Column operations for sorption of chromium and lead from aqueous solution using industrial wastes

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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 pH, sorbent dosage, adsorbate concentration, temperature, and contact time 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 adsorbents is suitable for sorption of Pb(II) and Cr(VI). In addition, fixed-bed studies were performed to simulate real-life conditions. The experiments were also performed to regenerate the column by 0.2N HNO_3 for lead-dolochar system and 0.5M NaOH for chromium-dolochar system for reuse.

*Key Words***:** Adsorption; Dolochar; Isotherms; Column study; Breakthrough curve

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 (Dubey and Gopal 2007). Chromium is harmful heavy metal ion which exists in hexavalent and trivalent forms. The permissible limits of Cr (VI) and Pb (II) in industrial effluents are stipulated 0.5 mg/l and 0.1 mg/l respectively 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 (De Filippis and Pallaghy 1994). Safe disposal of heavy metal contaminated wastewater is a challenging task due to the fact that techno-enviro-cost-effective feasible treatments are scanty (Weng et al., 1994). 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 suggest that most versatile and widely method is the method of adsorption. Activated carbon has been a standard adsorbent for removal of heavy metals from industrial wastewaters since long (Fornwalt 1966) despite being an expensive material. In last few decades, the researchers have shown lot of interest to develop low-cost adsorbents as a substitute to activated carbon.

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 2015-16. The details of materials and methods of the study are as follows;

2.1. Reagents

Stock solutions of the test sorbates were made by dissolving analytical reagent (AR) grade of potassium dichromate ($K_2Cr_2O_7$) and lead nitrate ($Pb(NO_3)_2$) in double-distilled water.

2.2. Equipments

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 (Systronics AU-2701) 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 by chemical analysis (Vogel 1989). A scanning electron microscope with an electron dispersive X-ray spectrometer (SEM/EDX, JEOL, JSM-6300F) was used to study the surface morphologies and elemental analysis of the dolochar

2.3. Preparation of adsorbent

The waste material (dolochar) was collected from the 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 one hour. The condition of actiation 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 materials was kept in a desiccator until used.

2.4. Preparation of adsorbate

The stock solutions of Pb(II) and Cr(VI) (1000 mg/L) were prepared by dissolving the required amounts of anhydrous lead nitrate and potassium dichromate (Analytical grade) respectively in 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.

2.5. Adsorption studies

Batch adsorption studies were conducted by taking a series of 50 mL test tubes filled with 10 mL of adsorbate varying initial concentrations from 10 to50 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 one hour, the supernatant solution was filtered and analyzed for aqueous metals. The effect of temperature on sorption was assessed at 30, 40, and 50°C. The effect of pH was studied from 1to 8.

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_e (mg/g) of both metal ions was calculated as

$$q_e = \frac{(C_0 - C_t)\ V}{W} \qquad\qquad\qquad (1)$$

where C_0 (mg/L) is the initial metal ion concentration, C_t (mg/L) is metal ion concentration at any time t (min), V (litre) is the volume of the solution and W (g) is the weight of adsorbent used.

2.6. Adsorption isotherms

Two adsorption isotherm models such as Langmuir and Freundlich isotherms were employed to understand the mechanism of the adsorption. The linear form of Langmuir isotherm is

$$q_e = \left(\frac{K_L b C_e}{1 + b C_e} \right) \tag{2}$$

where q_e (mg/g) is the amount adsorbed at equilibrium and C_e (mg/L) is the equilibrium concentration. The maximum amount of adsorption capacity (Q_0) and energy of adsorption (b) were determined from the slope and intercept of the linear plot of C_e/q_e against C_e. The linear form of Freundlich isotherm is

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{3}$$

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption and these are determined from the slope and intercept of the plot of $\ln C_e$ and $\ln q_e$.

2.7. Kinetic measurements

The known concentration of 10 ml metal solutions was taken in a number of glass tubes and placed in a temperature controlled mechanical shaker. Then, required quantity of adsorbent was added into each test tube, once the desired temperature was attained. At given time intervals, the test solutions were filtered and the aqueous metal ions in the supernatant were measured.

The pseudo-first order and 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 form of both the equations are as follows;

Ist order Kinetics: $\text{Log} (q_e - q) = \log q_e - \frac{Kad}{2.303} t \tag{4}$

2nd order kinetics: $\frac{t}{q} = \frac{1}{K_2 q_{e2}} + \frac{1}{q_e} t \tag{5}$

where q_e and q_t are the metal ion adsorbed per unit weight of adsorbent (mg/g) at equilibrium at any time t, respectively; K_1 is the rate constant for 1st order reaction and K_2 is the rate constant for 2nd order reactions. The above two models have been examined by each linear plot of $\log (q_e - q)$ versus t, and (t/q) versus t, respectively.

