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Removal of Cr(VI) from aqueous solution using fly ash of different sources

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ABSTRACT

The removal of Cr(VI) ions from aqueous solution using five different fly ash collected from different thermal power plants using batch mode is reported. The effect of different operating parameters on the selectivity and sensitivity is investigated. Kinetics studies are reported to understand the mechanistic steps of the adsorption process, and pseudo-second-order kinetic model is best suited for all the adsorbent used. Freundlich isotherm is better applicable compared to the Langmuir isotherm model. The sorption energy is calculated using Dubinin–Radushkevich isotherm indicated that the processes are chemisorption in nature. The thermodynamic parameters indicated the processes of the adsorption are spontaneous and endothermic.

Keywords: Fly ash; Freundlich isotherm; Rate kinetics; Sorption energy

1. Introduction

Cr(VI) has been reported to be a primary contaminant to humans, animals, plants, and microorganisms, and it is known to be carcinogenic (US Department of Health and Human services, 1991) [1]. Sources of chromium in wastewater include electroplating, steel fabrication, paints and pigments, mining, leather tanning, textile dyeing, aluminum conversion coating operations, plants producing industrial inorganic chemicals, and wood treatment units [2]. Tolerance limit of Cr(VI) for the discharge into inland surface water is 0.1 mg/L [3,4]. In order to comply with the given limit, industries have to treat their effluents to reduce the Cr(VI) concentration level in wastewater before it is discharged. Various technologies have been developed for the reduction of Cr(VI) to the permissible limit. Methods include chemical precipitation, membrane filtration, solvent extraction, and sorption to metal oxide, clay, activated carbon, and organic sorbents [5,6]. The above technologies suffer badly due to cost-ineffectiveness especially when metal concentration is very low. Adsorption process seems to be the most effective method for the removal of heavy metal if combined with appropriate regeneration steps. The high cost of activated carbon has motivated scientists into the search for industrial by-products such as waste slurry, kaolinite clay, fly ash, bentonite, red mud washed with water, red mud acid treated, blast furnace sludge, phosphatic clay, red mud, paper mill sludge, baggage fly ash, coffee residues binding with clay, calcined phosphate, clarified sludge, etc. as adsorbents for the metal remediation [7–19].

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Fly ash is finely divided residue resulting from the combustion of ground or powdered coal. It consists mainly of glassy spherical particles as well as residues of hematite and magnetite, char. Two major classes of fly ash as per ASTM C 618 on the basis of their chemical composition resulting from the type of coal burned. Class F—normally produced from burning anthracite or bituminous coal and Class C—normally produced from the burning of subbituminous coal and lignite. Class C—usually has cementitious properties in addition to pozzolanic properties due to free lime. Class F—rarely cementitious when mixed with water alone. Indian production of coal fly ash is approximately 135 million metric tons [20]. The percentage utilization of coal fly ash is only 54.53% and among them only 48.13% in cement production, 8.72% reclamation of low lying area, 13.02% for road and embankments, 6.76% for mine filling, 6.51% for brick and tiles making, 1.02% for agricultural uses, and the rest is for other purposes [20]. However, the rate of increase in demand in these applications is far less than the rate of increase in production. Fly ash also has potential application in wastewater treatment due to its major chemical components, such as alumina, silica, ferric oxide, calcium and magnesium oxide, and carbon, and its physical properties such as porosity, surface area, etc. [21].

Indian coal has high ash fraction and imported coal has low ash fraction. Power plants in eastern India import coal from Australia. Power plant generally mixes coal from different sources to optimize the useful heat value required. When imported coal is used, then less amount of fuel is required as it has high calorific value. Hence, it generates less ash and carbon dioxide. But imported coal contains more sulfur, so desulphurization for flue gas is necessary [22]. Literature review suggested that the fly ashes of different origin are characterized by different chemical compositions, structures, surface areas, and porosities [23,24].

In this study, a series of batch adsorption experiments are performed to investigate and explore the applicability of fly ash from different origins as industrial waste for the removal of Cr(VI) from aqueous solutions.

