Kinetics study of Cr(III) Adsorption onto low cost Fly Ash Adsorbent

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Abstract- Chromium removal from wastewater is becoming increasingly important both to meet discharge consents and prevent eutrophication of water resources. A series of simple batch tests were conducted to investigate the influence of fly ash dosage on chromium adsorption from synthetic wastewater containing Chromium trioxide. Chromium removal of up to 84.5% was obtained. Different adsorption and kinetic models were studied namely; Langmuir, Freundlich, First order, Second order, Factorial power and Elovich and their constants were calculated. Using K_L values, it is known that adsorption fits well in Langmuir isotherm. Second order kinetics is observed for the adsorption process carried out. Activated Fly ash is used in the treatment process. The effect of various parameters such as initial pH, contact time, adsorbent amount and initial Cr (III) concentration are studied. Adsorption capacity and adsorption intensity were calculated. Rate constants and order of the reaction were determined and final rate equation was developed.

Keywords:

Chromium removal, Chromium trioxide, Adsorption, Activated Fly ash, Adsorption capacity, Adsorption intensity.

INTRODUCTION

Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents[1]. The discharge of non-biodegradable heavy metals like Cu, Zn, Ni, Pb, Cd, and Cr into water stream is hazardous because the consumption of polluted water causes various health problems. Among these heavy metals, pollution by chromium is of major concern as 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[2].

Leather is a material that has a reasonable mechanical resistance, good chemical stability and acceptable thermal behavior. This material is obtained by means of specific reactions among carboxylic groups of the protein fiber network of animal skin (collagen) and tanning reagents. The basic chromium (III) sulfate $[Cr(OH)(H_2O)_5SO_4]$ is a primary tanning agent widely used at the present time[3]. Chromium exists in +3 and +6 oxidation states, as all other oxidation states are not stable in aqueous solutions. Both valences of chromium are potentially harmful[4].When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract and lung carcinoma are noticed. The discharge limit from industry is less than 1 mg/l. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/l. Several methods such as chemical precipitation, ions exchange, electrochemical precipitation, solvent extraction, reverse osmosis are being practiced for chromium removal in waste waters[5].

These methods are cost intensive and are unaffordable for large scale treatment of wastewater that is rich in chromium. Adsorption using the activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium and quite popular as compared to other methods [6]. The cost associated with the commercial activated carbon is very high which make the adsorption process expensive[7]. This indicates that the cost effective alternate adsorbents for treatment of chrome contaminated waste streams are needed.

MATERIALS AND METHODS

PREPARATION OF ADSORBENT:

The fly ash was collected from ACC cements, Madukarai. The composition of the fly ash was also collected from the Madukarai cement plant. The fly ash was washed with distilled water and dried at room temperature for 24 h. The activation of fly ash was carried out by treating it with concentrated sulfuric acid (98% w/w) and maintaining at the temperature range of 150ºC for 24 h. Again it was washed with distilled water to remove the free acid.

CHARACTERIZATION OF FLY ASH AS ADSORBENT:

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties including electrical conductivity.

The particle size of the fly ashes was measured using a laser based particle size analyzer, a Mastersizer 2000 of Malvern Instruments Ltd. It utilizes Fraunhofer diffraction of light formed by particles with a diameter larger than the incident laser beam wavelength. A combination of an optical filter, lens and photo detector coupled with a computer loaded with Mastersizer software enables one to compute the particle size distribution from the diffraction data and store it as volume percentage against the particle size.

BATCH EXPERIMENTS:

A stock solution of Cr(III) was prepared by dissolving 1.52 g of 99.9% chrome green in distilled water and solution made up to 1000 ml. This solution is diluted as required to obtain the standard solutions containing 50-500 mg/l of Cr(III). 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 were carried out in 250 ml conical flasks by shaking a pre-weighed amount of the fly ash with 50 ml of the aqueous Cr(III) solutions for a predetermined period.

Adsorption isotherm study is carried out with different initial Cr(III) concentrations ranging from 50 to 500 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 30ºC with an initial Cr(III) concentration of 100 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 2 to 16 g/l with the initial Cr(III) concentration of 100 mg/l at 30ºC. The concentration of free Cr(III) ions in the effluent is determined spectrophotometrically(Elico® Double Beam UV-Vis Spectrophotometer SL 244) by developing a standard curve with different concentration of chrome green. The absorbance of the chrome green solution is read at 520 nm.

Desorption studies are conducted by batch experiments. The 15 g of saturated fly ash obtained from adsorption studies is first treated with 150 ml of 1 N NaOH solution for 1 day. After the NaOH treatment, fly ash are separated from the solution and washed with distilled water. Washed adsorbent is further regenerated with 150 ml of 1 N HCl. The fly ash washed with distilled water and dried at room temperature (~30 ºC) for 6 h. Desorption experiments are carried out with different initial concentrations of Cr(III) ranging 50 to 500 mg/l.


