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Experimental, kinetic, equilibrium and regeneration studies for adsorption of Cr(VI) from aqueous solutions using low cost adsorbent (activated flyash)

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ABSTRACT

In the present study, activated flyash — a low-cost adsorbent, is used as for Cr(VI) removal from aqueous solutions. Flyash is activated by giving heat treatment and with the use of concentrated sulfuric acid (98% w/w). Batch adsorption experiments are carried out to investigate the effect of influencing process parameters such as initial pH, change in pH during adsorption, contact time, adsorbent amount, and initial Cr(VI) concentration. The maximum adsorption of Cr(VI) on activated flyash is found at an initial pH value of 1. The value of pH increases with increase in adsorption of Cr(VI). The equilibrium data for adsorption of Cr(VI) on activated flyash is tested with different adsorption isotherm models such as Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Tempkin, Dubinin–Radushkevich and generalized isotherm models. The Koble–Corrigon isotherm model is found to be the most suitable one for Cr(VI) adsorption using activated flyash. The maximum adsorption capacity obtained is 21.9 mg g^{-1} at a pH value of 1. The adsorption process follows the second order kinetics and the corresponding rate constants are obtained at different initial Cr(VI) concentrations. Desorption of Cr(VI) from activated flyash using acid and base treatment shows a higher desorption efficiency by more than 85%. A feasible methodic solution for the disposal of contaminant (acid and base solutions) containing high concentration of Cr(VI) obtained during the desorption process is proposed.

Keywords: Adsorption; Cr(VI); Activated fly ash; Heavy metal removal; Batch studies; Water pollution; Adsorption isotherm; Kinetics; Regeneration

1. Introduction

Hexavalent chromium [Cr(VI)] is present in many compounds and has a variety of industrial applications. 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 [1–4]. Concentration of Cr(VI) present in industrial effluent streams are in the range of 50–200 mg L^{-1} [1,5]. Cr(VI) is highly mobile and is considered severely toxic, carcinogenic and mutagenic to living organisms [6]. 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 chromosomic aberrations [7]. Hence, Cr(VI) is more hazardous than other heavy metals. According to the US Environmental Protection Agency and Indian standards, the permissible limit of Cr(VI) for industrial effluents to be discharged to surface water is 0.1–0.5 mg L^{-1} [8]. Consequently, the

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removal of Cr(VI) from industrial wastewater has become a research topic of great interest [9].

There are various treatment methods available to remove Cr(VI) from wastewater such as chemical precipitation [10], flocculation [11], ion exchange [12], membrane separation [13], ultrafiltration [14], solvent extraction [15], reverse osmosis [15], and electrodialysis [16]. These methods are expensive and are unaffordable for large scale treatment of wastewater that is rich in Cr(VI). Adsorption, using activated carbon as an adsorbent, is an effective method for the treatment of industrial effluents contaminated with Cr(VI), and quite popular as compared to other methods [17,18]. The cost associated with the commercial activated carbon is high which makes the adsorption process cost intensive. This has led to the search for new strategies for developing low-cost materials with a good capacity for Cr(VI) removal [19,20]. Hence, there is a need for low cost adsorbents available naturally in abundance which can be used for the removal of Cr(VI) from wastewater streams [3].

In the present study, flyash is activated with heat and concentrated sulfuric acid (98% w/w) for using as an adsorbent to remove Cr(VI) from aqueous solutions. The equilibrium data and kinetic data are tested with various isotherm models and kinetic models. The regeneration efficiency of flyash is evaluated for the removal of Cr(VI).

2. Materials and methods

2.1. Adsorbent preparation

Flyash is one of the residues generated in the combustion of coal which cannot be released into the atmosphere. The waste (flyash) management in power plants is a major environmental issue faced by the country. The flyash used in this study is collected from National Thermal Power Corporation (NTPC), Tanda. The flyash is obtained by the combustion of lignite coal and it has following chemical composition (wt%): SiO_2 – 30%, Al_2O_3 – 25%, Fe_2O_3 – 10%, CaO – 30%, loss of ignition (LOI) – 5%. 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

Batch experiments are conducted for the studies on the removal of Cr(VI) from aqueous solutions. The effect of various influencing parameters, such as initial solution pH, change in pH during adsorption, contact time, adsorbent amount and initial Cr(VI) concentration, are studied.

All the chemicals used are of analytical grade. 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^{-1} of Cr(VI). The pH of solution 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 conducted in 100 mL borosil conical flasks by shaking a pre-weighed amount of the activated flyash with 25 mL of the aqueous Cr(VI) solutions for a predetermined period (found out from the kinetic studies) at 30°C in water bath-cum-mechanical shaker. Afterwards, the activated flyash is separated from the resultant solution using a filter paper as reported by several studies [2,21]. Adsorption isotherm study is conducted with different initial Cr(VI) concentrations ranging from 20 to 400 mg L^{-1} while maintaining the activated flyash amount of 10 g L^{-1}. The effect of pH is studied at 30°C with an initial Cr(VI) concentration of 100 mg L^{-1}. The variation in the solution pH during adsorption of Cr(VI) is also measured with change in contact time and initial Cr(VI) concentration. The effect of the contact time is studied at 30°C with an initial Cr(VI) concentration ranging from 100 to 400 mg L^{-1} and an adsorbent amount of 10 g L^{-1}. The effect of the adsorbent amount is studied by varying it in the range of 4–24 g L^{-1} with the initial Cr(VI) concentration of 100 mg L^{-1} at 30°C. The batch experiments are conducted in replicates. The values obtained are more or less same after the repetition of experiments so the experiments are carried out twice and the average values are reported.

