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Removal of chromium and lead from aqueous solution using industrial wastes: batch and column studies

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ABSTRACT

The rotary kiln waste (dolochar) generated in sponge iron plants has been converted into a low-cost adsorbent by heat activation for the removal of chromium and lead from aqueous solution. The effects of particle size, contact time, sorbent dosage, adsorbate concentration, pH and temperature on the sorption of both the metal ions were studied in batch experiments. Kinetic studies were also conducted to have an idea on the sorption mechanism of the process. The uptake of lead was found to be more than that of chromium. Adsorption on dolochar followed Freundlich isotherm. The kinetics of the Cr(VI) and Pb(II) adsorption on the kiln waste was found to follow a pseudo-second-order rate equation. It was observed that the sorption process was spontaneous and the adsorbent is suitable for sorption of both ions. In addition, fixed bed studies were performed to simulate real-life conditions. The experiments were also performed to regenerate the column by 0.2 N HNO_3 for lead–dolochar system and 0.5 M NaOH for chromium–dolochar system for reuse.

Keywords: Adsorption; Dolochar; Heavy metals; Isotherms; Column study; Breakthrough curve

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1. Introduction

Water pollution due to toxic heavy metals such as chromium, lead, manganese, copper, iron, zinc, etc. has been a major cause of concern for the society. Among these heavy metals, chromium and lead are toxic metals found in several industrial discharges and effluents. The permissible limits of Cr(VI) of 0.5 mg/L and Pb(II) of 0.1 mg/L in industrial effluents are stipulated by the environment protection agency in India. But, these metal ions in the mining and industrial effluents are often found to be more than the permissible limits [1]. Safe and effective disposal of heavy-metal-bearing wastewater is a difficult task due to the fact that technical, environmental and cost-effective feasible treatments are scanty. Although number of methods such as ion exchange, reverse osmosis, precipitation and adsorption, etc. exist to remove these toxic metal ions from industrial effluents, the literature survey suggests that most versatile and widely used method is the method of adsorption. Activated carbon has been a standard adsorbent for removal of heavy metals from industrial wastewaters since long. In the last few decades, researchers have shown lot of interest to develop low-cost adsorbents as a substitute to activated carbon.

Literature survey suggests that all low-cost adsorbent materials ranging from industrial waste products to agricultural waste products have been developed for the removal of metals from natural and industrial wastewaters [2–8]. Such materials range from industrial waste products to agricultural waste products such as fly ash, carbonaceous material, metal oxides, zeolites, moss, lignin, clays, biomass, peanut hulls, human hair, goethite, etc. Still researchers are in the process of using new industrial wastes generated from different industries as adsorbents for removal of metals from wastewater.

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Sponge iron plants produce dolochar as a byproduct during the production of direct reduction of iron by rotary kiln. This material causes a disposal problem. In view of above facts, an attempt has been made to assess the sorption capacity of dolochar as an adsorbent considering its carbon content and inherent porosity. Further the adsorption studies for the removal of Cr(VI) and Pb(II) ions using the sponge iron plant wastes has not been reported.

2. Material and methods

This study was conducted in the Environmental Engineering Laboratory, Department of Civil Engineering, Veer Surendra Sai University of Technology, Odisha, in 2015–2016. The details of materials and methods of the study are as follows:

2.1. Reagents

The stock solutions of Pb(II) and Cr(VI) (1,000 mg/L) were prepared by dissolving the required amounts of analytical reagent grade of anhydrous lead nitrate ($Pb(NO_3)_2$) and potassium dichromate ($K_2Cr_2O_7$), respectively, in double-distilled water. Different concentrations of these two solutions were then made from the stock solutions. Dilute H_2SO_4 or NaOH solutions were added to maintain the pH of the solution.

2.2. Instruments

pH measurements were made using a Orion make pH meter. The lead concentrations were measured using Rayleigh WFX-1308 atomic absorption spectrophotometer. A UV-Visible spectrophotometer (AU-2701, Systronics, India) was used for measuring hexavalent chromium by complexing with 1,5-diphenyl carbazide in acid solution at 540 nm. The constituents of dolochar were analyzed following the routine standard methods of chemical analysis. A scanning electron microscope with an electron dispersive X-ray spectrometer (SEM/EDX, JEOL (Japan), JSM-6300F) was used to study the surface morphologies and elemental composition of the dolochar.