Figure 1: Chrome Green Powder and Solution

RESULTS AND DISCUSSION

1. CHARACTERIZATION OF FLY ASH AS ADSORBENT:

The SEM analysis also shows that after activation of fly ash there are many numerous pores developed on their surface, which indicates larger surface area is available for adsorption. Thus there is a significant increase in adsorption capacity of fly ash.

SEM MICROPHOTOGRAPHS OF FLY ASH UNDER DIFFERENT MAGNIFICATION
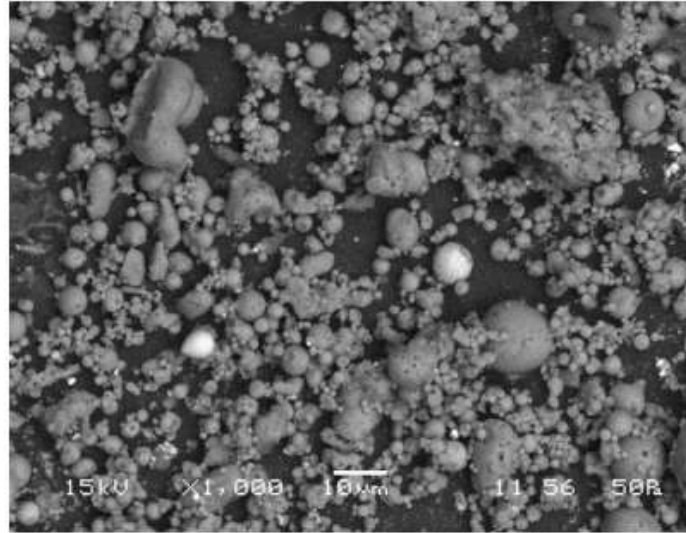
Magnification at 1000x
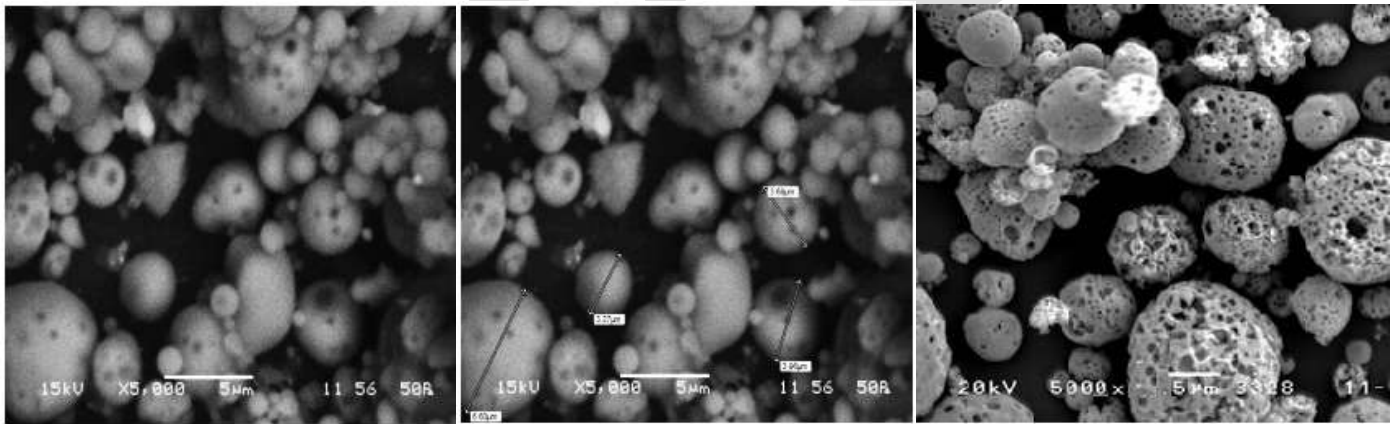
Before activation   **Before   activation**   **After activation**
Magnification at 5000x

Figure 2: SEM Analysis for Normal and Activated Fly ash with 1000x and 5000x Magnification