2. Materials and methods

2.1. Materials

Coal fly ash was collected from different origins—Bandal thermal power plant, Kolaghat thermal power plant, Kalahandi thermal power plant, Bakreswar thermal power plant, and NALCO thermal power plant. Bandal, Kolaghat, and Bakreswar are located in West Bengal and Kalahandi and NALCO in Odisha. After collection, fly ash was ground, homogenized, and dried at 105 ± 5˚C for 3 h and cooled to ambient temperature in desiccators. All the necessary chemicals used in the study were of analytical grade and obtained from M/S E. Merck India Limited, Mumbai, India.

2.2. Leaching behavior of fly ash [24]

It can be observed that when fly ash is put in double-distilled water, there is practically no significant change in pH value of water, hence, it can be concluded that there is practically no leaching of fly ash. However, it can be noticed that initially, there is a slight decrease in pH, but within 24 h, it attains a very close to normal value of pH 7. Table 1 shows the pH values.

2.3. Metal stock and standard solution

The stock solution containing 1,000 mg/L of Cr(VI) was prepared by dissolving 3.73 g of AR. grade K_2CrO_4, $2H_2O$ in 1,000 ml double-distilled water. The stock solution was diluted with double-distilled water to obtain the desired concentration.

2.4. Reagent and equipment used

Analytical grade chemicals are used in these studies and are purchased from E. Merck Limited, Mumbai, India. The pH of the solution was measured with a EUTECH-make digital microprocessor-based pH meter previously calibrated with standard buffer solutions. The Cr(VI) content in standard and treated solutions after adsorption experiments was measured

Table 1
pH of water fly ash sample after 24 h

	Fly ash collected from				
Parameter	Bandal	Kolaghat	Kalahandi	Bakrewar	NALCO
pH water with fly ash sample 24 h	6.9	6.7	6.8	6.4	6.9

Table 2
Physical characteristics of fly ash of different origin

Parameter	Fly ash collected from Bandal	Kolaghat	Kalahandi	Bakrewar	NALCO
Bulk density, g/cm^3	1.76	1.68	1.84	1.75	1.86
Surface area, m^2/g	6.42	6.36	9.46	7.59	4.37
Point of zero charge, pH_{pzc}	7.21	6.56	6.73	6.87	6.70

by UV spectrophotometer (U-4100 spectrophotometer, Hitachi, Japan). The Cr(VI) concentration was determined from the calibration curve prepared by measuring absorbance at λ_{max} 540 nm using a UV spectrophotometer. Scanning electron microscopic (S-3400 N, Hitachi, Japan) study was conducted to observe the surface texture of the adsorbents. The surface area was measured on Micromeritics surface area analyzer (ASAP 2020). The pH of the solution was measured with a 5500 EUTECH pH meter using FET solid electrode calibrated with standard buffer solutions. The point of zero charge (pH_{pzc}) was determined by solid addition method [25] and is shown in Table 2.

2.5. Characterization of fly ash

Scanning electron microscopic (SEM; Model S415A, Hitachi, Japan) studies were conducted to observe the surface texture of the fly ash. Fig. 1 shows the X-ray diffraction studies for fly ash from Bandal to find out the constituents. The physical properties and composition of fly ashes are shown in Tables 2–3 respectively. The point of zero charge (pH_{pzc}) was determined by solid addition method [25]. In a series of 100-ml conical flask, 40 ml of 0.1 M KNO_3 solution was transferred. The pH values were adjusted by adding 0.1 N HCl or 0.1 N NaOH solutions. Then, the total volume in each flask was made exactly 50 ml by adding KNO_3. The pH was noted (pH_i) and then 1 g of fly ash was added to each flask separately. The suspensions were shaken and allowed to equilibrate for 48 h with occasionally shaken. The pH of the supernatant liquid was noted (pH_f). The difference between the initial pH_i and the final pH_f value ($\Delta pH = pH_i - pH_f$) was plated against initial pH, pH_i. The point of intersection with ΔpH axis indicated the point of zero charge. The bulk density was measured according to ISO 697:1981 method.

