Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.833554

52 (2014) 7845–7855
December

Taylor & Francis
Taylor & Francis Group

Removal of hexavalent chromium from aqueous solution using biomass derived fly ash from Waste-to-Energy power plant

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Received 5 April 2013; Accepted 23 July 2013

ABSTRACT

Fly ash from the agricultural waste-based Energy Power Plant has been studied for the adsorption of hexavalent chromium [Cr(VI)]. In order to maximize the Cr(VI) removal from simulated aqueous solutions, effects of various parameters i.e. adsorbent dose (10–40 g/L), contact time (5–90 min), variation in pH (1–5), and initial metal ion concentration (10–80 mg/L) on Cr(VI) adsorption were investigated by batch adsorption experiments. It was observed that adsorption of Cr(VI) on the selected adsorbent was dependent on pH. Before optimization of experimental conditions, the percent removal of Cr(VI) from the aqueous solution (10 mg Cr/L) was approximately 4%, which increased to approximately 99% after optimization of experimental conditions. Maximum adsorption was observed upon adding 10 g/L of adsorbent to a 60 mg Cr/L aqueous solution at pH 1.0 and contact time of 90 min at 200 rpm. Equilibrium adsorption data were well fitted in Langmuir isotherm model which substantiate monolayer adsorption of Cr(VI) on fly ash. Kinetics of Cr(VI) adsorption on fly ash follows pseudo-second-order reaction.

Keywords: Adsorption; Hexavalent chromium removal; Fly ash; Isotherms; Kinetics

1. Introduction

Chromium (Cr) is a metal of transition series occurring commonly in environment as trivalent [Cr(III)] and hexavalent [Cr(VI)] forms [1]. Trivalent chromium occurs naturally in ores like ferrochromite, while hexavalent chromium does not occur naturally and is added to the environment through various industrial activities [2,3]. Exposure to chromium through inhalation, ingestion of contaminated food, or drinking water affects the respiratory tract, liver, kidney, gastrointestinal, and immune systems. Contact dermatitis, sensitivity, and ulceration of the skin may be caused by dermal exposure to hexavalent chromium [3]. Further, Cr(VI) is reported to be more water soluble, toxic, and carcinogenic as compared to Cr(III) [4–6].

A number of physico-chemical methods from simple methods like chemical reduction and precipitation to advanced methods like ion-exchange, electrolysis, ion-flotation, membrane processing, electrolytic methods, and carbon adsorption have been used for the removal of chromium from wastewater [7,8]. Many attempts have been made to develop low-cost adsorbent by using natural materials, waste, and

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by-products of many industries. The materials used in various studies include nonliving biomass of fresh water macrophytes [9], aquatic weeds [10], agricultural waste residue including coirpith [11], olive cake, sawdust, pine needles, almond shells, cactus leaves [12], cornelian cherry, apricot stone, and almond shells [13], modified activated coconut shell carbon [14], sugarcane bagasse, maize corn cob, Jatropha oil cake [15], neem leaves [16], coconut shell, coconut shell fibers and rice husk [17], paddy straw, coconut palm fiber, corn husk and pineapple crown top [18], walnut shells [19] etc. to remove heavy metals from contaminated water. Even waste material from various industrial processes like sugar industry waste [20–22], food industry waste including used black tea leaves [23], exhausted ground coffee waste [24], olive oil industry waste [25], cement kiln dust [26], fertilizer industry waste [27], power plant fly ash [28,29], and bottom ash [30,31] have also been explored in an endeavor for low-cost adsorbents. Using waste material from various industrial processes for the treatment of wastewater of other industries is a very good option in environmental and economical terms. This activity will not only solve the problem of waste management but will also provide ways for its beneficial use.

Fly ash generated from Waste-to-Energy power plant using agricultural waste as fuel located at Gidderwaha, Punjab (India), was selected as an adsorbent in the present study. The power plant uses a huge quantity of agricultural residues of seasonal crops as a primary fuel to produce electricity. The material was selected as adsorbent in current study keeping in view its easy availability, low cost, and problem in dumping the material. Moreover, there are a number of industries discharging chromium in their effluent in this area which can use the material in their effluent treatment plants. To the best of our knowledge, there is no study on the use of this type of material in removal of Cr(VI) from aqueous solution. It is thus suitable to use it as an adsorbent, as it will provide an alternative low-cost adsorbent.

2. Materials and methods

Fly ash from Waste-to-Energy power plant, Gidderwaha, Punjab (India), was collected in the month of March, 2011. The agricultural waste used as fuel comprised of 70–80% gram straw, 10–15% cotton straw, 5–10% wheat straw, and small percentage of leaves. Small amount of coal was supplemented for efficient burning. Fly ash was directly heated in the oven for 7–8 h at 105˚C and was then sieved using sieve shaker with mesh of size 300 μ. The ash particles of less than 300 μ were taken and stored in polythene bags for further use.

All the chemicals used in experimental work were of analytical grade and were procured from Loba Chemie Pvt. Ltd., Mumbai. The stock solution of hexavalent chromium (500 mg Cr/L) was made by dissolving 1.414 g of potassium dichromate in 1 L of distilled water. The stock solution was further diluted with distilled water to obtain the desired concentrations and was subsequently used as adsorbate. The pH of the solutions was adjusted using 1 N H_2SO_4. Other chemicals used for the estimation of metal ion were H_2SO_4, H_3PO_4, 1, 5-diphenylcarbazide, acetone etc.

2.1. Characterization of fly ash

2.1.1. Particle size analysis

Particle size analysis of fly ash sample was conducted by Dynamic Light Scattering using Laser Beam, Particle Size Analyzer (Mastersizer 2000, Malvern instruments Ltd.), and Hydro 2000MU (A) accessory in the size range of 0.100–1000.00 μm. Water was used as dispersant for analysis.