The particle size of fly ash collected from ACC cements plant was found to be Minimum-3.44 µm Mean-8.080 µm Max-18.585 µm from Figure 3. The size, density, type of reinforcing particles and its distribution have a pronounced effect on the properties of particulate composite.
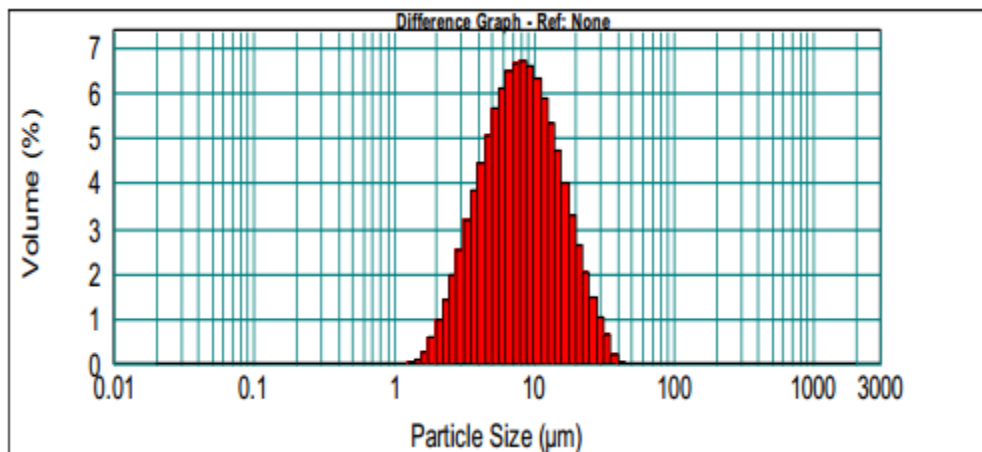
PARTICLE SIZE DISTRIBUTION

Figure 3: Particle Distribution Analysis using Mastersizer 2000

BATCH EXPERIMENTS:

In the present study, fly ash is used as an adsorbent for Cr(III) removal from aqueous solutions. Fly ash is activated by giving heat treatment and with the use of concentrated sulfuric acid (98% w/w). The effect of the activation of adsorbent was studied at 30°C with an initial Cr(III) concentration of 100 mg/l and an adsorbent amount of 10 g/l for 6 hours. There is a significant increase of 12% in the percentage removal of Cr(III) with activated fly ash as shown in Fig 4. Hence, for further batch adsorption studies fly ash with activation is used. The effect of various parameters such as initial pH, contact time, adsorbent amount and initial Cr(III) concentration are studied and discussed in detail in the following sections.
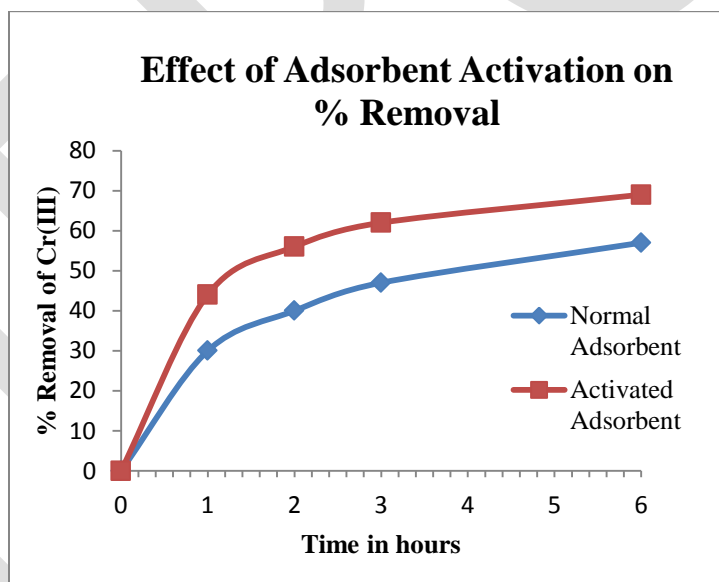

Figure 4: Effect of Adsorbent Activation on Cr(III) removal (C_0=100mg/l, M=10g/l, t_T = 6 h)

