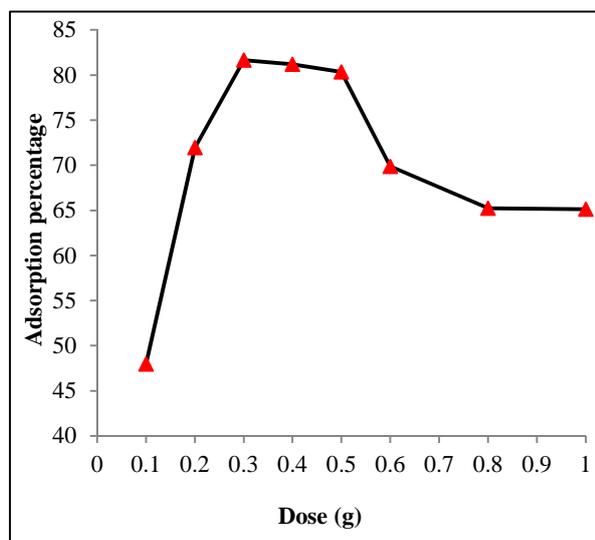

Fig. 8 Effect of adsorbent dose

3.3 Adsorption Isotherms

Langmuir isotherm relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. Adsorption isotherm curve is an invaluable curve describing the phenomena governing the retention or mobility of the adsorbent from the aqueous phase to a solid phase at constant temperature and pH (Allen et. al., 2004; Foo et. al., 2010). In order to model the adsorption behaviour of Cr(VI) ions on CFA, Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) adsorption isotherm were studied.. It is expressed as-

$$\frac{1}{q_e} = 1/bq_m + 1/q_m \times 1/C_e$$

where, q_e is the amount of Cr(VI) adsorbed per unit weight of the adsorbent (mg/g) at equilibrium, C_e is the equilibrium concentration (mg/L), b and q_m are Langmuir constant related to the energy of adsorption and monolayer adsorption capacity of adsorbent (mg/g) respectively. The plot of $1/q_e$ vs $1/C_e$ is shown in Fig. 9 and the values of q_m and b were be calculated from the intercept and slope of the plot.

Freundlich isotherm is an empirical equation which was applied for adsorption of Cr(VI) and is represented as-

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

where, C_e is the equilibrium metal ion concentration (mg/L) q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g). K_f and n are the Freundlich constant indicates adsorption capacity and adsorption intensity respectively. The plot of log q_e vs log C_e is shown in Fig. 10 and the values of K_f and n were calculated from the intercepts and slop of the plots.

In order to evaluate the fitness of the experimental data on Langmuir model, $1/q_e$ were plotted against $1/C_e$ as shown in Fig. 3.9 and on Freundlich model, $\log q_e$ were plotted against log C_e as shown in Fig. 3.10, respectively. The monolayer adsorption capacity of CFA was found to be 7.057 mg/g and the value R_L which is less than 1 indicating that the adsorption of Cr(VI) on CFA is favourable. The linearity of the graph and values of the correlation coefficient (R^2) and other parameters shown in Table 1 revealed that the experimental data were more appropriately fitted on Freundlich isotherm model. The value of n was found to be greater than 1 (n=2.150) indicated that adsorption of Cr(VI) on CFA is favourable and chemical in nature. The validity of data to Freundlich isotherm further suggested that adsorption of Cr(VI) ions on CFA occurs by the formation of homogeneous monolayer followed by multilayer formation.

Table:1 Langmuir and Freundlich isotherm constants for the adsorption of Cr(VI)

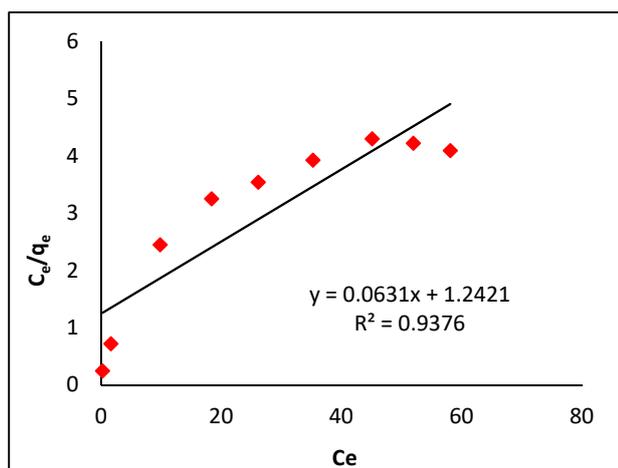| Metal Ions	Langmuir isotherm				Freundlich isotherm			
	q_m	b	R^2	R_L	1/n	n	K_F	R^2
Cr(VI)	7.057	0.6512	0.9376	0.0869	0.4651	2.150	1.740	0.9745

Fig. 9 Langmuir adsorption isotherm model
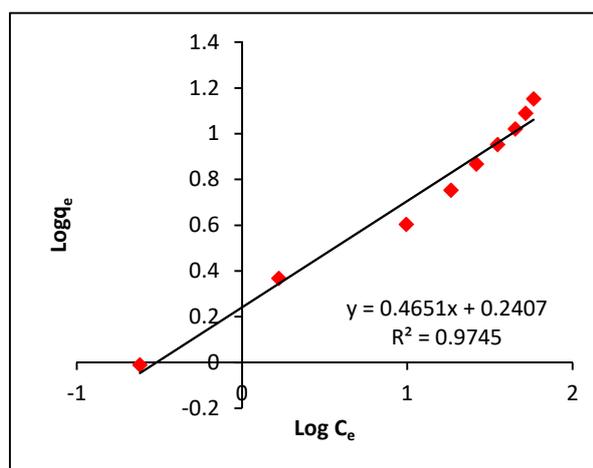