2.1.2. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis

Surface structure and elemental composition of the fly ash were analyzed by scanning electron microscopy (ZEISS EVO 40 EP) and energy dispersive X-ray analysis (BRUKER LN_2 Free X-Flash 4010 SDD Detector), respectively, using Quantax 200 analytical software.

SEM-EDX analysis of collected fly ash sample and chromium (60 mg Cr/L at initial pH 1.0) treated fly ash sample was carried out. Both the samples were dried in the oven at 70˚C for 3–4 h. For the analysis, samples were mounted on a stainless steel stub using a double sticky carbon tape.

2.1.3. Fourier transform infrared (FTIR) analysis

FTIR spectra were recorded on a Fourier transform infrared spectrometer (BRUKER TENSOR 27) for fly ash, acidified fly ash (treated with distilled water acidified to pH 1 using H_2SO_4), and chromate adsorbed fly ash samples. All the samples were dried in the oven at 70˚C for 3–4 h. Samples for FTIR were prepared and analyzed as KBr pellets.

2.2. Batch experiments

The batch experiments were carried out by shaking a pre-weighed amount of fly ash with 200 mL of the aqueous solution of hexavalent chromium for a predetermined period in Erlenmeyer flasks incubated at 25 ± 1˚C. The adsorbent was separated by filtration through filter paper (Whatman no. 1) and aqueous phase concentration of metal ion was determined spectrophotometrically using UV-VIS double beam spectrophotometer (Systronics-2202) by 3500-Cr B Colorimetric method given in Standard Method for Examination of Water and Wastewater, 21st edition, APHA [32].

2.2.1. Effect of adsorbent doses

The effect of adsorbent dose was studied by varying the adsorbent doses (10, 20, 30, and 40 g/L) in 200 mL of 10 mg Cr/L aqueous solution at 25 ± 1˚C. The flasks were shaken for 2 h at 200 rpm and then left for 22 h for the equilibrium.

2.2.2. Effect of pH

The effect of pH on the adsorption of Cr(VI) was studied by adding 10 g/L adsorbent doses in 200 mL aqueous solution of 10 mg Cr/L of varying pH within the range 1.0–5.0 and shaking for 2 h at 25 ± 1˚C and 200 rpm followed by equilibrium period of 22 h.

2.2.3. Effect of contact time

The effect of contact time and adsorption kinetics was studied by shaking different sets of flasks having 200 mL aqueous solution of 10 mg Cr/L having pH 1.0 and 10 g/L fly ash for different time intervals (5, 30, 60, and 90 min) at 200 rpm and 25 ± 1˚C temperature.

2.2.4. Effect of initial metal ion concentration

The effect of initial metal ion concentration and adsorption isotherm study was carried out by shaking 10 g/L fly ash with aqueous solutions of varying initial metal ion concentration (10, 20, 40, 60, and 80 mg Cr/L) at pH 1.0 for 90 min at 25 ± 1˚C and 200 rpm followed by equilibrium period.

2.2.5. Metal uptake

Metal uptake by sorbent after equilibrium (mg/g) was determined by applying mass balance equation to the data collected from above experiments.

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where q_e = metal uptake by sorbent after equilibrium, mg/g; C_o = initial concentration of metal ion, mg/L; C_e = final concentration of metal ion after adsorption has occurred, mg/L; V = volume of liquid treated, L; W = weight of adsorbent used, g.

Further, the percentage of Cr(VI) ions removed ($R\%$) was calculated using the following equation:

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

2.3. Adsorption isotherm

The linear form of Langmuir isotherm was applied to the data generated in the study of variation in initial ion concentration. Langmuir isotherm is expressed by the following equation:

$$\theta = \frac{(q_e)}{q_m} = \frac{(bC_o)}{(1 + bC_e)} \tag{3}$$

where θ = fractional coverage; $b = k_a/k_d$; $k_{a=}$constant for adsorption; k_d = constant for desorption; q_m = quantity of adsorbate required to form a single monolayer on unit mass of adsorbent, mg/g; q_e = amount adsorbed on unit mass of the adsorbent at equilibrium, mg/g.

The above equation can be rearranged as below:

$$\frac{(C_e)}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} \times C_e \tag{4}$$

where C_e = equilibrium concentration of solute in bulk solution (mg/L); b = Langmuir constant related to the free sorption energy (L/mg).

Further, Langmuir equation also predict that whether the process is favorable or not on the basis of dimensionless separation factor. R_L can be derived using equation:

$$R_L = \frac{1}{(1 + bC_e)} \tag{5}$$

where value of R_L represents the following adsorption characteristics: $R_L > 1$: unfavorable adsorption; $R_L = 1$: linear adsorption; $0 < R_L < 1$: favorable; $R_L = 0$: irreversible adsorption.

2.4. Adsorption kinetics

The linear form of Lagergren pseudo-first-order and pseudo-second-order adsorption kinetic model was applied to the data generated in the study of variation in contact time.

The linearized form of pseudo-first-order Lagergren equation can be expressed as:

$$\log(q_e - q_t) = \log\ q_e - \frac{k_{1,\text{ads}}}{2.303} \times t \tag{6}$$

and linearized form of pseudo-second-order Lagergren equation is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} \times t \tag{7}$$

where q_e = mass of metal ion adsorbed at equilibrium (mg/g); q_t = mass of metal ion adsorbed at time t (mg/g); $k_{1,\text{ads}}$ = the pseudo-first-order reaction rate of adsorption (per min); $h = k_2\ q_e^2$; k_2 = the pseudo-second-order rate constant of adsorption mg/g/min.

3. Results and discussion

3.1. Characterization of fly ash

3.1.1. Particle size analysis

Particle size analysis of fly ash revealed that major fraction, 92.40% (approx.), of fly ash particles are in the size range of 1–150 µm (Fig. 1). Based on the particle size, the specific surface area of fly ash is found to be 0.404 m^2/g, whereas uniformity of fly ash is 0.867.