EFFECT OF INITIAL PH

The effect of the initial pH of solution on Cr(III) removal is shown in Fig. 5. The effect of pH was studied at 30°C with an initial Cr(III) concentration of 50 mg/l and an adsorbent amount of 10 g/l for 20 hours. Removal efficiency is found increasing with increase in the initial pH and reached 84% at initial pH value of 13. Although insoluble in water, it dissolves in acid to produce hydrated chromium ions, $[Cr(H_2O)_6]^3$ while the surface of adsorbent is positively charged [8]. Chrome green dissolves in concentrated alkali to yield chromite ions CrO^{-2}. The poly-nuclear species at a high Cr(III) concentration and hence the high pH value of 13 results in a higher percentage removal of Cr(III) using fly ash. Since there is no significant increase in the % removal of Cr(III) ions pH=9.0 is chosen to be the optimum value and the experiment is proceeded with it.
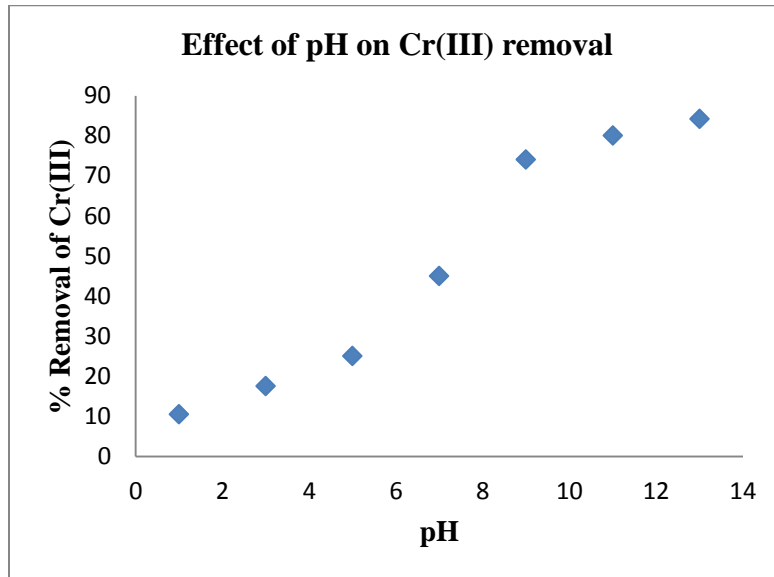
Figure 5: Effect of pH on Cr(III) removal (C_0=50mg/l, M=10g/l, t_T=20 h)

EFFECT OF CONTACT TIME

Fig. 6 shows the percentage removal of Cr(III) for different values of the initial Cr(III) concentration ranging from 50 to 500 mg/l at pH value of 1. It is apparent from Fig. 6 that till 6 h, the percentage removal of Cr(III) from aqueous solution increases rapidly and reaches up to 72% to 31% of the Cr(III) removal for 50 to 500 mg/l of the initial Cr(III) concentration respectively. After that, the percentage removal of chromium (III) increases slowly till 22 h and becomes constant. A further increase in the contact time has a negligible effect on the rate of adsorption of Cr(III). Therefore, the contact time of 20 h could be considered for the adsorption of Cr(III) on fly ash for entire batch studies. The rate of adsorption of Cr(III) 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(III) adsorption as intra particle diffusion becomes predominant and may be due to the slow pore diffusion of the Cr(III) into the bulk of the adsorbent.
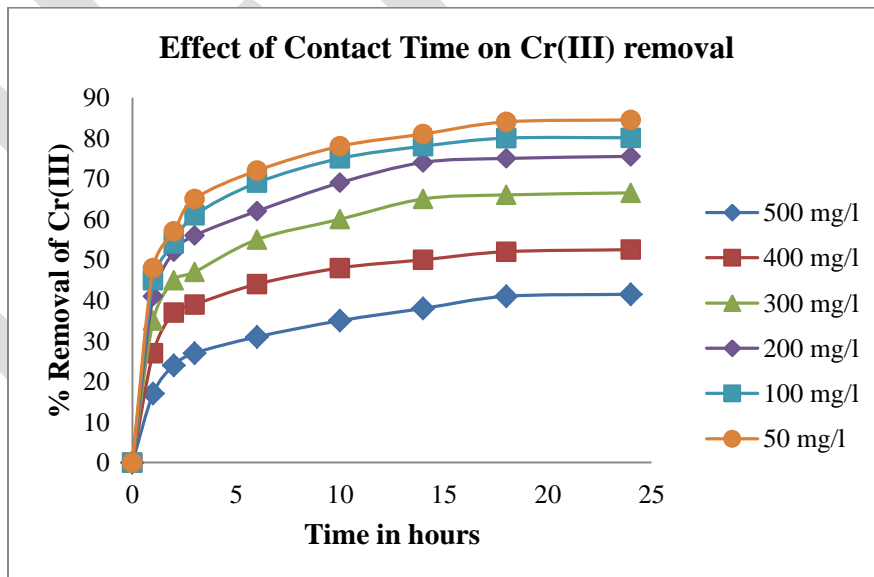

Figure 6: Effect of contact time on Cr(III) removal (pH=9.0, M=10g/l)

EFFECT OF ADSORBENT AMOUNT:

The effect of the fly ash amount on the adsorption of Cr(III) is shown in Fig. 7. The percentage removal increases from 76.4% to 83% by increasing the adsorbent amount from 2 to 16 g/l respectively and the adsorption capacity also dropped from 18.8 to 3.5 mg/g. The increase in Cr(III) removal with an increase in the fly ash amount is due to the increase in surface area and adsorption sites available for adsorption of Cr(III). However, the decrease in adsorption capacity by increasing the adsorbent amount is basically due to the sites remaining unsaturated during the adsorption process.
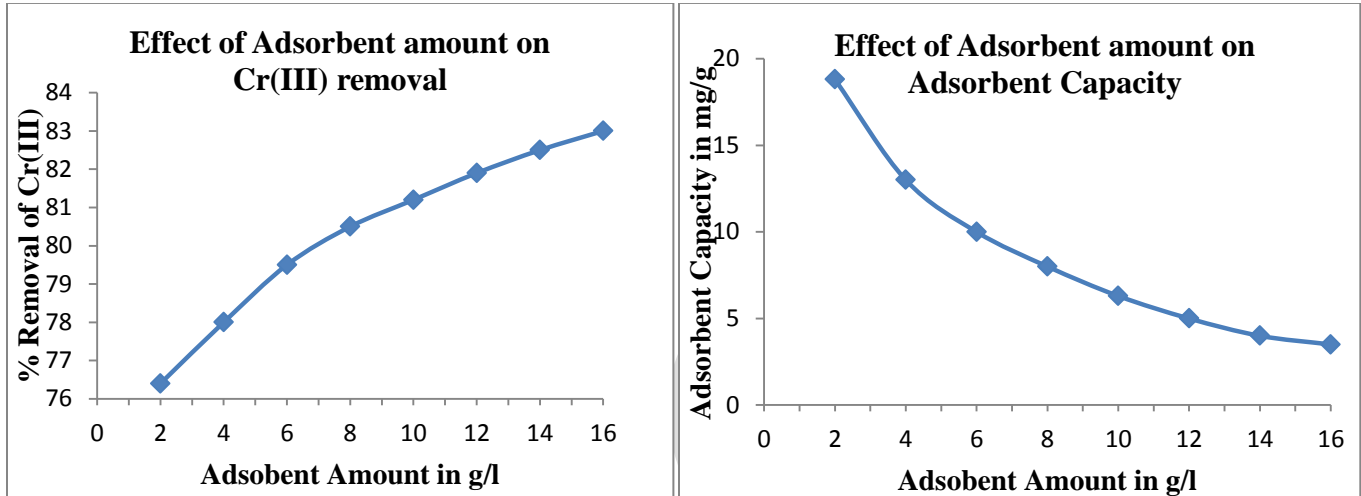

Figure 7: Effect of Adsorbent amount on Cr(III) removal and Adsorbent activity (C_0=100mg/l, pH=9.0, M=10g/l, t_T=20 h)

EFFECT OF INITIAL CHROMIUM(III) CONCENTRATION:

Fig. 8 predicts the effect of initial Cr(III) concentration on the percentage removal of Cr(III) and the adsorption capacity of fly ash. The percentage removal decreases from 84.5% to 41.5% and the adsorption capacity increases from 4.3 to 41.8 mg/g with increase in the initial Cr(III) concentration from 50 to 500 mg/l, respectively. The decrease in the percentage removal of Cr(III) 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(III) concentration. The increase in the adsorption capacity with increase in the initial Cr(III) concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration.
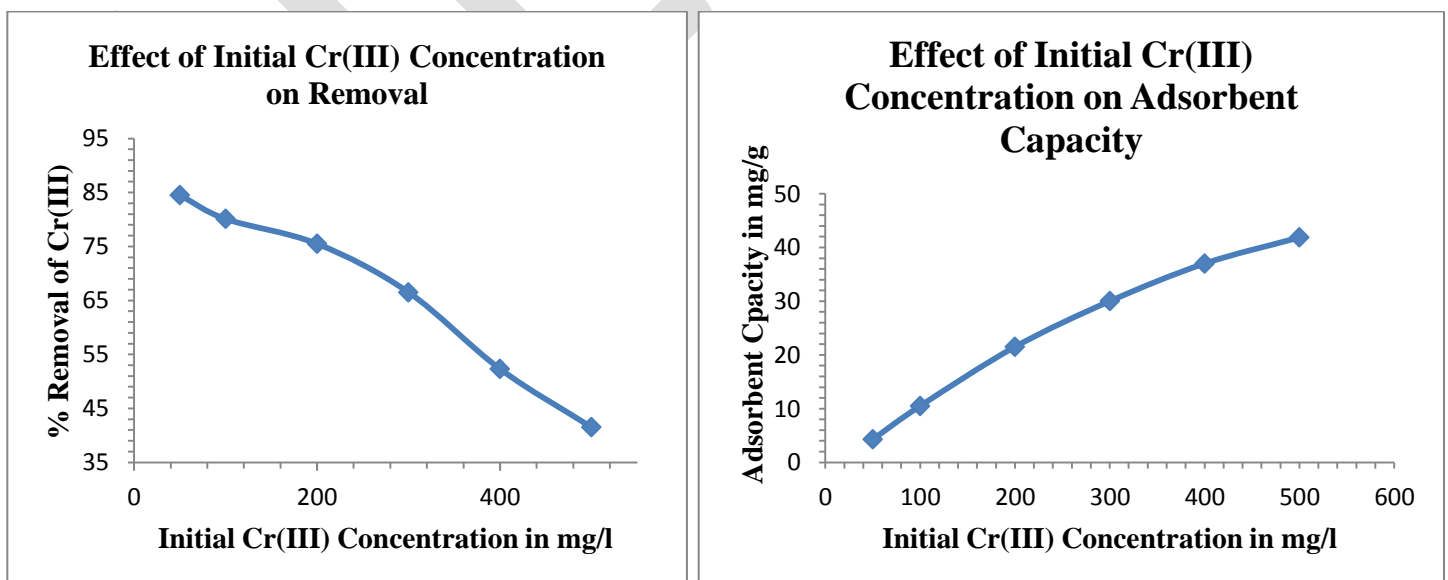