The quantity of Cr(VI) adsorbed by the activated flyash and the percentage removal of Cr(VI) are calculated using the following Eqs. (1) and (2), respectively.

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$\text{\% Removal of Cr(VI)} = \frac{C_i - C_0}{C_i} \times 100 \tag{2}$$

The concentration of Cr(VI) ions in the aqueous solutions is determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as a complexing agent [22]. In this study, the experiments are conducted for the removal of Cr(VI) from the aqueous solutions which are prepared by dissolving the potassium dichromate into distilled water. So it mainly comprises of Cr(VI). Di-phenyl carbazide method is used for the analysis of Cr(VI) in the solution which only measures the quantity of Cr(VI). This method is usually used and reported in several studies for determination of Cr(VI) at low pH [2,23,24]. Though in principle, there is a chance of reduction of Cr(VI) into Cr(III) ions at low pH. The earlier studies reported that the quantity of total Cr and Cr(VI) at low pH is more or less same [1], which indicates that the presence of Cr(III) in the resultant solution is unimportant. So the quantity of Cr(III) is not determined in this study. The absorbance of the purple-violet colored solution is measured at 540 nm after 20 min. The analytical study of Cr(VI) is conducted in triplicates and the average values are taken for the further analysis of data. The standard deviation is obtained as 0.00453 for the calibration curve which is indicative of a good fit of the data and within the error limits of ±1.64%. This ensured high confidence limits of the experimental measurements.

Desorption studies are carried out by performing batch experiments. The procedure used for the desorption of Cr(VI) from saturated activated flyash is taken from the literature [25]. The 15 g of saturated activated flyash obtained from adsorption studies (effect of initial concentration) is initially treated with 150 mL of 1 N NaOH solution for 1 day. Afterwards, activated flyash are separated from the base solution and washed with distilled water. Washed activated flyash is further treated with 150 mL of 1 N HCl. The activated flyash are washed with distilled water and dried at room temperature (30°C) for 6 h. The performance of regenerated activated flyash is evaluated by conducting adsorption experiments with different initial concentrations of Cr(VI) ranging from 20 to 400 mg L^{-1} while maintaining the activated flyash amount of 10 g L^{-1} and an initial pH value of 1 at 30°C.

3. Results and discussion

In this study, activated fly ash is used for Cr(VI) removal from aqueous solutions. The effect of influencing parameters such as initial pH, change in pH during adsorption, contact time, activated flyash amount and initial Cr(VI) concentration are investigated and discussed in detail in the following sections.

3.1. Effect of initial pH

The initial pH of solution is a significant parameter in the adsorption of Cr(VI) [6]. The effect of initial pH of the solution on the removal of Cr(VI) using activated flyash is obtained in the initial pH range of 1–13 and is shown in Fig. 1. The percentage removal of Cr(VI) is decreased from 81.0 to 2.0% with increasing the initial solution pH from 1 to 13. At a lower solution pH value of 1, the dominant forms of Cr(VI) exists in the solution is $HCrO_4^-$ and the surface of activated flyash is charged positively [3,26]. Hence the low value of solution pH (pH = 1) results in a higher percentage removal of Cr(VI) using activated flyash. For the pH values more than 1, the percentage removal decreases with increasing solution pH. The lime (crystalline CaO) content in flyash is significant which influence Cr(VI) removal using flyash [27].

The equilibrium pH is found increasing from 1.09 to 1.38 with an increase in the initial Cr(VI) concentration ranging from 40 to 400 mg L^{-1} with an interaction time of 22 h. This signifies that the change in the final value of solution pH is insignificant, which confirms the higher acidic medium in the final solution of Cr(VI). The change in solution pH is measured with time at an initial Cr(VI) concentration of 400 mg L^{-1} by keeping the activated flyash quantity constant (10 g L^{-1}) and is shown in Fig. 2. It is found that the value of pH increases from 1.1 to 1.39 with an increase in time of adsorption from 0.5 to 24 h (Fig. 2). It is observed that with an increase in the adsorption of Cr(VI) on activated flyash, the pH of solution is found increasing.

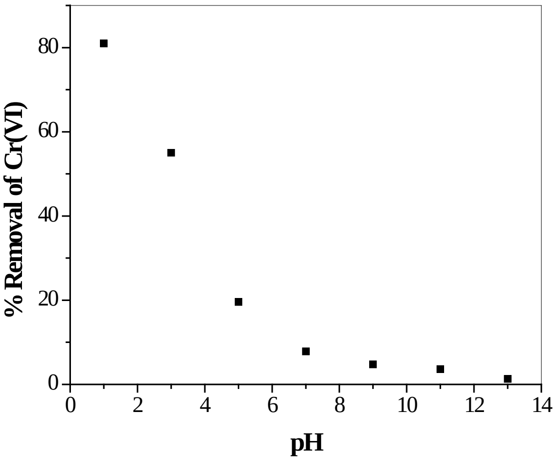

Fig. 1. Effect of pH on the adsorption of Cr(VI) using activated flyash (T = 30°C, W = 0.25 g, C_0 = 100 mg L^{-1}, t = 22 h and initial pH = 1).