3.1.2. SEM-EDX analysis

Electron micrographs (Figs. 2 and 3) of fly ash and fly ash treated with 60 mg/L Cr(VI) solution at pH 1.0 show heterogeneous morphology of the adsorbent. The elemental distribution of fly ash obtained by EDX of fly ash and Cr(VI) treated fly ash (Figs. 4 and 5) shows high percentage of carbon, magnesium, silicon, potassium, calcium and oxygen, and very low (<2%) amount of sodium, aluminum and iron. Fly ash samples upon treatment with Cr(VI) solution showed a significant increase in sulfur content due to the addition of sulfuric acid to maintain the pH. Fig. 5 shows the presence of Cr indicating its actual adsorption on fly ash.

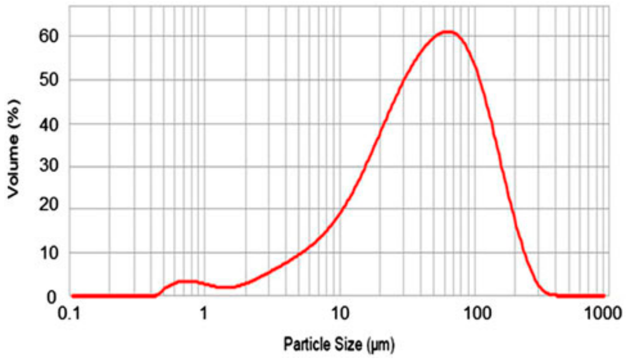

Fig. 1. Particle size distribution of fly ash.

3.1.3. FTIR analysis

The FTIR spectra of the fly ash, acidified fly ash (treated with distilled water acidified to pH 1 using H_2SO_4), and chromate adsorbed fly ash have been presented in Fig. 6. The FTIR spectrum of the fly ash sample (Fig. 6(A)) shows sharp bands at 3,644 and 3,699 cm^{-1} corresponding to the nonhydrogen bonded hydroxyl groups. Further, a broad band at 3,424 cm^{-1} was observed for the hydrogen bonded hydroxyl group present in the fly ash sample. Presence of absorption bands at 1,418, 875 and 713 cm^{-1} indicates the presence of carbonate ions in the fly ash sample [33]. The sharp absorption bands at 1,128 and 1,046 cm^{-1} may be due to the presence of the tetrahedral moieties, generally represented by TO_4^{4-} (T = Si, Al) [34].

Further, when fly ash was acidified with sulfuric acid (pH 1), a significant change in the FTIR spectrum was observed (Fig. 6(B)). Appearance of broad absorption bands at 3,613, 3,553, 3,386, and 3,243 cm^{-1} could be accounted for the strongly hydrogen bonded hydroxyl groups present in the acidified fly ash sample. The appearance of hydrogen bonded hydroxyl groups represents the protonation of the silicates and aluminates present in the fly ash. Further, presence of absorption bands at 1,686 and 1,621 cm^{-1} in acidified sample indicate the presence of water molecules and hydroxide moieties. The absence of absorption bands at 1,418, 875, and 713 cm^{-1} indicates complete removal of carbonate groups under acidic conditions [35]. Appearance of broad absorption bands in the range of 1,200–1,000 cm^{-1} is further an indication of protonation of TO_4^{4-} system upon acidification.

Further, FTIR spectra of fly ash treated with Cr(VI) solution under acidic conditions (pH 1) (Fig. 6(C)) showed few significant changes, particularly with the absorption bands of the protonated sites of fly ash i.e. at 3,600–3,200, 2,300–2100, and 1,200–1,100 cm^{-1}. These are indicative of the hydrogen bonding interaction between the chromate ion and the protonated sites of fly ash.

Based on the literature and the FTIR analysis, the proposed mechanism for the adsorption of chromate ion on fly ash under acidic conditions is depicted in

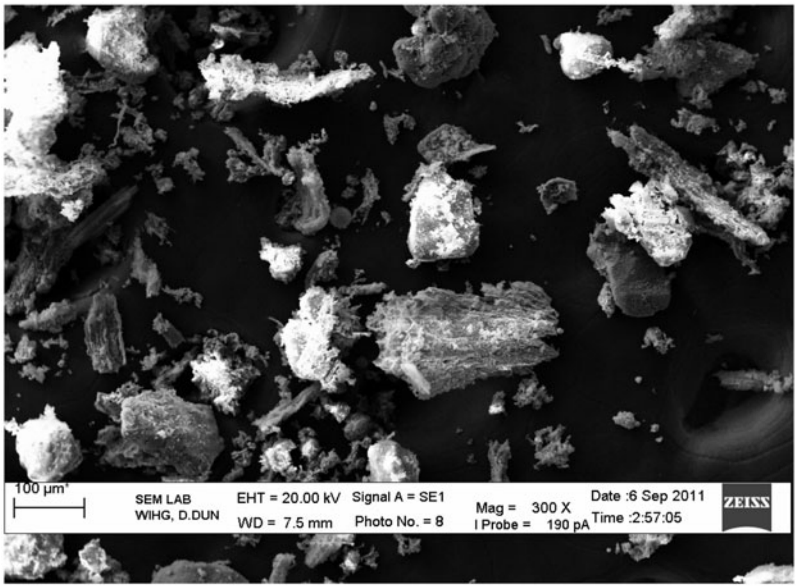

Fig. 2. Electron micrograph of raw fly ash.