2.3. Preparation of adsorbent

The waste material (dolochar) was collected from one of the sponge iron plants operating in the western part of Odisha, India. The impurities present in the dolochar were removed by washing it thoroughly with distilled water followed by drying the dolochar at 200°C. Then the product was cooled at room temperature and activated in a muffle furnace at 600°C for 1 h. The condition of activation was optimized to obtain the best sorption capacity. The product so obtained was sieved to obtain in the range of three particle sizes viz. 360, 505 and 795 micron. Finally, the material was kept in desiccators until used.

2.4. Adsorption method

Batch sorption studies were mainly conducted to obtain data on the rate and extent of sorption. The studies were conducted by taking a series of 50 mL test tubes filled with 10 mL of adsorbate with varying initial concentrations from 10 to 50 mg/L and adjusted to desired pH and temperature. The dolochar of known quantity was added into each test tube and put in a mechanical shaker at 150 rpm for attaining equilibrium concentration. After 1 h, the supernatant solution was filtered and analyzed for aqueous metals. The effect of temperature on sorption was assessed at 30°C, 40°C and 50°C. The effect of pH was studied from 1 to 8.

2.5. Column studies

Fig. 1 shows the schematic of the experimental setup used in the study. The column was made up of perspex having 4.5 cm in diameter and 55 cm in length. The column was packed with dolochar having layers of glass wool at top and bottom of adsorbent. The column was placed in a vertical position and operated in up-flow mode having flow regulation device at the inlet and outlet of column. The column was then filled with water and the required amount of dolochar was put inside the column. Then the column was allowed to remain in quiescent condition for full settlement of adsorbent. The column was operated up to a point when 90% of the breakthrough capacity was attained. Regeneration of column with suitable chemicals has also been undertaken to restore the sorption efficiency of the column for reuse.

3. Results and discussion

Figs. 2(a) and (b) show the SEM photograph of dolochar before and after adsorption. Fig. 2(a) clearly reveals the porous texture of the product. The density, porosity and point of zero charge of the material were found to be 3.25 g/cc, 67.5% and 6.4, respectively. Surface area of the sample as determined by the Brunauer-Emmett-Teller method was 15.36 m^2/g. Fig. 3(a) shows the EDX spectrum before adsorption indicating that

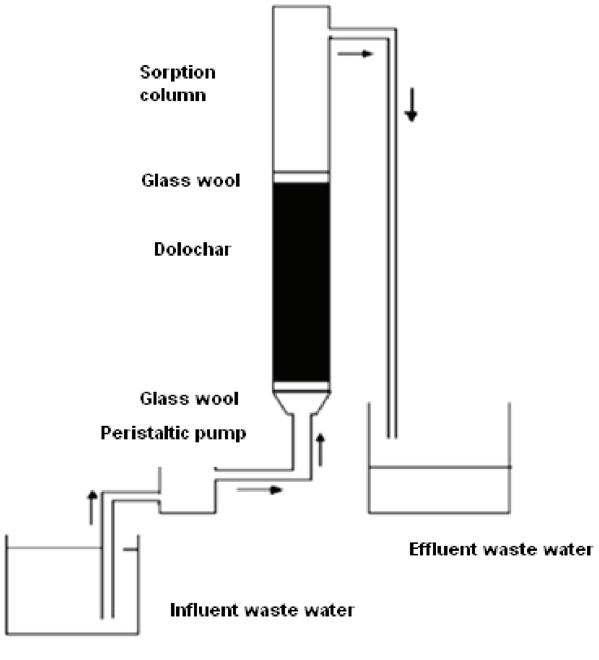

Fig. 1. Schematic diagram of fixed bed column experimental setup.

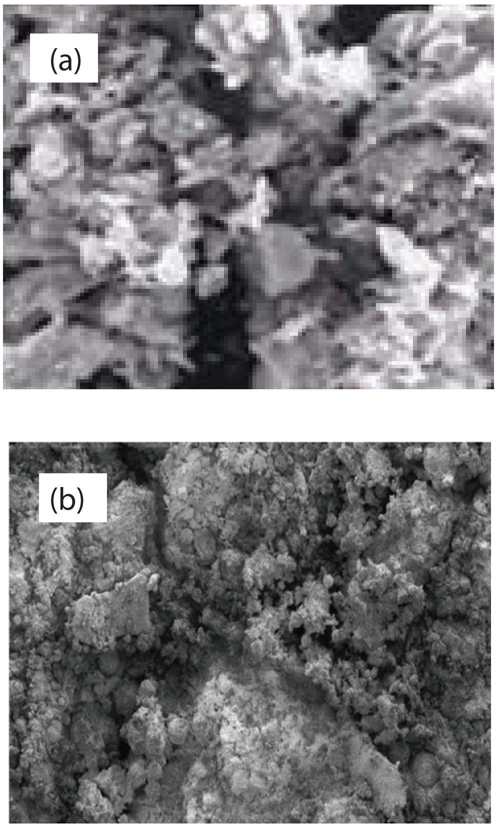

Fig. 2. SEM photograph of dolochar (a) before adsorption and (b) after adsorption.