3.2. Effect of contact time

The percentage removal of Cr(VI) with time for different values of the initial Cr(VI) concentration ranging from 100 to 400 mg L^{-1} at pH value of 1 is shown in Fig. 3. The percentage removal of Cr(VI) from aqueous solution increases rapidly up to 6 h and reaches up to 69% to 43% of

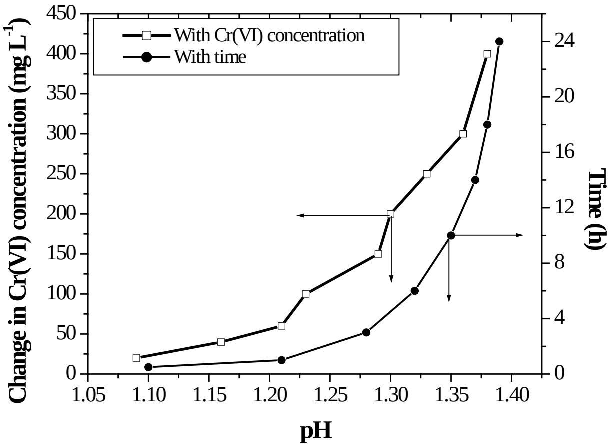

Fig. 2. Change in pH of solution with change in time of adsorption and Cr(VI) concentration (T = 30°C, W = 0.25 g, and initial pH = 1).

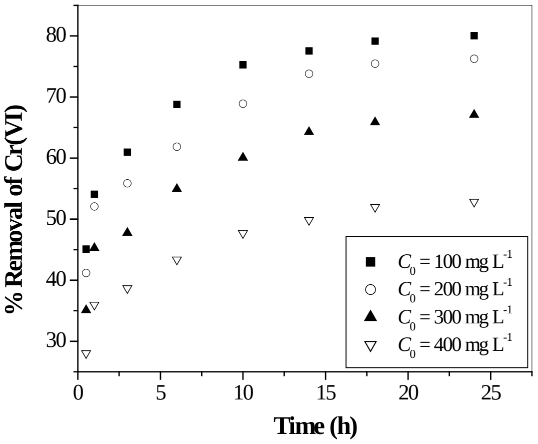

Fig. 3. Effect of contact time on the adsorption of Cr(VI) using activated flyash (T = 30°C, W = 0.25 g, and initial pH = 1).

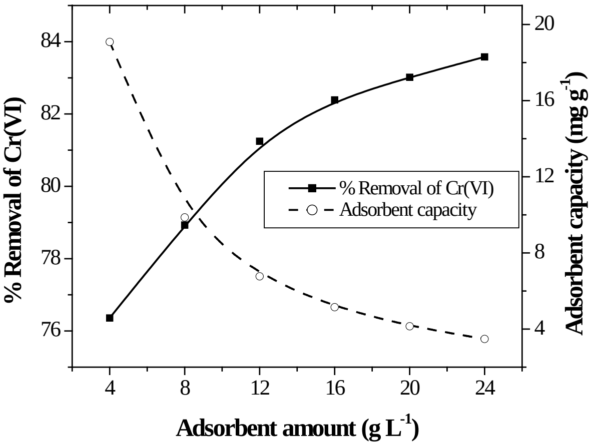

Fig. 4. Effect of amount of activated flyash on the adsorption of Cr(VI) (T = 30°C, C_0 = 100 mg L^{-1}, initial pH = 1 and t = 22 h).

the Cr(VI) removal for 100–400 mg L^{-1} of the intial Cr(VI) concentration respectively (Fig. 3). This indicates that the rate of adsorption of Cr(VI) is faster in the early time of adsorption. The rate of adsorption of Cr(VI) is depends on the nature of the adsorbent and the available adsorption sites. The mechanism of Cr(VI) transfer from aqueous solution to the activated flyash surface is proposed based on the results obtained in the present study. The concentration difference between the film and the available adsorption sites is higher in the initial time of adsorption of Cr(VI) which causes the faster removal of Cr(VI). After 6 h, the percentage removal of Cr(VI) increases slowly and becomes constant up to 22 h. A further increase in the contact time has a negligible effect on the percentage removal of Cr(VI). Therefore, 22 h could be considered as the equilibrium time for the adsorption of Cr(VI) using activated flyash for entire batch experiments. 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 intra-particle diffusion mechanism becomes predominant. This results the slow diffusion of Cr(VI) ions from pore liquid present in the pore mouth to the internal adsorbent sites. Hence, the rate of adsorption decreases in the later stages of adsorption.