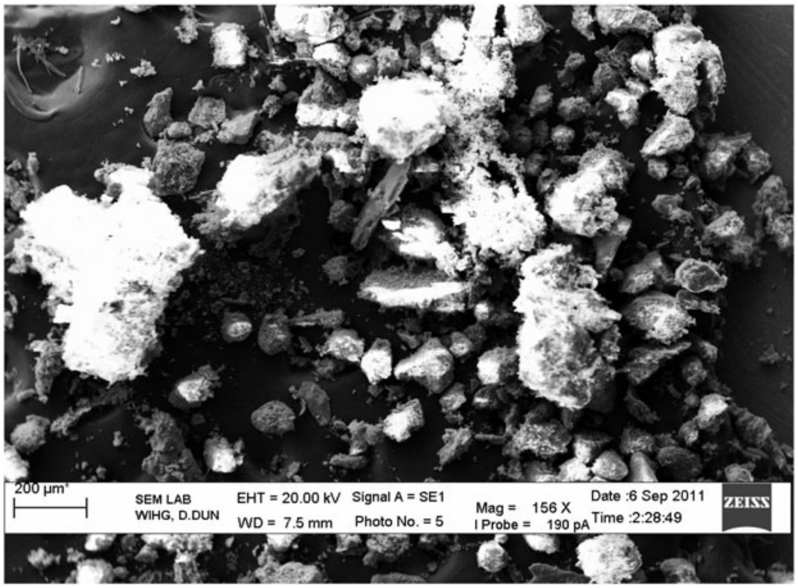

Fig. 3. Electron micrograph of fly ash after treatment of aqueous solution (60 mg/L Cr(VI) solution at initial pH 1.0).

Fig. 7. Under strong acidic conditions, the chromate ion exists predominantly in the form of hydrogen chromate ion and the fly ash surface gets protonated [36] (Fig. 7(A)). The hydrogen chromate ion is a monovalent ion with a weak hydration sphere. When hydrogen chromate ion comes in contact with the protonated TO_4^{4-} moieties of acidified fly ash, it forms hydrogen bonded complex hence the adsorption (Fig. 7(B)).

3.2. Batch adsorption studies

3.2.1. Effect of adsorbent (fly ash) dose

The effect of adsorbent dose on percent chromium removal was studied by varying the adsorbent dose from 10 to 40 g/L, at 10 mg/L hexavalent chromium concentration (Fig. 8). The result indicated an increase in percentage chromium removal from 4.0 to 10.1% with the increase of fly ash dose from 10 to 40 g/L.

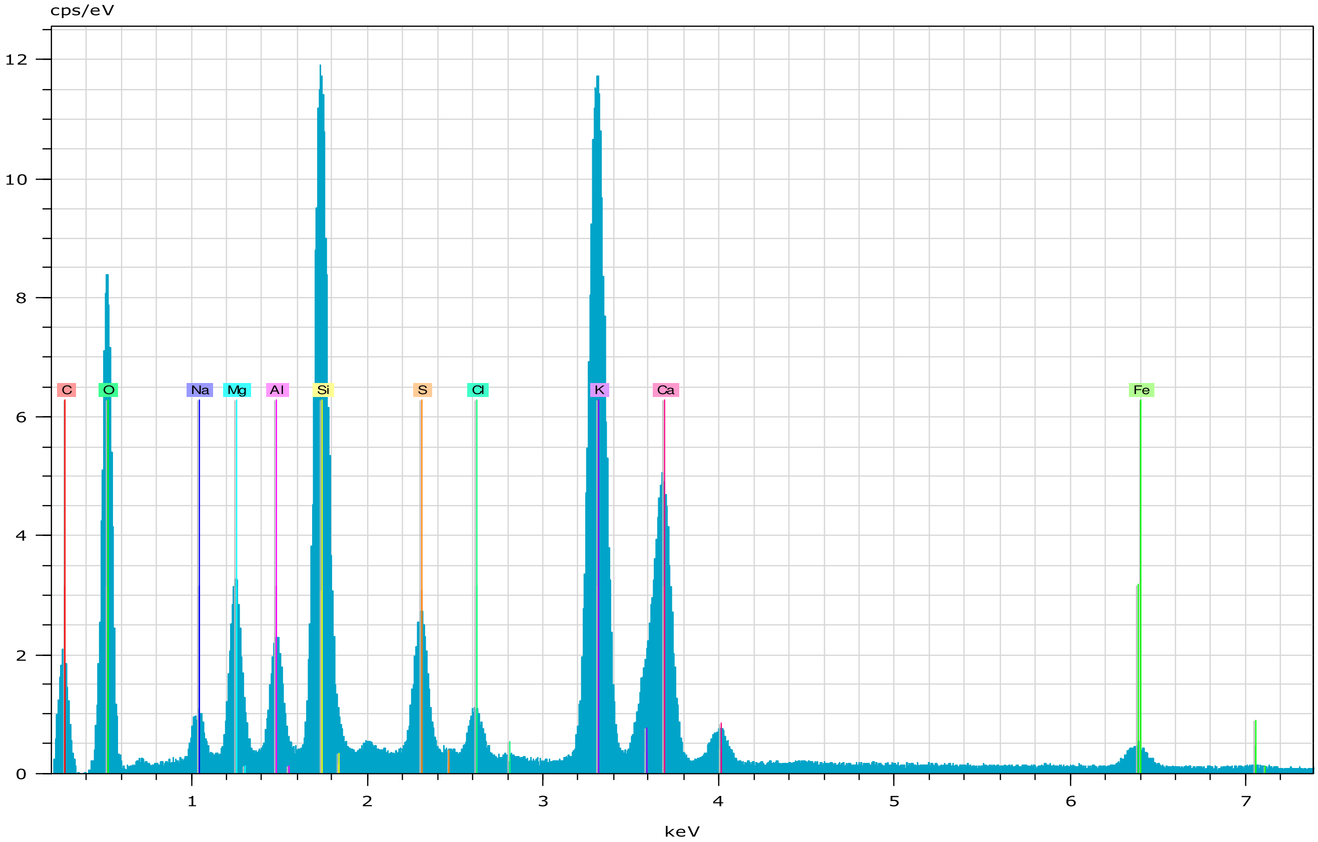

Fig. 4. EDX spectra of fly ash.