2.6. Method used

Experiments were conducted at room temperature, that is 30 ± 2℃. The necessary amount of fly ash is taken in a 250-ml stopper conical flask containing 100 ml of desired concentration of the test solution at the desired pH value. Different initial concentration of metal solutions was prepared by proper dilution from stock 1,000 ppm metal standard. pH of the solution was monitored by adding 0.1 N HCl and 0.1 N NaOH solution. The flask was shaken for the desired contact time in an electrically thermostated reciprocating shaker (120–130 strokes/min) at 30℃. The shaking time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time. The contents of the flask were filtered through filter paper, and the filtrate was analyzed for remaining metal concentration in the sample using a UV–vis Spectrophotometer with 1,5-diphenylcarbazide in acid medium as per procedure laid down in APHA, AWWA standard methods for examination of water and wastewater, 1998 edition [26]. The amount of Cr (VI) adsorbed at time any time t was determined using the following equation:

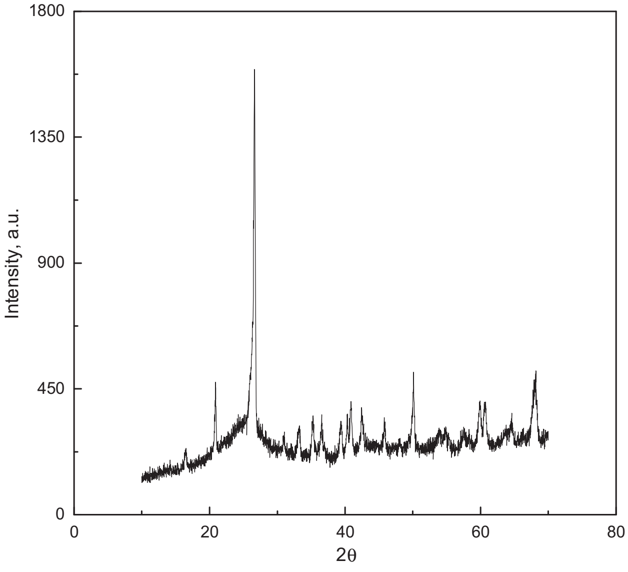

Fig. 1. X-ray diffraction for Bandal fly ash.

Table 3
Chemical composition of fly ash (%wt) from different power plant

	Fly ash collected from				
Constituent	Bandal	Kaloghat	Kalahandi	Bakrewar	NALCO
Fe_2O_3	8.33	3.77	5.64	5.39	4.75
Al_2O_3	22.01	26.38	30.40	23.42	30.63
CaO	2.57	1.54	0.96	2.54	3.28
MgO	0.91	0.39	0.28	0.16	1.33
SiO_2	57.82	61.43	58.67	62.94	56.10
Na_2O/K_2O	0.00/0.45	0.10/0.30	0.10/0.25	0.10/0.20	0.10/0.25
Loss of ignition	12	5.89	3.7	5.45	0.50

$$q_t = \frac{(C_0 - C_t)V}{m_S} \tag{1}$$

The percentage removal of Cr(VI) is calculated using the following equation:

$$R = \frac{C_i - C_o}{C_i} \times 100 \tag{2}$$

In all the experiments, the contact time was varied from 0 to 360 min, the pH of the solution from 2 to 9, the initial metal ion concentration from 3 to 50 mg/L, and the amount of adsorbent from 2.5 to 30 g/L. All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the reproducibility and the relative deviation of the order of ±0.5 and ±2.5%, respectively.

3. Results and discussion

3.1. Effect of pH

Fig. 2 shows the percentage removal of Cr(VI) as a function of pH using different fly ashes. It is clear from the figure that the adsorption characteristics of the adsorbents are highly pH dependent. The percentage removal reached a maximum value at an initial pH of the solution at 2. In general, adsorption of cation is favored at $pH > pH_{pzc.}$ At a very low pH, chromium ions exist in the form of $HCrO_4^-$, while the increase in pH (up to pH 6) in different forms such as $Cr2O_7^{2-}$, $HCrO_4^-$, and $Cr_3O_{10}^{2-}$ coexists, of which $HCrO_4^-$ predominates. As the pH increases, equilibrium shifts from $HCrO_4^-$ to CrO_4^{2-} and $Cr2O_7^{2-}$ [27]. At very low pH values, the surface of adsorbent would be surrounded by the hydronium ions, which enhance the Cr(VI) interaction with binding sites of the fly ash by greater attractive forces. As the pH is increased, the overall surface charge becomes negative and adsorption decreases [5,28]. Adsorption of Cr(VI) was not significant at pH values of more than six due to dual complexation of the anions (CrO_4^{2-}, $Cr2O_7^{2-}$, and OH^-) to be adsorbed on the surface of the adsorbents, of which OH^- predominates [29].