Fig.10 Freundlich adsorption isotherm

3.4 Adsorption Kinetics

In order to investigate the adsorption kinetics, pseudo first-order given by Researcher (Lagergren, 1898) and pseudo second order kinetics models by researcher (Ho et. al., 1999) were applied. The pseudo second order model was found to be obeyed closely as the value of correlation coefficient is close to 1 i.e. $R^2 = 0.99$. The pseudo first-order kinetic equation of Lagergren is represented as:

$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$

where, k_1 is the Lagergren rate constant for adsorption (min^{-1}), q_e is the amount of metal adsorbed at equilibrium ($mg \ g^{-1}$), q_t is the amount of metal adsorbed ($mg \ g^{-1}$) at any time t. The time, t was plotted against $\log(q_e - q_t)$ as shown in Fig. 11 and the values of k_1 and q_e was calculated from slope and intercept of lines of the plot.

The equation of pseudo second order model is:

$$t / q_t = 1 / k_2 q_e^2 + 1 / q_e t$$

where, k_2 is the equilibrium rate constant of second order kinetics model ($g \ mg^{-1} \ min^{-1}$), q_e is the equilibrium capacity, q_t is the adsorption capacity at any time t. The time t, was plotted against t/q_t as shown in Fig.12 and the values of k_2 and q_e were calculated from the slope and intercepts of the plot.

In order to investigate the adsorption kinetics, pseudo first-order and pseudo second order kinetics models were applied. The experimental data obey pseudo second order model more appropriately when the value of correlation coefficient is greater than 0.99($R^2 > 0.99$). The value of correlation coefficient and other parameters for kinetic models used are listed in Table 2. The straight line of the graph and value of correlation coefficient (R^2 0.99) and other parameters indicated that adsorbate-adsorbent system obeyed pseudo second order model more closely than pseudo first order. Furthermore, the applicability of pseudo second order model confirmed that Cr(VI) ions during adsorption formed multilayer on the surface of particles of CFA.

Table: 2 Pseudo-first order and pseudo-second order kinetic model constants

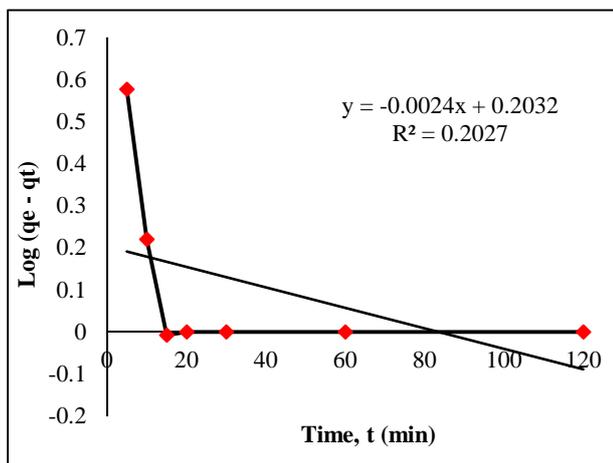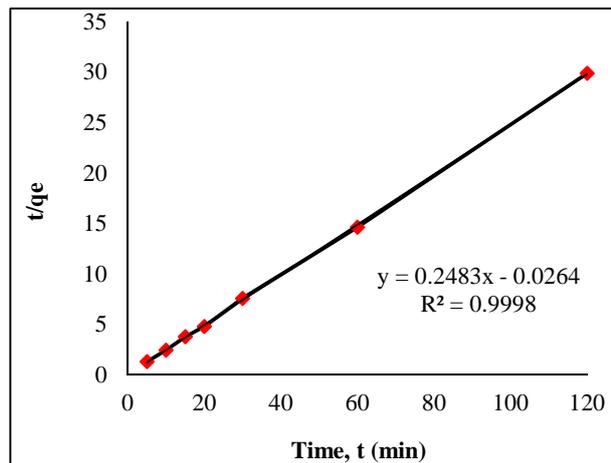| Metal ions	Pseudo-first order			Pseudo-second order		
	q_e	K_1	R^2	q_e	K_2	R^2
Cr(VI)	1.5966	0.0055	0.2027	4.027	-2.3359	0.999

Fig. 3.12 Pseudo second order model

Fig. 3.11 Pseudo first order model

4.   CONCLUSIONS

This present study was conducted to evaluate coal fly ash (CFA) as possible potential adsorbent for removal of Cr(VI) from synthetic wastewater by batch process. It was found that the adsorption of Cr(VI) ions by CFA was pH dependent and the optimum pH for the maximum removal (81.66%) of Cr(VI) was pH 3. The equilibrium data was found to be obeyed Freundlich model more appropriately than Langmuir model. The study of kinetic data was found to obey pseudo second order model best. It is also important to remark that the CFA is economically and easily available material. After treatment with heavy metals a very low amount of sludge is produced which may be disposed off without causing any harm to the environment. The results showed that the CFA has been found very effective and environment friendly adsorbent which can remove sufficient amount of Cr(VI) from aqueous solution in very small period of contact time (in this case 30 minutes). Hence, CFA can be utilized in wastewater treatment containing Cr(VI) as pollutants without any chemical treatment.

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