Increase in percent removal is accounted to the increase in surface area and number of adsorption sites with the increase in adsorbent dose [16,37]. On the other hand, a decrease in the chromium ion uptake (q_e) was observed with an increase of fly ash dose. The decrease in chromium ion uptake (q_e) may be due to the availability of lesser number of Cr(VI) ions per unit mass of the fly ash due to which the active sites may remain unsaturated during the adsorption process [16,38].

3.2.2. Effect of pH

The pH of solution is the most important parameter among all other parameters, as it determines the adsorption efficiency [39–42]. It influences the speciation of metal ions and the charge on the sorption sites [43–45].

When pH of the solution was lowered from 5 to 1, an increase in chromium adsorption was observed (Fig. 9) The adsorption at pH 5 was 8.2% which increased to 81.4% at pH 2 and 98.6% at pH 1. The fact has already been discussed under FTIR analysis.

3.2.3. Effect of contact time

The plot between percent Cr(VI) removal and time (Fig. 10) indicates that the rate of Cr(VI) adsorption was faster at the initial stage and then became slow after 30 min till the attainment of equilibrium. It was observed that 69.9% chromium ion removal took place in the first 5 min upon addition of fly ash. When contact time was increased from 5 to 60 min, the percentage removal of chromium ions subsequently increased from 69.9 to 98.1% and then becomes almost constant (Fig. 10).

Various studies have postulated that initially diffusion occurs by external mass transfer followed by intraparticle diffusion [46–48]. Initially, there is a large concentration gradient between the fluid and the adsorbent surface leading to a faster transfer of adsorbate onto the adsorbent surface. However, with the passage of time, predominantly intraparticle diffusion of adsorbate from surface of adsorbent to internal adsorption sites of adsorbent occurs, which is a slow process [16]. The postulate is further supported by applying Weber-Morris model for intraparticle diffusion. According to Weber-Morris model for

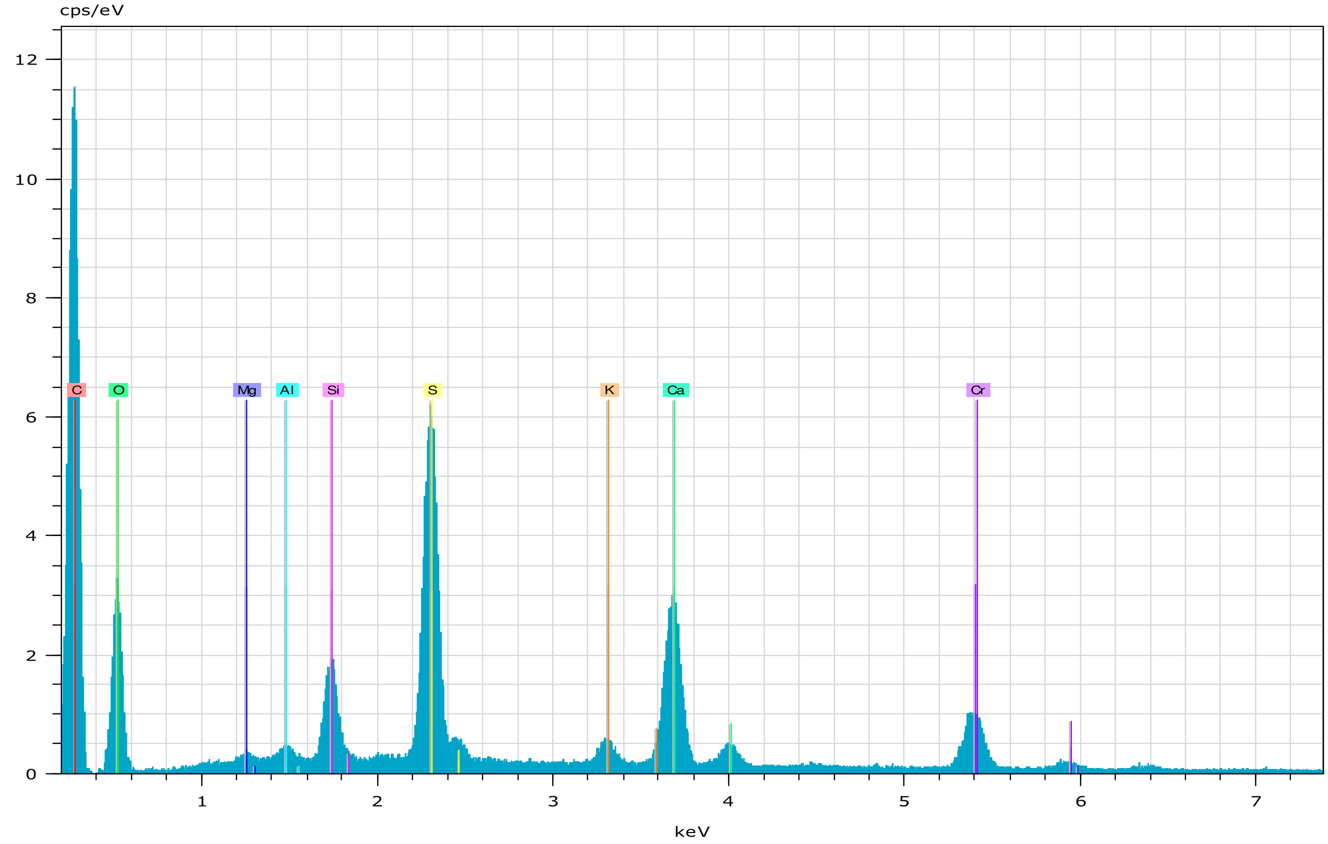

Fig. 5. EDX spectra of fly ash after treatment of aqueous solution (60 mg/L Cr(VI) solution at initial pH 1.0).