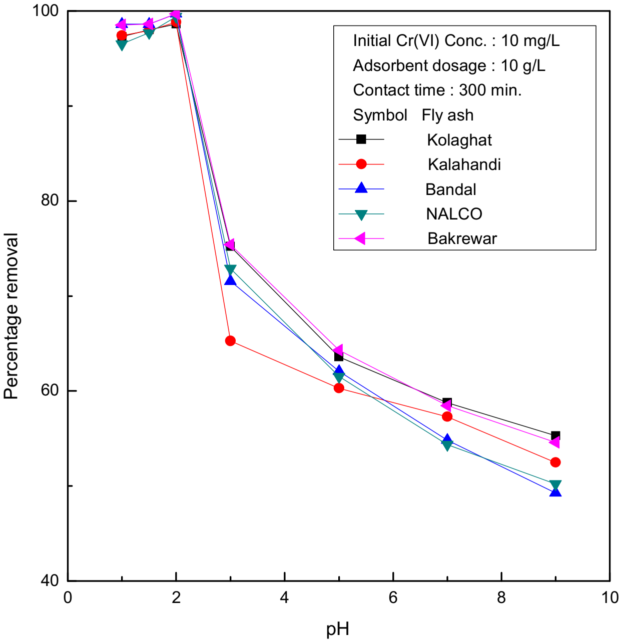

Fig. 2. Variation in pH on the percentage removal of Cr(VI).

3.2. Effect of adsorbent dosage and initial Cr(VI) ion concentration

Variation in adsorbent dosage on the percentage removal of Cr(VI) was studied using adsorbent dosage varying from 2.5 to 30 g/L of adsorbents dosage and is shown in Fig. 3.

The Cr(VI) removal was increased rapidly as adsorbent dosage increases from 2.5 to 30 g/L. After these dosages, the metal ion removal was very slow and it

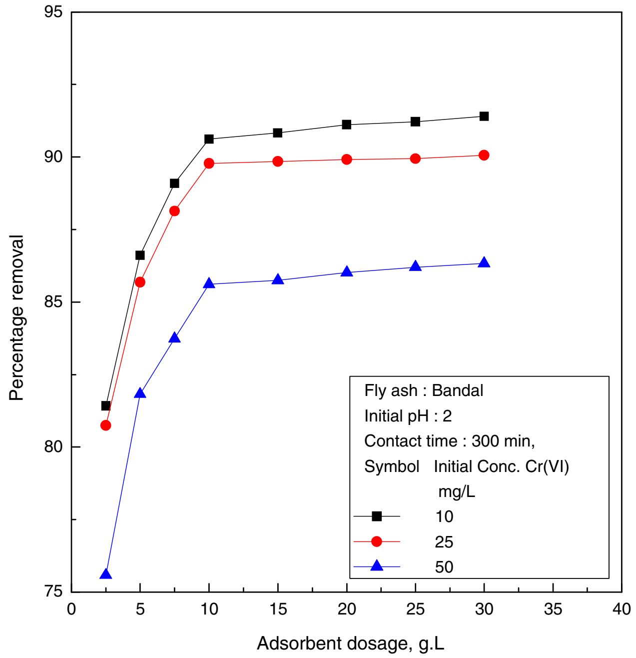

Fig. 3. Variation in adsorbent dosage on the percentage removal of Cr(VI).

was due to surface Cr(VI) ion concentration, and the solution Cr(VI) ion concentration reached equilibrium. Hence with further increase in adsorbent dosage above 10 g/L, the removal percentage was almost constant. So the optimum adsorbent dosages were 10 g/L for all the adsorbents. This figure also indicates that there is a decrease in percentage of Cr(VI) ion removal as the initial Cr(VI) ion concentration increases.

3.3. Effect of contact time

Fig. 4 shows the effect of contact time on the batch adsorption of Cr(VI) ion at 3°C. During the experiment, contact time varied from 0 to 360 min. The initial rapid adsorption gives away a very slow approach to equilibrium. The equilibrium time for the Cr(VI) adsorption was 4 h for all types of fly ash used.