2.8. Mass transfer parameter

The particle, film diffusion and mass action-controlled mechanism of exchange are the basis of sorption/ion exchange kinetics (Boyd et al., 1947; Reichenberg 1953). It is necessary to identify the step that governs the overall removal rate of the adsorption process. The linearity behavior of the Boyd plots passing through the origin establish the fact that the rate controlling step in the adsorption process is the internal diffusion, and vice versa.

2.8.1. Boyd model

For the design purposes, it is required to distinguish between film diffusion and particle diffusion applied (Doner et al., 2003). In order to identify the slowest step in the adsorption process, Boyd kinetic equation was employed. The kinetic data was also analyzed by the procedure given by Reichenberg (1953) and Helfferich (1962). The following equations were used as:

$$F = 1 - \frac{6}{\pi r^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-D_L t \pi^2 n^2}{r^2}\right]$$

(6)

$$F = 1 - \frac{6}{\pi r^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 Bt\right]$$

(7)

Where F is the fractional attainment of equilibrium at time t and is obtained by the expression

$$F = \frac{q}{q_m}$$

(8)

Where q is the amount of metal ion adsorbed at time t and q∞ is the maximum equilibrium uptake. Bt is a function of F, which can be calculated for each value of F such as:

$$Bt = -0.04977 - \ln(1 - F)$$

(9)

$$B = \frac{\pi^2 D_l}{r^2} = \text{time constant}$$

Where, D_i is the effective diffusion coefficient of ion in the adsorbent phase, r is the radius of the adsorbent particle, assumed to be spherical and is an integer that defines the infinite series of solution. The values of Bt were plotted versus time and the linearity was employed to distinguish between the film diffusion and particle diffusion controlled adsorption. If the plot of Bt versus time is a straight line passing through the origin, then the adsorption rate is governed by particle diffusion mechanism otherwise it is governed by film diffusion.

2.8.2. Film diffusion parameter

The rate of change of metal ion concentration for film diffusion is as follows:

$$\frac{dC}{dt} = k_L A_s (C - C_s)$$

(10)

Where C is the bulk liquid phase concentration of metal ion at a time t, C_s is the surface concentration of metal ion, k_L is the external mass transfer coefficient and A_s is the specific surface area for mass transfer. It is assumed that during the initial stages of adsorption, the intraparticle resistance is negligible and the transport is mainly due to film diffusion mechanism. At t = 0 in the surface concentration of metal ion, CS is negligible and C = C_0. With this assumption equation (10) can be simplified as:

$$\left[\frac{d(C/C_0)}{dt}\right] = -k_L A_s$$

(11)

Assuming the adsorbent particles to be spherical, A_s is calculated from equation (12).

$$A_s = \frac{6S_S}{d_P \rho_P}$$

(12)

Where Ss are the sorbent mass concentration in the solution, d_p is the average particle diameter and ρ_p is the density of the sorbent. By plotting C/C_0 against t, the value of k_L may be determined from the slope at t = 0.

2.9. 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

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
(13)

The ΔG∘ value was calculated by using the equation

$$\Delta G^0 = -RT \ln K_C$$
(14)
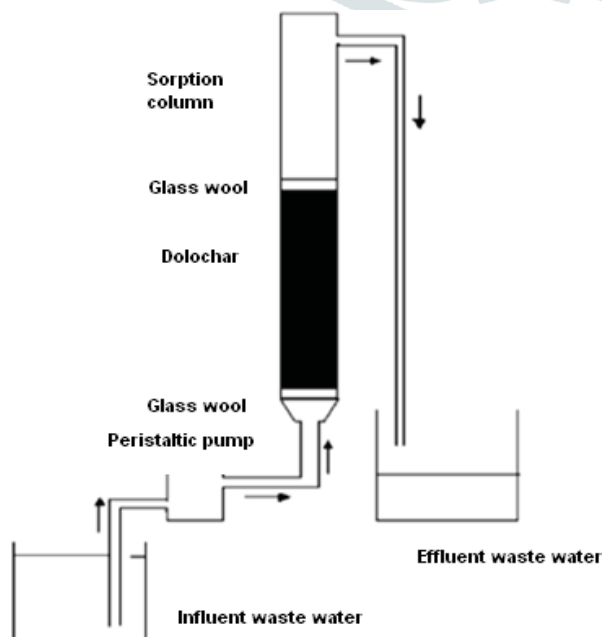
where R is the gas constant, T is the temperature in Kelvin and Kc is equilibrium constant, determined as

$$K_C = \frac{C_A}{C_e}$$
(15)

In the above equation, C_A is the adsorbed amount of adsorbate at equilibrium (mg/L) and Ce is the equilibrium concentration in solution (g/L). The plot of log Kc vs. 1/T for both metal ions can be examined to determine ΔH∘ and ΔS∘ from the slope and intercept of the plot respectively.