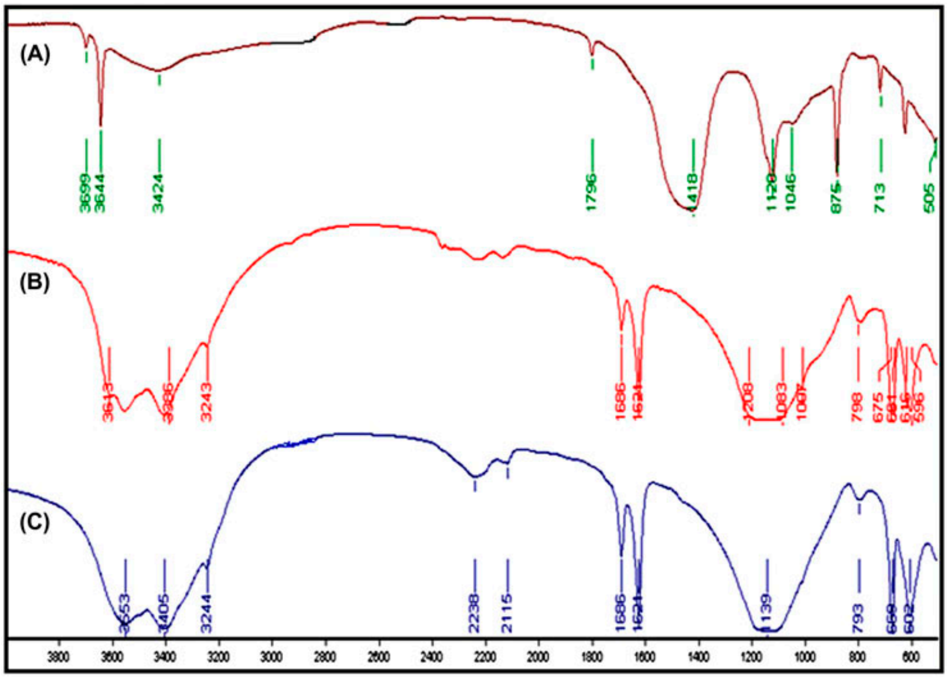

Fig. 6. FTIR spectra of (A) fly ash, (B) acidified fly ash (treated with distilled water acidified to pH 1 using H_2SO_4), and (C) fly ash treated with potassium dichromate under acidic conditions (pH 1).

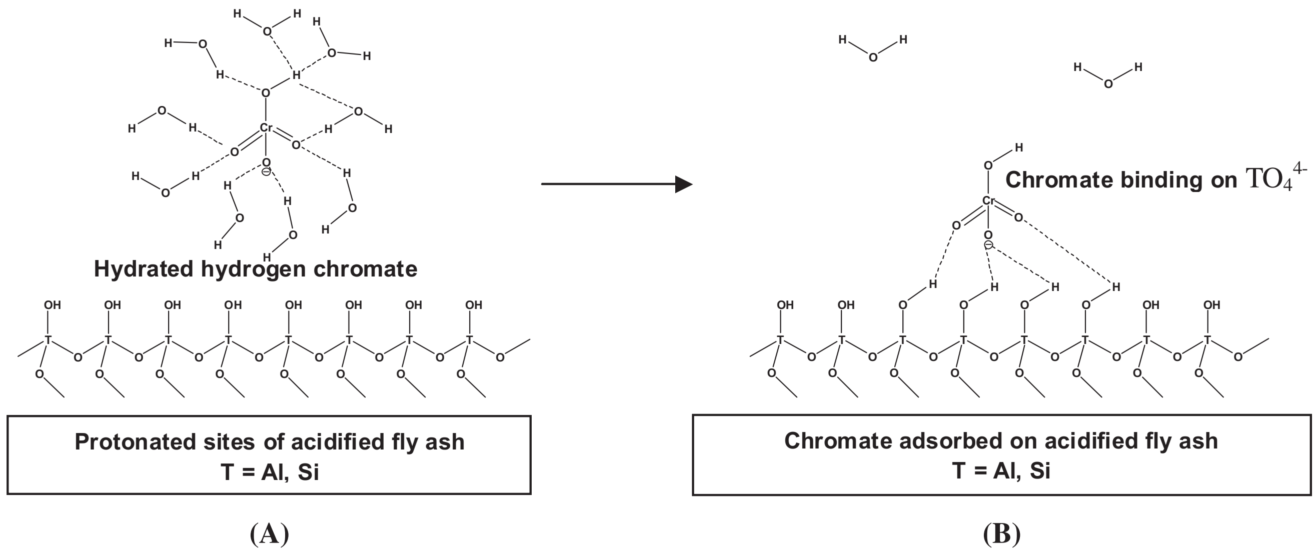

Fig. 7. Proposed mechanism for the adsorption of chromate ion on the acidified fly ash material (A) before adsorption (B) after adsorption.

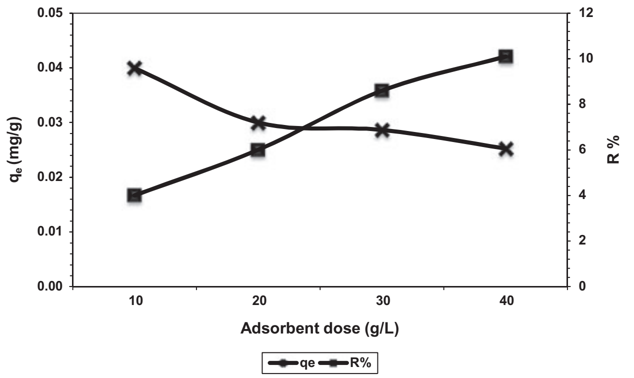

Fig. 8. Effect of adsorbent (fly ash) dose on % chromium removal and its uptake (conc. of Cr(VI) in aqueous solution—10 mg/L, contact time—2 h at 200 rpm, pH—5.5, temperature—25 ± 1 ˚C).