3.4. Adsorption kinetics study

The kinetics of Cr(VI) adsorption was studied from the time vs. percentage removal curves. The study of adsorption kinetics describes the solute uptake rate, and evidently, these rates control the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the fly ash as well as on the mass transfer process.

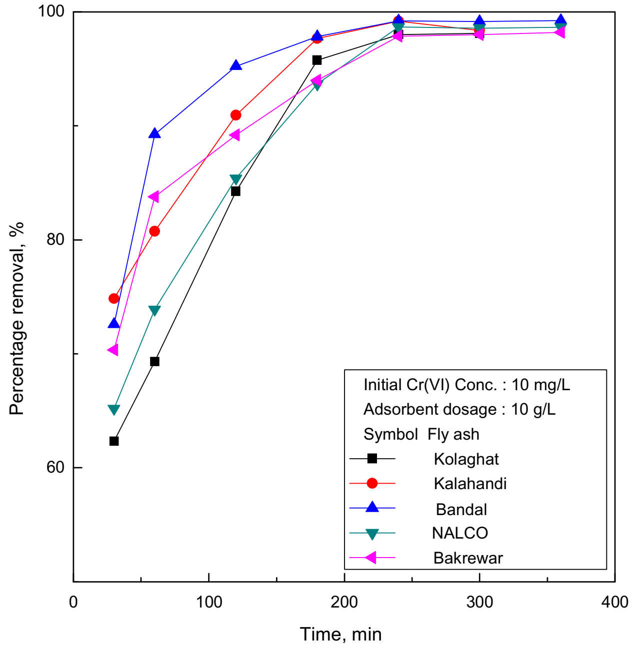

Fig. 4. Variation in contact time on the percentage removal of Cr(VI).

3.5. Lagergren model

The pseudo-first-order kinetic model was proposed by [30]. The integral form of the model is generally expressed as follows:

$$\log\,(q_e - q) = \log q_e - \frac{K_{ad}t}{2.303} \tag{3}$$

3.6. Pseudo-second-order model

The kinetics of adsorption process may also be described pseudo-second-order rate equation [31]. The linearized form of equation is expressed as

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

The applicability of the Lagergren and pseudo-second-order models was examined by each linear plot of log ($q_{e\,-}\,q$) vs. t and (t/q) vs. t, respectively. In order to quantify the applicability of each model, the correlation coefficient, r^2, was calculated from these plots. The linearity of these plots indicates the applicability of these three models. Values of rate constant and correlation coefficient for each of the model are shown in

Table 4
Rate kinetics parameters

Model parameters	Fly ash collected from				
	Bandal	NALCO	Bakreswer	Kalandhi	Kolaghat
Pseudo first order model					
K_{ad} (min^{-1})	0.02168	0.0147	0.0178	0.0285	0.02381
r^2	0.8751	0.8133	0.9134	0.8636	0.9278
χ^2	4.4718	6.2453	4.4987	5.7865	3.2936
Pseudo second order model					
K_2(mg/g/min)	0.0123	0.0240	0.02956	0.0365	0.2768
r^2	0.9972	0.9993	0.9934	0.9998	0.9912
χ^2	0.0031	0.0014	0.0012	0.0009	0.0003

Table 4. Correlation coefficients, r^2, indicated that the pseudo-second-order model fits best with the experimental data. The following expressions may be described as the reaction of the metal ion, M, binding to the binding sites of the fly ash, FA

$$M + 2FA \leftrightarrow FA_2M \tag{5}$$

$$r = k[M][FA]^2 \tag{6}$$

This means that the adsorption rate would be proportional to the metal ion concentration and the square of the number of free sites of the fly ash, which corresponds to the term $(q_e - q_t)^2$ in the second-order model.

3.7. Adsorption isotherms

The adsorption equilibrium data are generally represented by adsorption isotherms. The interaction between adsorbate and adsorbent are frequently interpreted using the Langmuir and the Freundlich isotherm models [32,33]. The Langmuir model is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented as follows,

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{7}$$

Webi and Chakravort [34] expressed the essential characteristics and feasibility of the Langmuir isotherm in terms of a dimensionless constant, separation factor, or equilibrium parameter, R_L. If this value ranges in between 0 and 1, then the sorption process is favorable. All the experimental data were lying between 0 and 1, indicating favorable sorption.