3.3. *Effect of adsorbent amount*

The effect of the flyash amount on the adsorption of Cr(VI) is shown in Fig. 4. This study is important to get the trade-off between the adsorbent capacity and the percentage removal of Cr(VI) which results in an optimum amount of activated flyash. The increase in the adsorbent amount from 4 to 24 g L^{-1} increases the percentage removal of Cr(VI) from 76.3% to 83.6% respectively. This may be due to the increase in surface area and adsorption sites available for the adsorption with increase in activated flyash amount. Adsorption capacity is defined as the mass of Cr(VI) adsorbed per unit mass of adsorbent. The adsorption capacity dropped from 19.1 mg g^{-1} to 3.5 mg g^{-1} by increasing the adsorbent amount from 4 to 26 g L^{-1} respectively. If the activated flyash amount is increased by keeping the Cr(VI) concentration constant, the amount of Cr(VI) adsorbed per unit mass of activated flyash decreases due to the availability of less number of Cr(VI) ions. This results in unsaturated adsorbent sites during adsorption process due to which adsorption capacity decreases. As the percentage removal of Cr(VI) and the amount of Cr(VI) adsorbent show an increasing trend, hence with the use of adsorption amount of Cr(VI), the optimum amount of adsorbent used cannot be calculated. So in this study the adsorption capacity of activated flyash is used for the discussion of results obtained. Earlier studies have also reported in terms of the adsorption capacity [3,28]. For the activated flyash amount of 8.9 g L^{-1}, the optimum values of Cr(VI) removal and the adsorption capacity are found to be 79.0% and 9.7 mg g^{-1}, respectively.

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

The initial concentration of Cr(VI) has a significant effect on Cr(VI) adsorption from aqueous solutions. Fig. 5 predicts the effect of initial Cr(VI) concentration ranging from 20 to 400 mg L^{-1} on the percentage removal of Cr(VI) and the adsorption capacity of activated flyash while maintaining the adsorbent amount of 10 g L^{-1} at an initial pH value of 1. The percentage removal of Cr(VI) decreases from 80.3% to 52.5% and the adsorption capacity increases from 1.57 to 21 mg/g with increase in the initial Cr(VI) concentration from 20 to 400 mg L^{-1}, 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 satu-

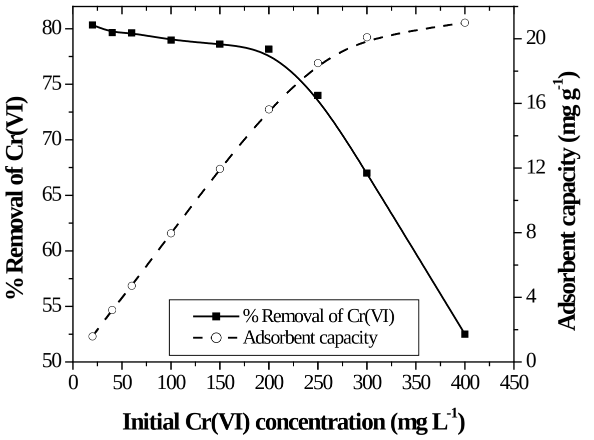

Fig. 5. Effect of initial Cr(VI) concentration on adsorption of Cr(VI) using activated flyash (T = 30°C, W = 0.25 g, initial pH = 1, and t = 22 h).

rated 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 rate of adsorption and the utilization of all the active sites available for the adsorption of Cr(VI) at higher concentration. For an initial Cr(VI) concentration of 234 mg L^{-1}, the optimum values of Cr(VI) removal and the adsorption capacity are found to be 76.0% and 17.9 mg g^{-1}, respectively.

3.5. Adsorption mechanism

While comparing with other expensive and low-cost adsorbents, the results of this study indicates that the activated flyash shows a better adsorption capacity in almost all cases (S. Nos. 7–21 in Table 1) except for few adsorbents (S. Nos. 1–5 in Table 1). This signifies that the activated flyash prove to be a cost effective adsorbent that can be used for the removal of Cr(VI) from aqueous solutions.

The acid-treated adsorbents are more suitable for adsorption of Cr(VI) [38]. Commonly acidic oxides are developed on the surface of acid treated adsorbents (activated flyash). The ionic state of the functional group present on the activated flyash surface depends on the pH_{zpc} (zero point of charge) value of activated flyash. In this study, the pH_{zpc} value of activated flyash is obtained as 6.4. The value of the pH_{zpc} of activated flyash is much higher than the value of solution pH, hence the surface of adsorbent is positively charged [1,9,40].

The stable form of Cr(VI) is $HCrO_4^-$ at lower solution pH. There is an electrostatic attraction between positively charged groups of adsorbent surface and $HCrO_4^-$ ions which results in increase in Cr(VI) adsorption. In addition,

Table 1
Maximum adsorbent capacity of various commercial and low cost adsorbents

S. No.	Adsorbent	Maximum adsorbent capacity, q_m (mg/g)	Optimum pH	Reference
1	Activated neem leaves	62.97	2.0	[3]
2	Activated carbon (Filtrasorb-400)	57.7	—	[29]
3	Sawdust	41.52	1.0	[6]
4	Activated tamarind seeds	29.7	2.0	[4]
5	Coconut husk fiber	29	2.05	[30]
6	Activated flyash	21.9	1.0	Present study
7	Pine needles	21.50	2.0	[31]
8	Coconut shell based activated carbon	20	2.5	[32]
9	Sugar beet pulp	17.2	2.0	[33]
10	Palm pressed-fibers	15.0	2.0	[30]
11	Maize cob	13.8	1.5	[33]
12	Sugar cane bagasse	13.4	2.0	[33]
13	Almond	10	2.0	[31]
14	Maple saw dust	8.2	4.0	[34]
15	Cactus	7.08	2.0	[31]
16	Coal	6.78	2.0	[31]
17	Biomass residual slurry	5.87	2.0	[26]
18	Distillery sludge	5.7	2.5	[35]
19	Waste tea	1.55	—	[36]
20	Fe(III)/Cr(III) hydroxide	1.43	5.7	[37]
21	Walnut shell	1.33	—	[38]
22	Soya cake	0.28	1	[39]