C, Si, O, Ca, Mg and Fe are the major elements present in the dolochar. Analysis of the sample indicates that both carbon and silica can be considered as a good source of adsorption. Fig. 3(b) shows the EDX spectrum after adsorption indicating the adsorption of metal ions on dolochar.

3.1. Adsorption studies

The adsorption of metal ions on sample was obtained by calculating the difference between the initial and final concentration in solution. The removal capacity *q* (mg/g) of both metal ions was calculated as follows:

$$q_e = \frac{\left(C_0 - C_t\right)V}{W} \tag{1}$$

where C_0 (mg/L) is the initial metal ion concentration, C_t (mg/L) is the metal ion concentration at any time *t* (min), *V* (L) is the volume of the solution and *W* (g) is the weight of adsorbent used. This equation was used to compare the adsorption capacity of dolochar by varying various physical and chemical parameters.

3.1.1. Effect of particle size

Batch adsorption experiments were conducted at pH 6 ± 0.1, room temperature at 30°C with an initial concentration of 10 mg/L and a sorbent dose of 10 g/L for different particle size. Fig. 4 shows the effect of the particle sizes on the metal sorption capacity of Cr(VI) ions. It was observed that by decreasing the particle size from 795 to 505 μm, the equilibrium concentration was decreased from 1.42 to 0.62 mg/L, the percentage uptake and sorption capacity was increased from 0.858 to 0.938 mg/g, respectively.

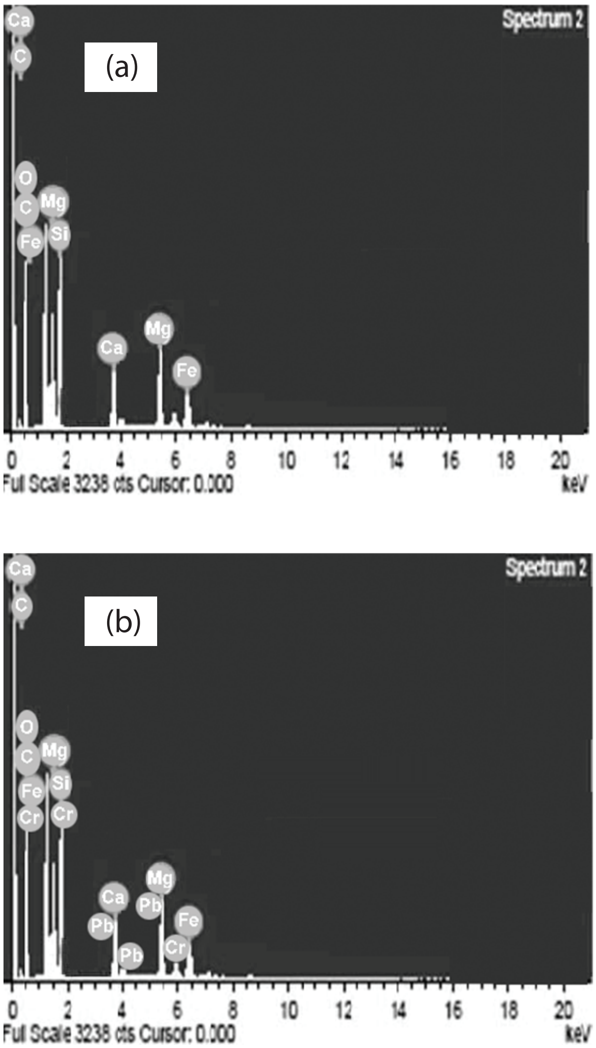

Fig. 3. EDX spectrum of dolochar (a) before adsorption and (b) after adsorption.

As the particle size was further decreased from 505 to 360 μm, the equilibrium concentration was decreased from 0.62 to 0.56 mg/L, and the percentage uptake and sorption capacity was increased from 0.938 to 0.944 mg/g, respectively. Similar observations were made for Pb(II).

Hence it was observed that the percentage uptake of metal ion increased with decrease in particle size of dolochar. It is fact that decreasing the particle size will increase the surface area per gram of the sorbent, which will provide more number of binding sites, thus increases the sorption capacity. However, there was no substantial increase in metal uptake capacity due to decrease of particle size from 505 to 360 μm. Therefore, the particle size of 505 micron was selected for detail kinetic study.