Figure 8: Effect of Initial Cr(III) concentration on Cr(III) removal and Adsorbent capacity (C_0=100mg/l, M=10g/l, t_T=20 h)

ADSORPTION ISOTHERMS

The analysis and design of adsorption process requires equilibrium data for better understanding of the process. In the present investigation, the equilibrium data has been analyzed for various adsorbents using Freundlich and Langmuir isotherms.

1. FREUNDLICH ADSORPTION ISOTHERM

The expression for the Freundlich adsorption isotherm[9] is given below

$$q_e = k_f C_e^{1/n}$$

Where, k_f and n are Freundlich constants. The above equation can be linearized in to a logarithmic form to determine the Freundlich constants.
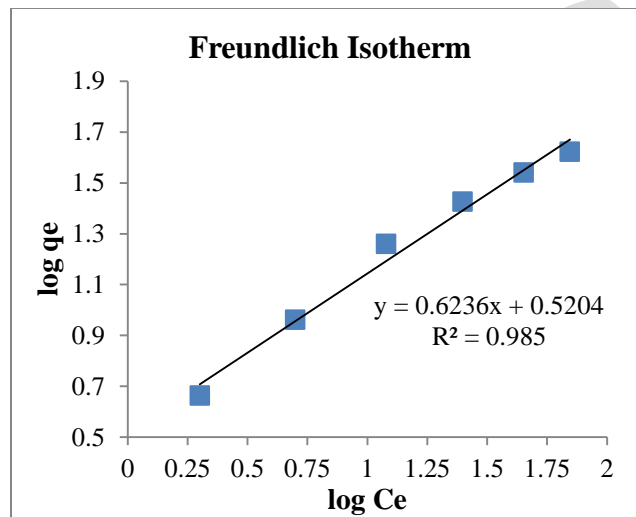

Freundlich Isotherm

y = 0.6236x + 0.5204
R² = 0.985

Figure 9: : Freundlich isotherm plot for adsorption of Cr(III) (C_0=50-500mg/l, M=10g/l, t_T=20 h)

From the values of k_f and 1/n, it is found that the isotherm is linear. The k_f parameter is a measure of adsorption capacity, which gets increased with increase in the efficiency of the adsorbent.

2. LANGMUIR ADSORPTION ISOTHERM

The expression for the Langmuir adsorption isotherm[10] is given below

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$$

Where, q_e is the adsorption capacity (mg/g) at equilibrium, C_e is the concentration of the solution at equilibrium, q_{max} represents the maximum adsorption capacity and b is the Langmuir constant.
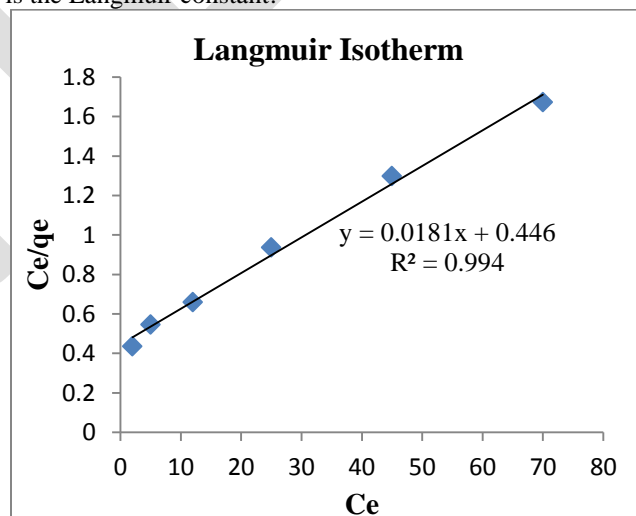