another key parameter which dominates the adsorption of Cr(VI) on activated flyash is the available specific surface area. The specific surface area of activated flyash is obtained using BET surface area analyzer (Smart Sorb 92/93, Smart Instruments Co. Pvt. Ltd., Thane) and is obtained as 0.5 $m^2\ g^{-1}$. This value of specific surface area is comparable with other low cost adsorbents such as tea factory waste (0.39 $m^2\ g^{-1}$) [2], sawdust (0.86 $m^2\ g^{-1}$) [6], modified coir pith (1.9 $m^2\ g^{-1}$) [41], and Aspergillus niger (1.36 $m^2\ g^{-1}$) [42].

3.6. Adsorption isotherm

In this study, as the adsorbent developed is new, it is essential to get a proper equilibrium relationship between the solid and liquid phase concentrations of Cr(VI). It is desirable to check the obtained experimental equilibrium data for Cr(VI) removal using activated flyash with variety of isotherm models available in the literature so as to identify which one is the best matched out of all the reported isotherm models. In this work, Langmuir [43], Freundlich [44], Redlich–Peterson [45], Koble–Corrigan [46], Tempkin [47], Dubinin–Radushkevich [48], and generalized isotherm [49] models are tested with the experimentally obtained equilibrium data.

3.6.1. Langumir isotherm model

Langmuir isotherm has been widely used for the adsorption of heavy metals, dyes, organic pollutants, etc. [6,50]. The linear form of isotherm equation is represented by Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \tag{3}$$

A plot of (C_e/q_e) vs. C_e should yield a straight line and the slope and the intercept of this line then yield the values of constants Q_m and b respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by Eq. (4):

$$R_L = \frac{1}{1+bC_0} \tag{4}$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

The Langmuir constant Q_m, which is a measure of the monolayer adsorption capacity of activated flyash, is obtained as 42.3 mg g^{-1} in the equilibrium pH value in the range of 1.1–1.38. This obtained value of Q_m for activated flyash (42.3 mg/g) is conflicting with the experimental results (21.9 mg/g). This may be due to the fact that the equilibrium data for activated flyash is not fitting well to the Langmuir isotherm model ($R^2 = 0.853$). Equilibrium data for activated flyash are not fitting well to Langmuir isotherm model because experimental data do not attain the isotherm "plateau" as is required when applying this equation. This does not confirms the monolayer adsorption of Cr(VI) onto the activated flyash. The Langmuir constant, b, which denotes adsorption energy, is obtained as 0.011 L mg^{-1} (Table 2). The value of R_L remained between 0.19 and 0.82 ($0 < R_L < 1$) consistent with the requirement for a favorable adsorption process. As the R^2 value obtained is not reasonably high (0.853), in order to find out a better fit isotherms, the experimental data are tested with other six isotherms available in the literature.

3.6.2. Freundlich isotherm

For adsorption of solute from solution, the linear form of Freundlich isotherm is expressed by Eq. (5):

$$\log q_e = \log K_f + n_F \log C_e \tag{5}$$

The Freundlich constants, K_f and n can be calculated from the plot of log q_e vs. log C_e. The values of K_f and n are obtained as 0.5604 and 0.8402, respectively, and also listed in Table 2. It is obtained that the coefficient of determination estimated from the Freundlich isotherm model for activated flyash is 0.968 which is higher than that for Langmuir isotherm model as given in Table 2. The obtained results show that the equilibrium data is fitted well with the Freundlich isotherm model.

3.6.3. Redlich–Peterson isotherm

Redlich–Peterson isotherm has three parameters and is an improvement over the Langmuir and Freundlich isotherms. It can be described by Eq. (6):

$$q_e = \frac{AC_e}{1+BC_e^g} \tag{6}$$

where A, B and g ($0 < g < 1$) are the Redlich–Peterson constants. Redlich–Peterson isotherm constants are not feasible to obtain using graphical method because of three unknown parameters which makes it highly non-linear. So three isotherm constants are obtained by a method of non-linear least squares using professional graphics software package ORIGIN (version 6) and are listed in Table 2. The obtained coefficient of determination for Redlich–Peterson isotherm model is 0.953 which indicates a good applicability of this model for the adsorption of Cr(VI) using activated flyash. The obtained coefficient of determination for Redlich–Peterson isotherm model is greater than that of Langmuir isotherm model but less than that of Freundlich isotherm model. For activated flyash, g value is 0.483 (between 0–1), which indicates the suitability of Redlich–Peterson isotherm for the obtained data [45].

3.6.4. Koble–Corrigan isotherm

Koble–Corrigan model is another three-parameter empirical model for representing the equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm models and is given by Eq. (7):

$$q_e = \frac{aC_e^n}{1+b_c C_e^n} \tag{7}$$

where a, b_c and n are the Koble–Corrigan constants. The three isotherm constants of Koble–Corrigan model are also evaluated by method of non-linear least squares and using a professional graphics software package ORIGIN (version 6) and are listed in Table 2. The obtained value of coefficient of determination for Koble–Corrigan isotherm model is 0.995 which is greater than the Langmuir isotherm, Freundlich isotherm and Redlich–Peterson isotherm model and also indicates the applicability of Koble–Corrigan isotherm model to describe equilibrium data obtained for the adsorption of Cr(VI) using activated flyash. The comparison between experimental data and model predicted data is shown in Fig. 6.