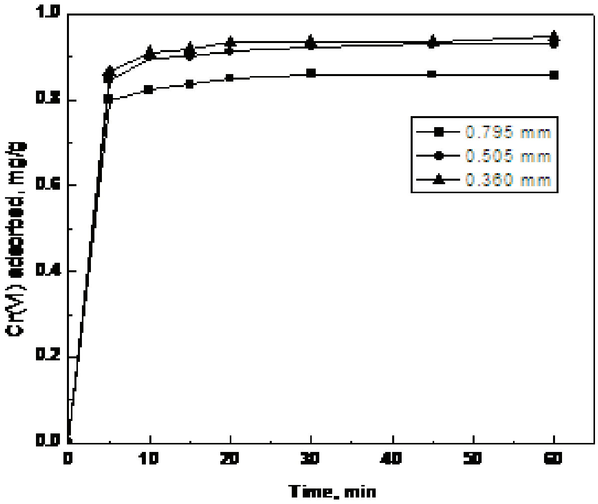

Fig. 4. Effect of particle size on Cr(VI) adsorption capacity (initial concentration 10 mg/L, pH 6, temperature 30°C, adsorbent dose 10 g/L).

3.1.2. Effect of contact time

The effect of contact time between adsorbent and adsorbate was studied by varying the contact time in the range of 5–60 min. Experiments were conducted varying the metal ions concentration from 10 to 50 mg/L keeping other parameters such as pH, temperature, particle size, adsorbent dose constant. Figs. 5(a) and (b) show the effect of contact time on uptake capacity of Cr(VI) and Pb(II) by dolochar at different time intervals. It was observed that the rate of adsorption of metal ions was rapid during the initial period. Beyond 30 min, slower rate of sorption indicated the conditions of equilibrium.

3.1.3. Effect of adsorbent dosage

The potential of adsorbent dosage to adsorb metal ions for a given initial concentration of the sorbent was studied. Fig. 6 shows the effect of adsorbent dosages on Cr(VI) uptake for 10 mg/L at 303 K. The Experimental results revealed that the percentage of adsorption increased with increase in adsorbent dosages. This was in fact expected since increasing the adsorbent dosage provides greater surface area or higher adsorption sites for a fixed metal concentration [9–11]. The sorption capacity at equilibrium for the doses of 5, 10 and 15 g/L was obtained as 1.820, 0.938 and 0.630 mg/g, respectively. There was a marginal decrease in the sorption capacity for 10 and 15 g/L. Similar observations were also made for Pb(II). Hence, the sorbent dose of 10 g/L of dolochar seemed to be optimum and was selected for the detailed kinetic study.

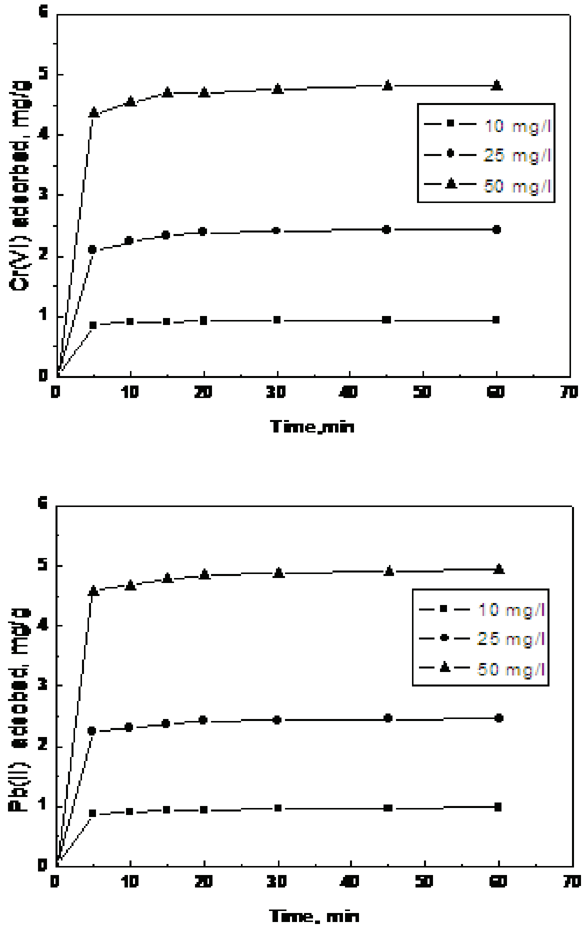

Fig. 5. Effect of contact time on Cr(VI) and Pb(II) adsorption efficiency (pH 6, temperature 30°C, particle size 505 micron, adsorbent dose 10 g/L).