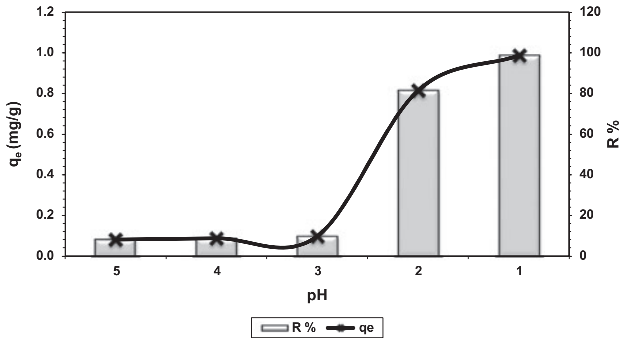

Fig. 9. Effect of pH on % chromium removal and its uptake (conc. of Cr(VI) in aqueous solution—10 mg/L, contact time—2 h at 200 rpm, adsorbent dose—10 g/L, temperature—25 ± 1 ˚C).

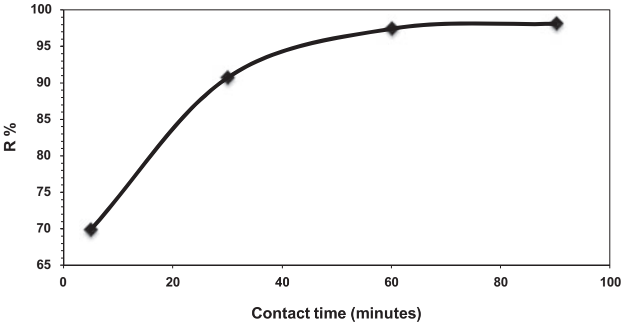

Fig. 10. Effect of contact time on % chromium removal ($[\mathrm{Cr(VI)}]_{\mathrm{in}}$ = 10 mg/L, adsorbent dose—10 g/L, pH—1, temperature—25 ± 1 ˚C).

intraparticle diffusion during adsorption, solute uptake varies almost proportionally with $t^{0.5}$ [48,49]. The Weber-Morris equation for intraparticle diffusion can be written as:

$$q_t = k_{\mathrm{int}} t^{0.5}$$

where k_{int} = intraparticle diffusion rate constant.

Fig. 11 depicts the plot between q_e vs. $t^{0.5}$. The plot is multilinear in shape and does not pass through origin, suggesting intraparticle diffusion is not the sole rate-controlling step in the adsorption of Cr(VI) on fly ash. As can be predicted from the Fig. 11, initial slope is steep indicating fast adsorption at the external surface and there is a decrease in the slope of the plot indicating intraparticle diffusion and nearly horizontal plot in the final stage indicating the equilibrium

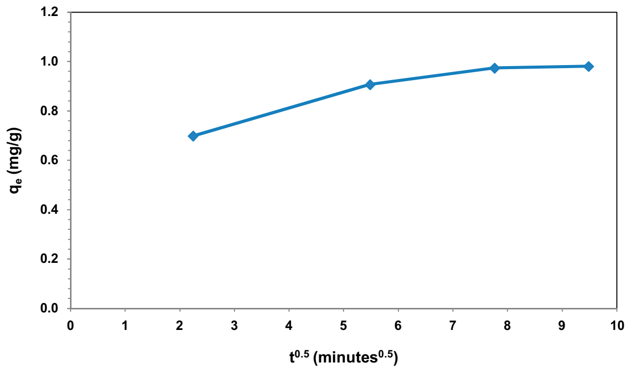

Fig. 11. Webber-Morris plot for intraparticle diffusion of Cr(VI) upon adsorption on fly ash.

condition. This indicates that the adsorption is controlled simultaneously by external mass transfer and intraparticle diffusion process.

3.2.4. Effect of initial ion concentration

It is evident from the Fig. 12 that chromate ion uptake increases with the increase in initial Cr(VI) concentration of aqueous solution. When initial metal ion concentration of Cr(VI) in aqueous solution increased from 10 to 80 mg Cr/L, percentage removal decreased from 98.60 to 16.13%. Increase in the number of Cr(VI) ions for the same amount of adsorbent may be the reason for the decrease in removal efficiency [16]. The Cr(VI) uptake increased with the increase in initial ion concentration of Cr(VI) up to 60 mg Cr/L. Because increase in Cr(VI) ions leads to complete utilization of adsorption surface and available active sites, which was otherwise not possible at low concentration [16]. A decrease in chromate ion uptake was observed after 60 mg Cr/L. This may be accounted to the saturation of the active adsorption site of the adsorbent at 60 mg Cr/L concentration.

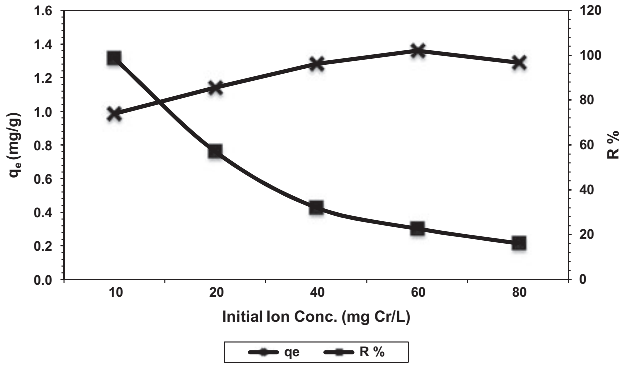

Fig. 12. Effect of initial Cr(VI) concentration on % chromium removal and uptake (adsorbent dose = 10 g/L, pH = 1, contact time = 90 min at 200 rpm, temperature = 25 ± 1˚C).