3.6.5. Tempkin isotherm

The linear form of Tempkin equation is given by Eq. (8):

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{8}$$

where $B_T = (RT)/b_T$. A plot of q_e vs. ln C_e at constant temperature is used to evaluate the Tempkin isotherm constants, A_T and b_T. The calculated values of Tempkin isotherm constants A_T and b_T, are 0.2182 and 387.14 and also listed in Table 2. The R^2 for Tempkin isotherm model is obtained as 0.958 which confirms the better fit of equilibrium data as compared with the Langmuir isotherm (R^2 = 0.85) and Redlich–Peterson isotherm (R^2 = 0.953) models. The obtained value of R^2 for this model is less than the R^2 values obtained for Freundlich isotherm (R^2 = 0.968) and Koble–Corrigon isotherm (R^2 = 0.995) models.

3.6.6. Dubinin–Radushkevich (D–R) isotherm

This isotherm is applied to estimate the mean free energy of adsorption (E). The linear form of D–R isotherm is given by Eq. (9):

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{9}$$

The D–R constant, ε, can be calculated from Eq. (10).

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \tag{10}$$

The D–R isotherm constants, K and Q_m are calculated from the slope and intercept of the plot between ln q_e and ε^2. The obtained values of D–R isotherm constants, Q_m and K, are 12.085 and 8×10^{-6}, respectively. The obtained value of coefficient of determination (R^2 = 0.746) indicates that the Dubinin–Radushkevich isotherm model does not fit well the equilibrium experimental data as compared with the other isotherm models used in this study. The value of Q_m obtained using Dubinin–Radushkevich isotherm model is 12.085 mg g^{-1} for the adsorption of Cr(VI) by activated flyash which is less than the Q_m value obtained using the experimental data (21.9 mg g^{-1}). The adsorption of Cr(VI) on activated flyash can be physical adsorption or chemisorption. In this study, the value of mean free energy of adsorption, E, is obtained as 0.25 kJ mol^{-1} which is close to 1 kJ mol^{-1}.

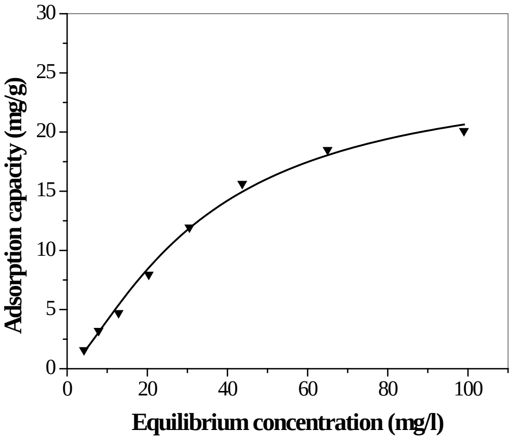

Fig. 6. Plot of equilibrium experimental data and calculated equilibrium data using Koble–Corrigan isotherm model for the adsorption of Cr(VI) onto activated flyash (T = 30°C, W = 0.25 g, t = 22 h, and initial pH = 1).

3.6.7. Generalized isotherm

The linear form of the generalized isotherm is given by Eq. (11):

$$\log\left(\frac{Q_m}{q_e}-1\right) = \log K_G - N_b \log C_e \tag{11}$$

The generalized isotherm constants K_G and N_b are obtained from the slope and intercept of the plot of log $[(Q_m/q_e)^{-1}]$ vs. log C_e and are listed in Table 2. The Q_m value is taken from the Langmuir isotherm model. The obtained value of coefficient of determination for the generalized isotherm model is 0.985 which is higher than the other isotherm models except Koble–Corrigon isotherm model as given in Table 2.

Adsorption isotherm studies show that the Koble–Corrigon isotherm model gives a better relationship for the equilibrium data obtained for Cr(VI) removal using activated flyash (Fig. 6). This equilibrium relationship is needed in the design of a fixed-bed adsorption column. Adsorption isotherm also characterizes the shape of the breakthrough curve and breakthrough time which is

Table 2
Isotherm constants and regression data for various adsorption isotherms for adsorption of Cr(VI) on activated flyash

S. No.	Adsorption isotherms	Isotherm parameters		R^2
1	Langmuir	Q_m	42.3	0.850
		b	0.011	
2	Freundlich	K_F	0.5604	0.968
		n_F	0.8402	
3	Redlich– Peterson	A	1.6271	0.953
		B	0.6868	
		g	0.4826	
4	Koble–Corrigan	a	0.2091	0.995
		b_c	0.0082	
		n	1.3668	
5	Tempkin	A_T	0.2182	0.958
		B_T	6.507	
		b_T	387.14	
6	Dubinin–Radushkevich	Q_m	12.085	0.746
		$K \times 10^8$	8×10^{-6}	
		E	0.25	
7	Generalized	N_b	1.05	0.985
		K_G	107.12	

governing design parameter in designing of fixed-bed adsorption columns. The equilibrium isotherm also indicates the favorability of adsorption process and also useful for an estimation of unused bed-length of the fixed-bed adsorption column.