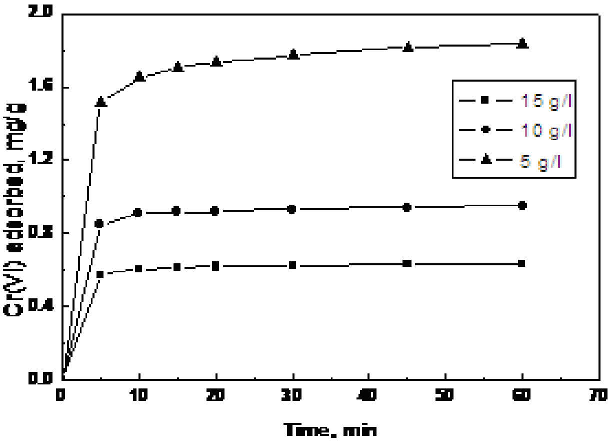

Fig. 6. Effect of adsorbent dose on Cr(VI) adsorption efficiency (initial concentration 10 mg/L, pH 6, temperature 30°C, particle size 505 micron).

3.1.4. Effect of pH

In the adsorption process, the adsorbent surface acquires positive or negative charge depending on pH of the solution. Fig. 7 shows the effect of pH varying from 1 to 8 on the uptake capacity of Pb(II) and Cr(VI). It was observed from the figure that with increase in pH from 1 to 8, the lead uptake capacity increased from 0.56 to 0.98 mg/g, whereas chromium uptake by dolochar decreased from 0.97 to 0.76 mg/g. This indicates that the adsorption of chromium is better at acidic pH in comparison with alkaline pH [12–17]. At pH 6, uptake capacity of dolochar for both the metal ions was same. Therefore, optimum pH for removal of both ions was chosen as 6 for all the studies.

3.1.5. Effect of temperature

Figs. 8(a) and (b) show the temperature dependence of Cr(VI) and Pb(II) adsorption by dolochar, respectively. The study was conducted at a constant initial metal ion concentration of 10 mg/L for different temperatures (288, 303, 313 and 323 K). From the figures, it was found that increase in temperature increased the metal uptake capacity indicating chemisorption.

3.1.6. Adsorption isotherms

Isotherm studies were conducted by varying the sorbent dose and keeping other parameters such as metal concentration, sorbent size, temperature and pH constant. The relative parameters of two adsorption isotherm models, Langmuir and Freundlich, determined at 30°C temperature are shown in Table 1. The best-fit equilibrium model was determined on the basis of regression correlation coefficient R^2. It follows Freundlich model closely. The adsorption capacity of dolochar for both Cr(VI) and Pb(II) was compared with the reported values [1,18–23] for waste materials and shown in Table 2. From the results, it is evident that dolochar is comparable with many adsorbents for treating wastewater containing Cr(VI) and Pb(II) metal ions.

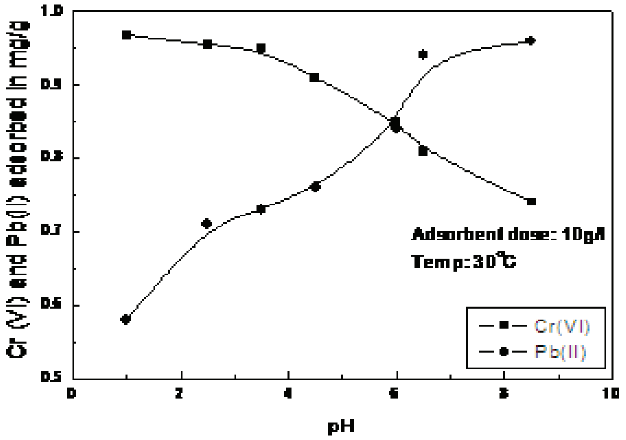

Fig. 7. Effect of pH on Cr(VI) and Pb(II) adsorption capacity (contact time 60 min, initial concentration 10 mg/L, temperature 30°C, particle size 505 micron, adsorbent dose 10 g/L).