The Freundlich isotherm model is applied to describe heterogeneous systems characterized by a heterogeneity factor of $1/n$. This model describes reversible sorption and is not restricted to the formation of the monolayer. The Freundlich isotherm model is expressed as,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

Table 5 indicates the Langmuir and Freundlich constants along with the statistical parameters. The values of n in the Freundlich constant lies between 1 and 10 for all biosorbents representing favorable sorption.

3.8. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm [35] was employed in the following linear form,

$$\ln C_{abs} = \ln X_m - \lambda \varepsilon^2 \tag{9}$$

where λ is constant related to energy and X_m is maximum adsorption capacity.

The Polanyi potential [36], ε, can be expressed as,

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

A plot of C_{abs} vs. ε^2 gave a straight line from which values of λ and X_m were evaluated from the slope and intercept, respectively. Using the calculated value of λ, it was possible to evaluate the mean sorption energy, E, from

Table 5
Isotherm parameters

Model parameters	Fly ash collected from Bandal	NALCO	Bakrewer	Kalandhi	Kolaghat
Langmuir model					
$q_{\max}$ (mg/g)	23.86	25.95	21.67	24.49	28.70
b (L/mg)	0.043	0.0563	0.0352	0.0482	0.0398
r^2	0.9790	0.9652	0.9782	0.9649	0.9530
χ^2	4.3422	2.3571	2.1083	3.5189	2.6354
R_L value for initial conc. of Cr(VI) 3 g/L	0.8857	0.8550	0.9045	0.8737	0.8933
R_L value for initial conc. of Cr(VI) 30 g/L	0.4367	0.3719	0.4864	0.4083	0.4558
Freundlich Model					
K_f (mg/g)/(mg/L)$^{1/n}$	2.6196	3.4112	2.3782	2.8391	3.4578
n	2.5954	3.3156	2.1493	2.7493	3.2851
r^2	0.9863	0.9926	0.9848	0.9956	0.9974
χ^2	1.3848	1.8762	1.5284	0.9298	0.8965

$$E = \frac{1}{\sqrt{-2\lambda}} \tag{11}$$

This is the free energy transfer of 1 mol of solute from infinity to the surface of the adsorbent. The estimated value of sorption energy was 12.845, 14.712, 15.394, 13.762 and 15.295 kJ/mol, for adsorption on fly ash collected from Bandal, Kolaghat, Kalahandi, Bakreswar, and NALCO, respectively. As the calculated values of E are greater than 8 kJ/mol in the present work, it follows that any bond formation between Cr (VI) ion and fly ash may be chemical in nature [25].

3.9. Thermodynamic parameters for adsorption

The thermodynamic equilibrium constant (K_c^0) for each system was obtained by calculating the apparent equilibrium constant, K'_C at different initial concentration of Cr(VI) ions and extrapolating to zero.

$$K'_c = \frac{C_a}{C_e} \tag{12}$$

The Gibbs free energy (ΔG°) for the adsorption process was obtained at 30 ± 2°C using the formula

$$\Delta G^\circ = -RT \ln K_C^0 \tag{13}$$

The process of metal ion adsorption can be summarized by the following reversible process, which represents a heterogeneous equilibrium

$$\text{Cr(VI) ion in solution} \leftrightarrow \text{Cr(VI) ion in adsorbent} \tag{14}$$

For determination of enthalpy and entropy change of the adsorption process, the temperature dependence of adsorption on the different fly ashes were studied, and were evaluated using equation,

Table 6
Thermodynamic parameters

Parameter	Temperature (K)	Fly ash collected from Bandal	NALCO	Bakreswer	Kalandhi	Kolaghat
$-\Delta G$ (kJ/mol)	303	7.2845	6.1247	5.9361	7.3812	6.2351
	313	7.8256	6.9856	6.2746	7.8537	7.2356
	328	7.9651	8.2341	7.948	8.2671	9.2569
ΔH (kJ/mol)		27.3246	27.3614	26.7232	28.4934	31.2564
$-\Delta S$ (kJ/mol K)		0.1531	0.0965	0.0784	0.1373	0.1254
E (kJ/mol)		12.845	15.295	13.762	15.394	14.712

$$\ln K_c^\circ = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{15}$$

From the slope and intercept of the plot, the values of ΔH° and ΔS° have been computed. The values of the thermodynamic parameters thus calculated are recorded in Table 6. From Table 6, it is clear that Cr(VI) adsorption on different fly ash is endothermic. The positive value of ΔS° is an indicative of increased randomness at the adsorbent–adsorbate interface during the adsorption of Cr(VI). The negative value of ΔG° confirms the feasibility of the metal ion adsorption process.