3.7. Adsorption kinetics

In order to understand the kinetics of removal of Cr(VI) using activated flyash, the experimental data for kinetics are tested with different kinetic models such as pseudo first-order [51], second-order [52], and Elovich kinetic models [53].

3.7.1. Pseudo first-order kinetics

The linear form of the pseudo first-order equation is given by Eq. (12):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{ad} t}{2.303}\right) \tag{12}$$

The plot of log ($q_e - q_t$) vs. t gives a straight line by which the adsorption rate constant, k_{ad}, are calculated. The values of first-order rate constants, k_{ad} and q_e, for the initial Cr(VI) concentration ranging from 100–400 mg L^{-1} are calculated and listed in Table 3. The obtained value of coefficient of determination is in the range of 0.97–0.994 which seems to be good and indicates the applicability of pseudo first-order kinetic model for the removal of Cr(VI).

Pseudo first-order kinetic equation differs from a true first-order equation in two ways: (i) the parameter $k_{ad}(q_e - q_t)$ does not represent the number of available active sites, and (ii) the parameter log (q_e) is an adjustable parameter. It is often observed that log (q_e) is not equal to the intercept of the plot of pseudo first-order kinetics, whereas in a true first-order model the value of log (q_e) should be equal to the intercept [51]. The true values of q_e obtained from experiments for 100, 200, 300, and 400 mg L^{-1} of the initial Cr(VI) concentrations are 8.0, 15.25, 20.12, and 21.13 mg g^{-1}, respectively, which are not in agreement with the predicted values of pseudo first-order model as given in Table 3. Hence, pseudo first-order kinetic model [Eq. (12)] is used for estimating k_{ad} alone, which is considered as mass transfer coefficient in the design calculations.

3.7.2. Second-order kinetics

As pseudo first-order kinetic model can be used to obtain only k_{ad} and as q_e cannot be found using this model, applicability of the second-order kinetics has to be tested for the estimation of q_e with the rate equation given by Eq. (13):

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{13}$$

Eq. (13) can be expressed in a linear form, as given by Eq. (14):

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right) t \tag{14}$$

where $h = k_2 q_e^2$ that can be obtained as the initial sorption rate as $t \to 0$. Under such circumstances, the plot of t/q_t vs. t gives a straight line, which allows the computation of q_e and k_2. The values of second-order rate constant, k_2, predicted equilibrium capacity q_e, and the coefficient of determination (R^2) for the initial Cr(VI) concentration ranging from 100 to 400 mg L^{-1} are listed in Table 3. The estimated q_e values show a good agreement with the experimental values. The values obtained for coefficient of determination (R^2) are more than 0.996 which shows that the second-order kinetic model explains the kinetic of Cr(VI) removal using activated flyash.

3.7.3. Elovich kinetic equation

Elovich equation is expressed as a rate equation based on the adsorption capacity commonly given as Eq. (15):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{15}$$

Eq. (15) is simplified by assuming $\alpha\beta >> t$ and by ap-

Table 3
Calculated kinetic parameters for pseudo first-order, second-order and Elovich kinetic models for the adsorption of Cr(VI) using activated flyash as an adsorbent

S. No.	C_0 (mg L^{-1})	q_e (mg g^{-1}) (experimental)	First-order kinetic model			Second-order kinetic model			Elovich kinetic model		
			k_1×10^3	q_e	R^2	k_2×10^3	q_e	R^2	β	α	R^2
1	100	8.0	0.199	3.56	0.994	0.156	8.22	0.999	1.087	274.9	0.990
2	200	15.25	0.201	7.78	0.972	0.066	15.7	0.996	0.561	408.6	0.970
3	300	20.12	0.175	9.76	0.985	0.048	20.7	0.996	0.415	434.3	0.972
4	400	21.13	0.171	9.92	0.970	0.047	21.9	0.996	0.406	557.2	0.976

plying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, as given by Eq. (16):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{16}$$

The kinetic constants, α and β, are estimated by the slope and intercept of the plot of q_t vs. ln t and reported in Table 3. The values of coefficient of determination (R^2) are obtained in the range of 0.97–0.99 for all the initial Cr(VI) concentration (100–400 mg L^{-1}). These values are found to be almost similar than the values estimated using pseudo first-order and less than the values estimated using second-order kinetic model (Table 3).

The kinetics of Cr(VI) adsorption using activated flyash can be better understood by the second-order kinetic model. It is essential to obtain the rate of Cr(VI) adsorption onto the activated flyash surface which is helpful in the designing of a fixed-bed adsorption column. The breakthrough time and the shape of the breakthrough curve are governing design parameters of fixed-bed adsorption column which are dependent on the rate of adsorption.

3.8. Regeneration studies

The adsorption of Cr(VI) is a reversible process, hence the saturated activated flyash can be regenerated and reused for adsorption. The efficiency of regenerated activated flyash is checked by conducting the experiments at different initial Cr(VI) concentration in the range of 20–400 mg L^{-1} as used for fresh activated flyash. The comparison of the percentage removal of Cr(VI) using fresh and regenerated activated flyash is shown in Fig. 7. The percentage removal of Cr(VI) is found to decrease from 74% to 35% for 20 to 400 mg L^{-1} of initial Cr(VI) concentration respectively, as compared to the corresponding values for fresh adsorbent ranging from 82% to 52%. These results using regenerated activated flyash shows a higher desorption efficiency by more than 85% of the fresh activated flyash for the removal of Cr(VI).