Langmuir Isotherm

y = 0.0181x + 0.446
R² = 0.994

Figure 10: Langmuir isotherm plot for adsorption of Cr(III) (C_0=50-500mg/l, M=10g/l, t_T=20 h)

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant or separation factor or equilibrium parameter K_L which is defined as

$$K_L = \frac{1}{1 + bC_0}$$

Where, b is the Langmuir constant and C_0 is the initial concentration of the salt solution. The value K_L indicates the type of isotherm. To be reversible (K_L=0), favorable (0< K_L<1), linear (K_L=1) or unfavorable (K_L>1). In our kinetic studies, the value of K_L was found to be less than 1 and greater than 0, indicating favorable adsorption. The constants and R^2 value are listed in the Table 1 below.

Table 1

Isotherm constants for absorption of Cr(III) on activated fly ash

Langmuir Isotherm			Freundlich Isotherm		
Constants		Correlation Coefficient (R^2)	Constants		Correlation Coefficient (R^2)
q_{max} (mg/g)	b (l/mg)		k_f (mg/g)	n	
55.24	0.0405	0.994	3.11	1.562	0.9815

ADSORPTION KINETICS

In order to understand the kinetics of removal of Cr(III) using fly ash as an adsorbent, pseudo first-order and second-order kinetics are tested with the experimental data.

1. FIRST-ORDER KINETICS

The non-linear form of the pseudo first-order equation is given by

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

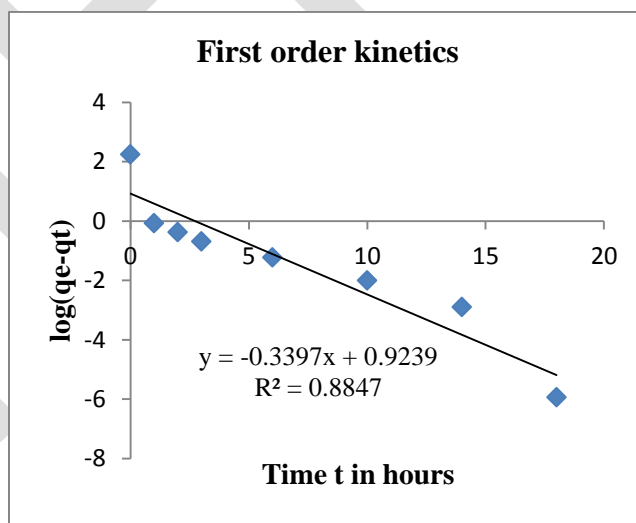$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303}$$

First order kinetics

y = -0.3397x + 0.9239
R² = 0.8847

Figure 11: First order kinetics plot for adsorption of Cr(III) (C_0=100mg/l, M=10g/l, t_T=20 h)

where, q_e and q_t are the amounts of Cr(III) 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(III) concentration ranges of 50-500 mg/l are calculated.

2. SECOND-ORDER KINETICS

The second-order kinetic rate equation is given by

$$\frac{d\boldsymbol{q_t}}{\boldsymbol{dt}} = k_{ad}(q_e - q_t)^2$$

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$$
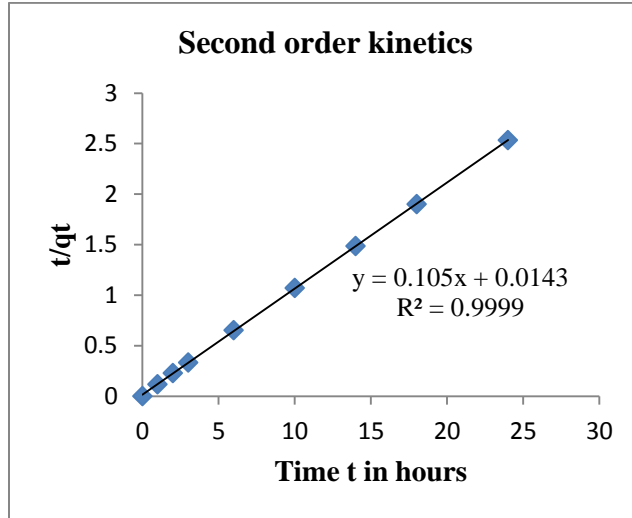
Second order kinetics

$$y = 0.105x + 0.0143$$
$$R^2 = 0.9999$$

Figure 12: Second order kinetics plot for adsorption of Cr(III) (C$_0$=100mg/l, M=10g/l, t$_T$=20 h)

k_2 is the second order rate constant, g/(mg) (min). The application of the second-order kinetics by plotting t/qt vs. t, yielded the second-order rate constant, k_2, estimated equilibrium capacity qe, and the coefficient of determination (R^2) for the initial Cr(III) concentration ranging from 50 - 500 mg/l.