3.10. Comparison of adsorption capacity reported in the literature

The adsorption capacity of Cr(VI) onto different ashes available in the literature is reported in Table 7.

Table 7
Comparison of adsorption capacities

Adsorbent	Adsorbent capacity (mg/g)	Reference
Rice husk ash	0.49	[37]
Rice husk ash modified with 0.1 M NaOH	0.84	
Untreated fly ash	16.876	[38]
Treated fly ash	12.854	
Charcoal of sugar cane bagasses	15.38	[39]
Activated rice husk carbon	0.8	[40]
Activated carbon from *Canarium schweinfurthii* seed shell with H_3PO_4	0.792	[41]
Activated carbon from *Canarium schweinfurthii* seed shell with $ZnCl_2$	0.12	
Bagasse fly ash	18.8679	[42]
Fly ash	0.01	[43]
Mango stone ash	4.7339	[44]
Cow dung ash	5.7481	
Corn cob ash	4.2125	
Granulated activated carbon	10.1694	
Fly ash collected from		Present study
Bandal	23.86	
NALCO	25.95	
Bakrewer	21.67	
Kalandhi	24.49	
Kolaghat	28.70	

4. Conclusions

In this study, batch adsorption experiments for the removal of Cr(VI) ions from aqueous solutions have been carried out using fly ash from different sources such as low cost, readily available adsorbent. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time, and adsorbent dosages. The obtained results can be summarized as follows,

1. The pH variation studies showed that the adsorption process for the metal ions was highly pH dependent. The optimum pH for the removal of all the metal ions was 2.
2. Increase in the concentration of adsorbent dosage and contact time were found to increase the percentage removal of Cr(VI).
3. SiO_2 and Al_2O_3 are the main groups present in the fly ash responsible for Cr(VI) adsorption.
4. Pseudo-second-order model was more suitable than the first-order model to describe the kinetics.
5. Freundlich adsorption isotherm model was better fitted than Langmuir adsorption isotherm model.
6. Sorption energy for the removal of Cr(VI) indicated the chemisorption process.
7. Thermodynamic parametric study indicated that the adsorption of Cr(VI) on fly ash was endothermic in nature.

Nomenclature

b — Langmuir constant, L/mg
C — concentration of metal ion after certain period of time, L/mg
C_a — concentration of metal ion on the adsorbent at equilibrium, L/mg
C_e — concentration of metal ion in solution at equilibrium, L/mg
C_{final} — final concentration of metal ion in solution, L/mg
C_{initial} — initial concentration of metal ion in solution, L/mg
C_0 — initial concentration of metal ion in solution, L/mg
C_t — concentration of metal ion after time t, L/mg
FA — fly ash
K' — pseudo-second-order rate constant of adsorption, mg/g min
K_{ad} — Lagergren rate constant, min^{-1}
K_c — thermodynamic equilibrium constant
K_f — measure of adsorption capacity, mg/g
K_{bq} — constant obtained by multiplying $q_{\max}$ and b

M — metal ion in Eq. (9)
m — amount of adsorbent added, g
n — Freundlich constants, intensity of adsorption
q — amount adsorb per gm of the adsorbent, mg/g
q_e — amount adsorb per gm of the adsorbent at equilibrium, mg/g
q_{max} — maximum adsorption capacity, mg/g
q_t — amount adsorb per gm of adsorbent at time t min
r^2 — correlation coefficient
R_L — separation factor
t — time, min
V — volume of the solution, ml
E — mean sorption energy, kJ/mol

Greek letter

λ — constant related to energy, mol^2/kJ^2
ε — polanyi potential, kJ^2/mol^2
χ^2 — Chi-square test

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