3.1.7. Kinetics of adsorption

For evaluating the adsorption kinetics of Cr(VI) and Pb(II), pseudo-first-order and pseudo-second-order kinetic models were employed to fit the experimental data obtained at different temperatures to evaluate the adsorption kinetics of metal ions. The linear forms of both the equations are as follows:

$$\text{Pseudo-first-order kinetics}: \log\left(q_e - q\right) = \log q_e - \frac{K_1}{2.303}t \qquad (2)$$

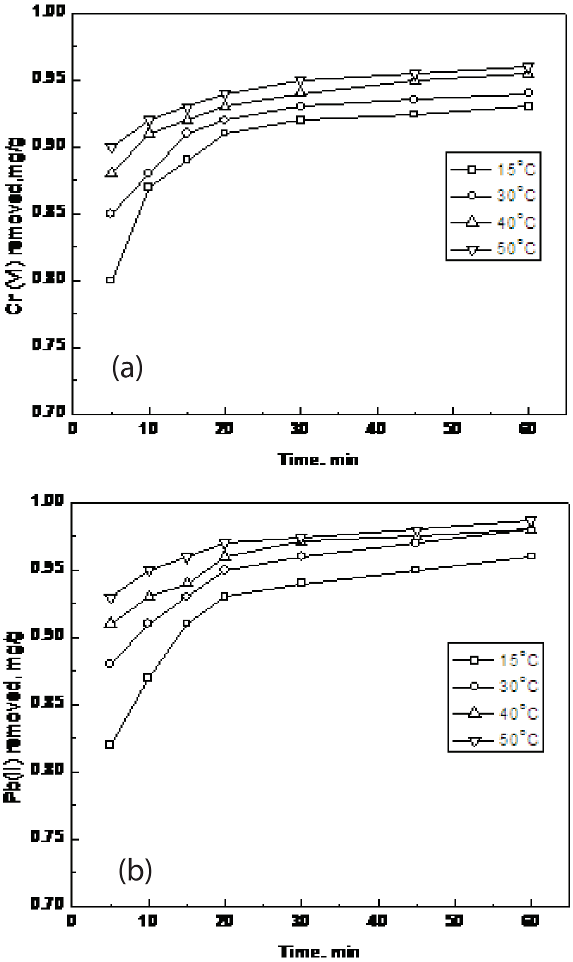

Fig. 8. Effect of temperature on (a) Cr(VI) and (b) Pb(II) adsorption capacity (initial concentration 10 mg/L, pH 6, particle size 505 micron, adsorbent dose 10 g/L).

Table 1
Sorption isotherm constants and correlation coefficients for lead and chromium ions

Metals	Langmuir isotherm constant $\left[q_e = \frac{Q_{\max} bC}{1+bC}\right]$			Freundlich isotherm constant $(q_e = K_F C^{1/n})$		
	$Q_{\max}$ (mg/g)	b (L/mg)	R^2	K_F (L/g)	$1/n$	R^2
Pb(II)	20.89	0.639	0.888	10.88	0.225	0.915
Cr(VI)	15.89	1.616	0.989	1.01	0.585	0.987

$$\text{Pseudo-second-order kinetics}: \frac{t}{q} = \frac{1}{K_2 q_e^{\ 2}} + \frac{t}{q} \tag{3}$$

where q_e and q_t are the metal ions adsorbed per unit weight of adsorbent (mg/g) at equilibrium at any time t, respectively; K_1 is the rate constant for pseudo-first-order reaction and K_2 is the rate constant for pseudo-second-order reaction. Kinetic parameters and correlation coefficients of different models are given in Table 3. The correlation coefficients of pseudo-second-order kinetic model were observed to be highest and almost equal to 1 which is the best fitted model in most of the cases as compared with pseudo-first-order kinetic model or other models [24–27].

Table 2
Comparison of adsorption capacities of various adsorbents for chromium and lead adsorption

Adsorbents	Adsorption capacity (Q_{max}) (mg/g)		Reference
	Chromium	Lead	
Wall nut sawdust	–	4.48	[18]
Bagasse fly ash	–	2.50	[19]
Groundnut husk	11.4	–	[20]
Imperata cylindrica leaf powder	–	13.50	[21]
De-oiled allspice husk	–	20.07	[22]
Exhausted coffee	1.4	–	[23]
Red mud	1.6	–	[24]
Dolochar	15.89	20.89	Present study

Table 3
Pseudo-second-order rate constant and correlation coefficients (R^2)

Models		Pseudo-first order		Pseudo-second order	
Initial metal ion concentration (mg/L)		K_1 (1/min)	R^2	K_2 (g/mg min)	R^2
Cr(VI)	10	0.069	0.967	1.669	1.0
	25	0.112	0.990	0.428	1.0
	50	0.985	0.984	0.246	1.0
Pb(II)	10	0.076	0.988	1.130	0.999
	25	0.057	0.979	0.633	1.0
	40	0.069	0.968	0.415	1.0

3.1.8. Thermodynamic parameters

The adsorption mechanism was also determined through the thermodynamic parameters such as ΔG°, ΔH° and ΔS°. The value of ΔH° and ΔS° was determined from Van't Hoff equation as given below:

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{4}$$

The ΔG° value was calculated by using the equation:

$$\Delta G° = -RT \ln K_C \tag{5}$$

where R is the gas constant, T is the temperature in Kelvin and K_C is the equilibrium constant, determined as:

$$K_C = \frac{C_A}{C_e} \tag{6}$$

In the above equation, C_A is the adsorbed amount of adsorbate at equilibrium (mg/L) and C_e is the equilibrium concentration in solution (mg/L). The values of these parameters were calculated and are presented in Table 4. Both ΔH° and ΔS° values are found to be positive suggesting chemisorption. The irreversible and stability of the adsorption process is confirmed from the positive value of entropy [28–31]. Also, as seen in Table 4, the ΔG° value is found to be negative indicating that the adsorption process is feasible and spontaneous.

4. Column operation studies

Adsorption isotherms are normally employed to obtain some preliminary parameters, but in practice the treatment plants use column-type operations. All the column experiments were conducted with distilled water spiked with 10 mg/L metal solutions for dolochar with particle size 505 micron, at bed depths of 10 cm and maintaining a constant flow rate of 10 mL/min (~2.10 $m^3/m^2/h$) for Cr(VI) and Pb(II). The studies were conducted at the room temperature of 30°C ± 2°C and the influent of pH were adjusted at 6.0 ± 0.2. The breakthrough point was considered when the ratio of effluent to influent concentration (C/C_0) reaches at 0.1. The breakthrough plots for ratio of effluent to influent concentration in the column vs. time at bed depths 10 cm are shown in Figs. 9(a) and (b) for Cr(VI) and Pb(II), respectively. It was observed that the time to achieve breakthrough was increased with the increase of bed depths. The samples were collected at certain time intervals and were analyzed for Cr(VI) and Pb(II) by using the atomic absorption

Table 4
Thermodynamic parameters for the adsorption of Cr(VI) and Pb(II)

Metal	C_0 (mg/L)	ΔH° (kJ/mol K)	ΔS° (J/mol)	ΔG° (kJ/mol)			
				288 K	303 K	313 K	323 K
Cr(VI)	10	13.88	69.92	–6.15	–6.83	–8.11	–8.51
Pb(II)	10	20.22	105.11	–7.56	–9.7	–10.31	–11.01

spectrophotometer. The volume of metal effluent treated and the requirement of dolochar up to breakthrough point have been shown in Table 5.

4.1. Column regeneration and reuse studies

The column desorption studies were subsequently carried out after complete exhaustion of the adsorption column by using 0.01 N HNO_3 for lead–dolochar and 1 M NaOH for chromium–dolochar systems, as it proved much effective to regenerate in batch studies. The metal concentration was measured after different time intervals. As the feed flows upward in the adsorption column, the lower portion of the bed is generally loaded more heavily than the upper portion. Upward regeneration results in the lightly loaded upper portion being exposed to a high concentration of the solute during regeneration and this may result in an unfavorable equilibrium during subsequent loading cycles. Hence, the regenerations were carried in the counter-current mode, that is, in the down flow mode. The counter-current operation generally reduces regeneration costs and to regenerate the volume, and increases the effluent quality. Desorption was carried out by HNO_3 and NaOH through the bed in the downward direction at a flow rate of 10 mL/min. The concentrations of metal ions were monitored after different time interval