The major problem of regeneration process is the disposal of the acid and base solution obtained. This solution is contaminated with high concentration of Cr(VI). One of the methods to handle this problem is precipitation of Cr(VI) from the aqueous solution using barium chloride which recover the Cr(VI) from aqueous solution before being disposed off [6,9].

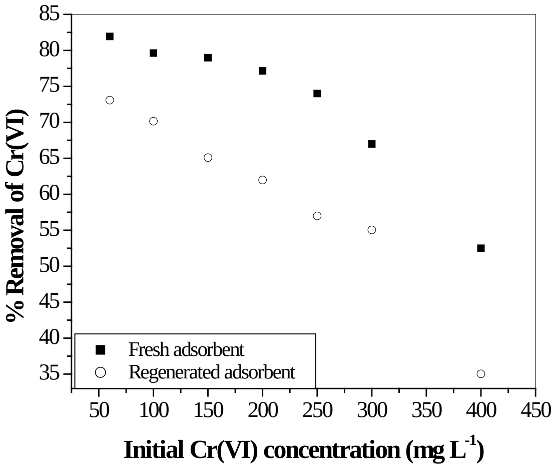

Fig. 7. Comparison for the percentage removal of Cr(VI) using fresh and regenerated activated flyash (T = 30°C, W = 0.25 g, t = 22 h and initial pH = 1).

6. Conclusions

A power plant waste material, flyash, is used for the removal of Cr(VI) from the aqueous solutions. The maximum percentage removal of Cr(VI) is obtained at initial solution pH value of 1. It is inferred that the dominant form of Cr(VI) is $HCrO_4^-$ and the surface of adsorbent is charged positively at a lower pH values. It is found from the kinetic studies that the rate of adsorption of Cr(VI) is higher for the initial 6 h and then it decreases in the later stage of adsorption. The equilibrium time for Cr(VI) adsorption on activated flyash is found as 22 h. The percentage removal of Cr(VI) increases and the adsorption capacity of activated flyash to adsorb Cr(VI) decreases, with the increase of adsorbent amount. With an increase in the initial Cr(VI) concentration, the percentage removal decreases and the adsorption capacity increases.

Activated flyash is found to be a better adsorbent for the removal of Cr(VI) as compared to many other low cost and commercially available adsorbents. The equilibrium data are tested with different isotherm models such as Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Tempkin, Dubinin–Radushkevich, Generalized isotherm models. The equilibrium data for Cr(VI) removal onto the activated flyash are best fitted with Koble–Corrigon isotherm model. The maximum adsorption capacity is obtained with the equilibrium experimental studies as 21.9 mg g^{-1}, which is comparatively good adsorption capacity. The kinetics of Cr(VI) adsorption using activated flyash is better explained by the second-order kinetic model for different values of initial Cr(VI) concentration. The saturated adsorbent is regenerated by acid and base treatment. The adsorption efficiency of the regenerated activated flyash is obtained to be more than 85% of fresh activated flyash for the removal of Cr(VI). The feasible solution for the major environmental problem of desorption process [i.e. the disposal of the acid and base solution obtained that contains high concentration of Cr(VI)] is the precipitation of Cr(VI) as barium chromate.

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Symbols

a — Koble–Corrigon isotherm constant, L mg^{1-n} g^{-1}
A — Redlich–Peterson parameter, L g^{-1}
A_T — Equilibrium binding constant, L min^{-1}
b — Adsorption equilibrium constant, L mg^{-1}
b_c — Koble–Corrigon isotherm constant, L^{n} mg^{-n}
b_T — Constant related to heat of adsorption
B — Redlich–Peterson parameter, L^{g} mg^{-g}
B_T — Tempkin isotherm constant, L g^{-1}
C_e — Concentration of Cr(VI) at equilibrium, mg L^{-1}
C_i — Inlet Cr(VI) concentration, mg L^{-1}
C_o — Final Cr(VI) concentration, mg L^{-1}
g — Redlich–Peterson isotherm constant
h — Initial sorption rate , mg g^{-1} min^{-1}
k_2 — Second-order rate constant, g mg^{-1} min^{-1}
k_{ad} — Pseudo first-order rate constant, L min^{-1}
K — Constant for adsorption energy, mol^{2} kJ^{-2}
K_G — Saturation constant, mg L^{-1}
K_F — Freundlich constant, L^{nF} mg^{-nF} g^{-1}
n — Koble–Corrigon isotherm constant
n_F — Freundlich isotherm constant
N_b — Cooperative binding constant, L mg^{-1}
q — Solid phase concentration of Cr(VI), mg g^{-1}
q_e — Equilibrium solid phase concentration of Cr(VI), mg g^{-1}
q_t — Solid phase concentration of Cr(VI) at time t, mg g^{-1}
Q_m — Maximum monolayer adsorption capacity, mg g^{-1}
R — Universal gas constant, J mol^{-1} K^{-1}
R_L — Dimensionless equilibrium parameter
t — Time, min
T — Temperature, °C
W — Weight of adsorbent, g

Greek

α — Initial adsorption rate, g mg^{-1} min^{-1}
β — Desorption constant, g mg^{-1}

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