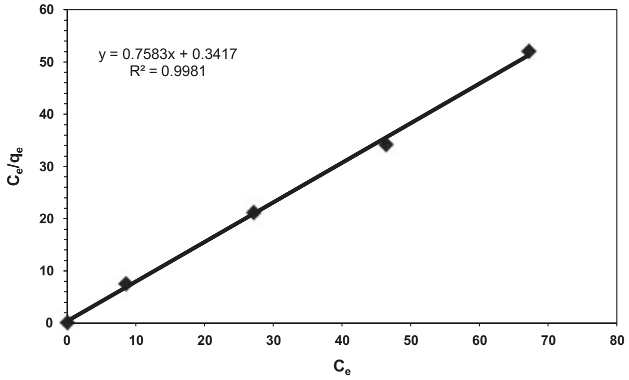

Fig. 13. Langmuir isotherm for fly ash.

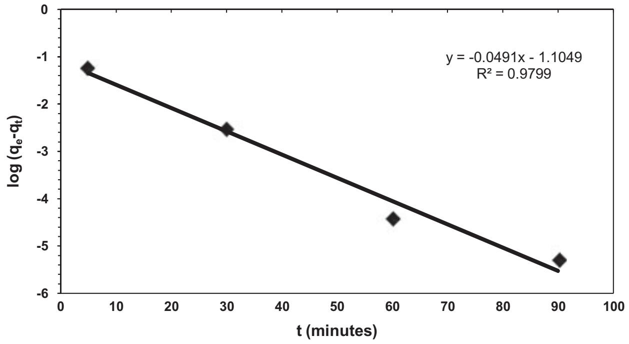

Fig. 14. Lagergren pseudo-first-order adsorption kinetic plot for adsorption of Cr(VI) on fly ash.

3.3. Equilibrium studies

The Langmuir isotherm is applied to the data generated from the study of variation in initial Cr(VI)

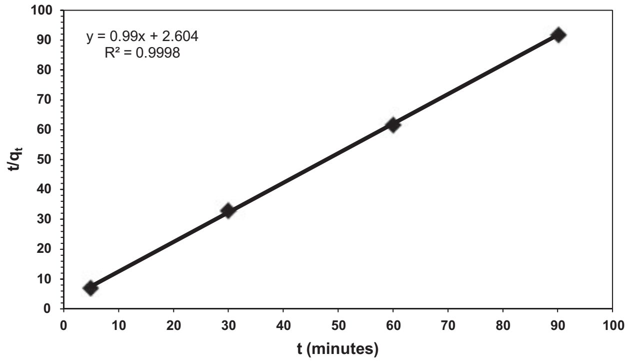

Fig. 15. Lagergren pseudo-second-order adsorption kinetic plot for adsorption of Cr(VI) on fly ash.

Table 1
Comparison of various kinetic model parameters for Lagergren pseudo-first-order and pseudo-second-order adsorption kinetic plot

Adsorbent	Exp. q_e (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q_e (mg/g)	$K_{1,\text{ads}}$ (min^{-1})	R^2	q_e (mg/g)	$K_{2,\text{ads}}$ (min^{-1})	R^2
Fly ash	0.986	0.137	0.1128	0.979	1.01	0.376	0.999

concentration. It was observed that Langmuir isotherm provides an excellent fit to the equilibrium adsorption data for fly ash.

Fig. 13 shows linear fit diagram of Langmuir adsorption model with good correlation coefficient of 0.998. High value of correlation coefficient confirmed the monolayer adsorption of Cr(VI) on the adsorbent surface. Values of q_m, adsorption energy (*b*), and dimensionless factor (R_L) were determined from this linear fit diagram.

The adsorption capacity to form a monolayer (q_m) was found to be 1.319 mg/g, while adsorption energy (*b*) was 2.22 L/mg. Further, separation factor R_L was calculated from the above graphs and it was found that R_L remained between 0.007 and 0.763 for fly ash. The value lies between 0 and 1 which indicates a favorable adsorption phenomenon.

3.4. Adsorption kinetics

Adsorption data obtained from the contact time variation experiment were fitted in the Lagergren pseudo-first-order and pseudo-second-order adsorption kinetic model. Figs. 14 and 15 depict the linear fit diagram of Lagergren pseudo-first-order and pseudo-second-order adsorption kinetic plot for raw fly ash with correlation coefficient of 0.979 and 0.999, respectively. From these linear plots q_e and rate constants were obtained. A comparison between both adsorption kinetic models is given in Table 1.

From Table 1 it is evident that coefficient of correlation is high for pseudo-second-order kinetic model and the values of q_e drawn for the same model are in agreement with experimental q_e for fly ash as adsorbent.

4. Conclusions

The present study focuses on the utilization of biomass derived fly ash generated from Waste-to-Energy power plant as an excellent material for the removal of Cr(VI) from aqueous solution. The adsorption is highly pH dependent and at low pH interaction between monovalent oxyanions of chromium and protonated fly ash surface leads to adsorption. The kinetic study suggests the presence of external mass transfer and intraparticle diffusion phenomenon in the adsorption of Cr(VI) by these material. The kinetics of Cr(VI) adsorption on fly ash follows pseudo-second-order kinetics and equilibrium adsorption data indicate monolayer adsorption of Cr(VI) on fly ash. Thus, the material is a waste which finds application as an adsorbent for remediation of wastewater system. Further studies are required to improve the efficiency of this material by modification and the material can further be explored with suitable modification for various water and wastewater pollutant remediation.

Acknowledgment

Ms Upma Vaid is thankful to the Central University of Punjab for granting the University fellowship for her PhD program. We are highly thankful to the Director, Wadia Institute of Himalyan Geology, Dehradun, and his other staff members for providing us Laser beam particle size analysis and SEM-EDX facility for determination of physico-chemical characteristics of the material.

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