3. FRACTIONAL POWER MODEL

The adsorption kinetics can also be described by the power fraction equation. The linear fractional power equation is given as
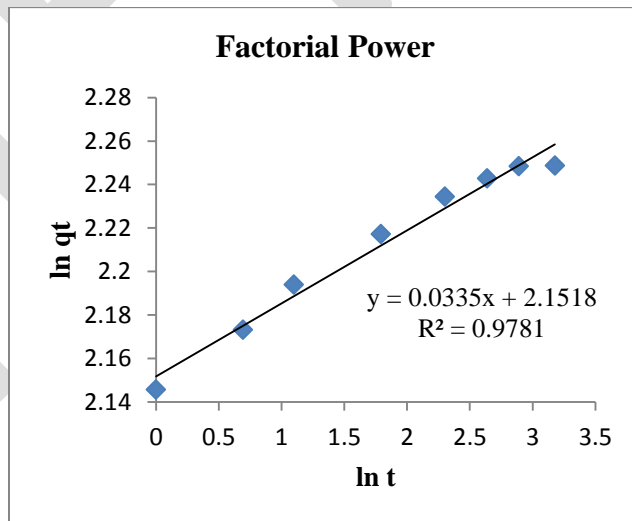
$$\ln qt = \ln K + \gamma \ln t$$

Factorial Power

$$y = 0.0335x + 2.1518$$
$$R^2 = 0.9781$$

Figure 13: Factorial Power Model plot for adsorption of Cr(III) (C$_0$=100mg/l, M=10g/l, t$_T$=20 h)

The plot ln qt vs ln t should give linear relationship from which γ and K can be calculated from the slope and intercept of the plot respectively.

4. THE ELOVICH EQUATION

The linear Elovich equation is given as follows

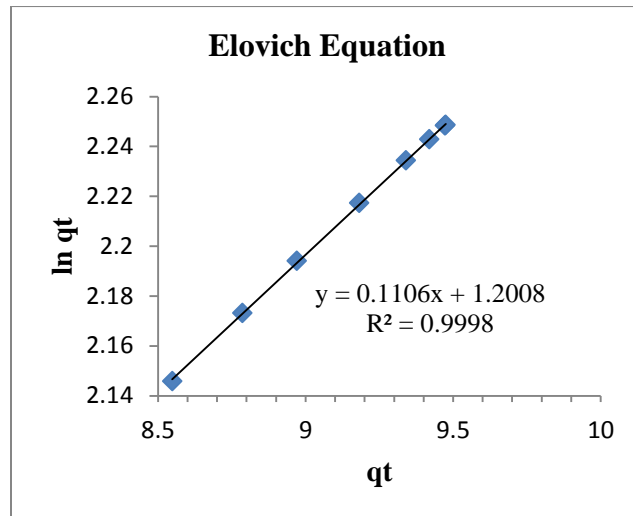$$qt = \frac{1}{\beta} ln\alpha\beta + \frac{1}{\beta}\ln t$$

Elovich Equation

$$y = 0.1106x + 1.2008$$
$$R^2 = 0.9998$$

Figure 14: Elovich Equation plot for adsorption of Cr(III) (C_0=100mg/l, M=10g/l, t_T=20 h)

Where α is the initial adsorption rate (mg/g). Parameter β is related to the extent of surface coverage and the activation energy for chemical adsorption (g/mg). The constants and R^2 value are listed in the Table 2 below.

Table 2

Kinetic constants for absorption of Cr(III) on activated fly ash

First order kinetics			Second order kinetics			Factorial Power			Elovich Equation		
Constants		Correlation Coefficient R^2	Constants		Correlation Coefficient R^2	Constants		Correlation Coefficient R^2	Constants		Correlation Coefficient R^2
q_e mg/g	k_{ad} 1/min		q_e mg/g	k_2 1/min		K mg/g	γ		α mg/g	β (g/mg)	
8.39	0.7823	0.8847	9.514	0.7726	0.9999	8.6	0.0335	0.9781	9.041	0.1263	0.9998

CONCLUSION

The following conclusions could be drawn from present study.
1. The maximum adsorption of Cr(III) took place in the initial pH value of 9.0.
2. The equilibrium time for the adsorption of Cr(III) on the activated fly ash was found to be 20 h.
3. The percentage removal of Cr(III) increases with increase in the adsorbent amount.
4. Adsorption of Cr(III) on the fly ash yielded maximum adsorption capacity of 55.24 mg/g.
5. Adsorption of Cr(III) obeys second order rate equation.

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