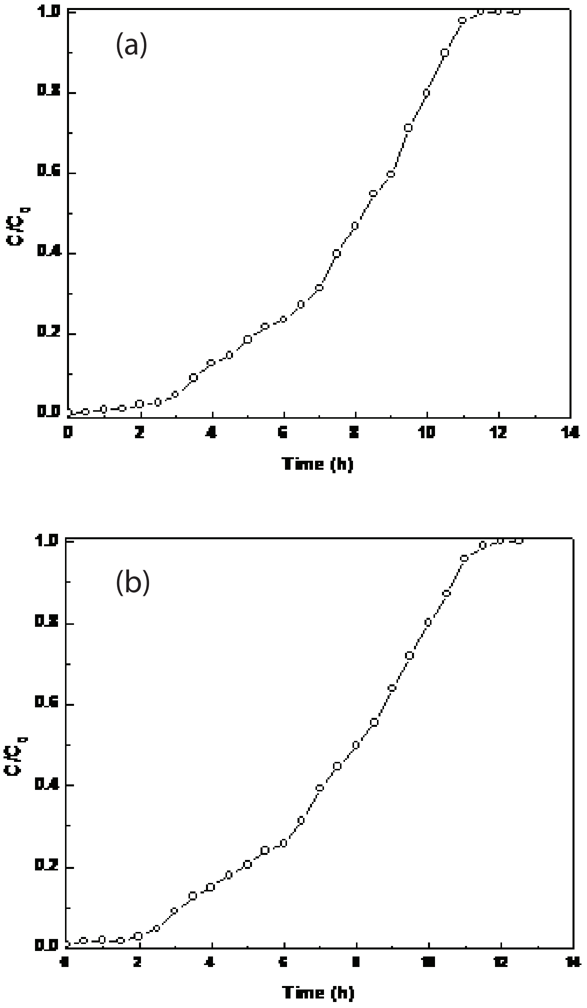

Fig. 9. Breakthrough curve for (a) Cr(VI) and (b) Pb(II) removal at initial concentration 10 mg/L.

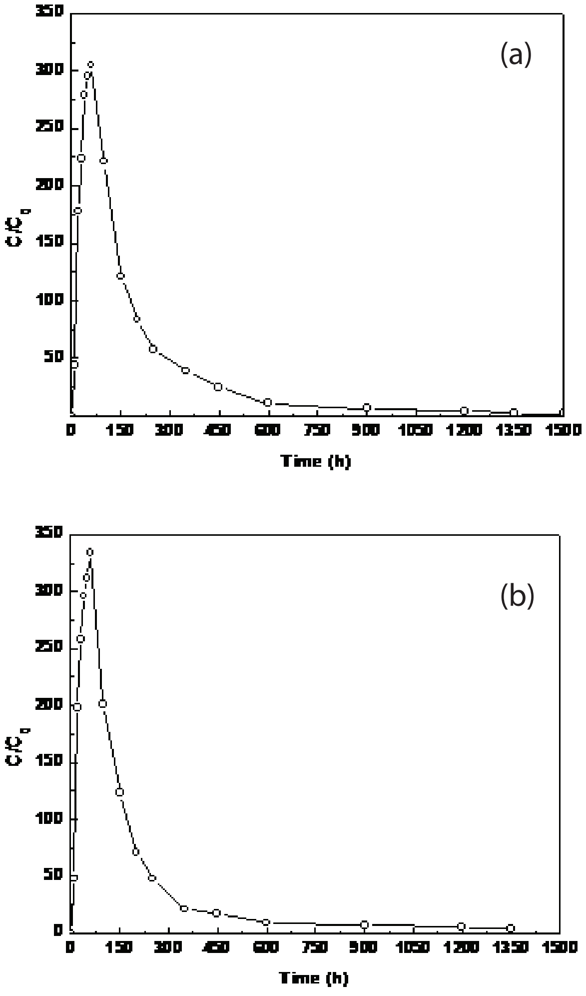

Fig. 10. Desorption profile for (a) Cr(VI) and (b) Pb(II).

Table 5
Volume of effluent treated and the mass of dolochar required up to breakthrough point

Metal	Initial concentration (mg/L)	Bed depth (cm)	10% breakthrough time (h)	Treated volume (L)	Total mass of dolochar (g)	Mass per liter (g/L)
Cr(VI)	10	10	3.8	2.26	88.39	39.10
Pb(II)	10	10	4.2	2.35	88.39	37.61

as is shown in Fig. 10. It was observed that desorption cycle took approximately 1 h, after which there was hardly any desorption. The total volume of this eluent at 1 h was 600 mL. The maximum concentration of Cr(VI) and Pb(II) was obtained at a contact time of 7 min and recorded as 300 and 330 mg/L, which is more than 30 times higher than the influent of Cr(VI) and Pb(II) concentration.

5. Conclusions

The present study reveals that the dolochar generated from the rotary kiln in the sponge iron plants can be efficiently used for the sorption of Pb^{2+} and Cr^{6+} in a wide range of concentration. The adsorbent was found to remove the metal ions more than 80% at normal conditions. The study indicated that the adsorption process is influenced by adsorbent dosages, particle size, metal ion concentration, contact time and solution pH, etc. Adsorption of Cr(VI) is highly pH-dependent. The kinetics of the Cr(VI) and Pb(II) adsorption on the adsorbent was found to follow a pseudo-second-order rate equation. The negative value of free energy and the positive values of entropy indicate the spontaneous process and higher affinity of the material for metal ions, respectively. The adsorption process is determined to be endothermic. The adsorption data fitted well to Freundlich isotherm model. The fixed bed studies have also been conducted to obtain a design model for real-life conditions. It has been possible to regenerate the column by 0.2 N HNO_3 for lead–dolochar system and 0.5 M NaOH for chromium–dolochar system.

Acknowledgments

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