2.10. Column studies

Fig 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

3.1. Characterization of adsorbent material

The chemical analysis of the dolochar as determined were having Moisture content - 3.3, Volatile matter-0.84, Fixed Carbon- 22.79 ,CaO- 3.6, SiO_2- 48.4, MgO- 1.7, Al_2O_3-15.1, Fe- 4.27 %t by weight. The density, porosity, and ZPC 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 BET method was 15.36 m^2/g. Fig. 2 shows the SEM photograph of dolochar which clearly reveals the porous texture of the product. The EDX spectrum (Fig.3) shows that C, Si, Al, O, Ca, K and Fe are the major elements present in the dolochar.
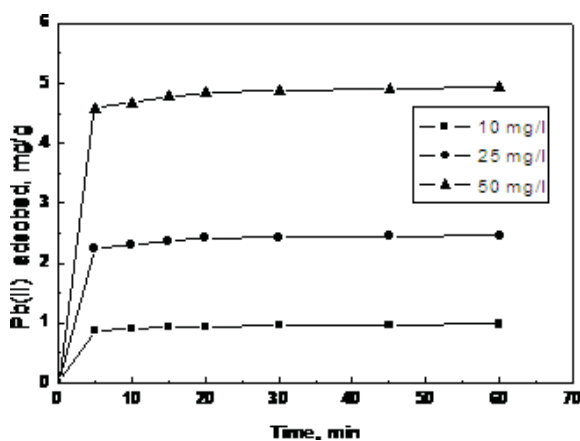
3.2. Effect of particle size

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 the effect of different 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 85.8 to 93.8% and 0.858 to 0.938 mg/g respectively.

As the particle size was further decreased from 505 to 360 μm, there was not much effect; however the equilibrium concentration was decreased from 0.62 to 0.56 mg/l, and the percentage uptake and sorption capacity was increased from 93.8 to 94.4 % and 0.938 to 0.944 mg/g respectively. Similar observations were made for Pb (II).

Hence it observed that, the percentage uptake of metal ion were increased with decrease in particle size of dolochar. Decreasing the particle size will increase the surface area per gram of the sorbent, which will provide more number of binding sites and the sorption capacity is increased. Also too small sizes will the cause of high head loss in the column operation. The particle size of 505 micron was selected for detail kinetic study.

3.3. Effect of contact time

The effect of contact time between adsorbent (10g/l) and adsorbate was studied by varying the contact time in the range of 5-60 min at 308 K. Fig. 5 & 6 shows 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 is rapid during the initial period. Beyond 30 min, slower rate of sorption indicates conditions of equilibrium.
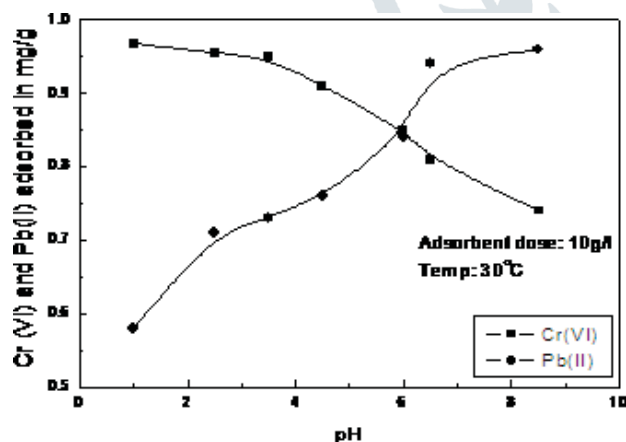
3.4. Effect of adsorbent dosage

The potential of adsorbent dosage to adsorb metal ions for a given initial concentration of the sorbent was studied. Fig. 7 shows the effect of adsorbent dosages on Cr (VI) uptake at 308 K. The initial concentration of chromium was kept at 10mg/l. The percentage uptake of metal ion at equilibrium was improved from 90.0 to 94.6 % by increasing the adsorbent dose from 5 to 15 g/l (Garg et al., 2004; Kannan and Veemaraj 2010; Potgieter et al., 2006). The percentage uptake for 10 and 15 gm/l was almost same. The sorption capacity at equilibrium for the doses of 5, 10 and 15 g/l were 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 gm/l. Similar observations were made for Pb (II). Hence, the sorbent dose of 10 g/l of dolochar seems to be optimum and was selected for the detailed kinetic study.

3.5. Effect of pH

In the adsorption process, the adsorbent surface acquires positive or negative charge depending on pH of the solution. Fig. 8 shows the effect of pH varying from 1 to 8 on the uptake capacity of Pb(II) and Cr(VI). It may be observed from the figure that with increase in pH from 1 to 8, the adsorption of Pb(II) increases from 56 to 98.5% , whereas removal of hexavalent chromium by dolochar at different pH values decreases from 97 to 76%. This indicates that the adsorption of chromium is better at acidic pH in comparison to alkaline pH. (Godea et al., 2010; Lalvani et al., 2000; Kobya 2004; Bishnoi et al., 2004). The optimum pH for removal of both ions is found to be at pH 6.

3.6. Effect of temperature

Figs. 9 and 10 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 (303, 313 and 323 K). From the figures, it may be found that increase in temperature increases the adsorption efficiency indicating chemisorption.

3.7. Adsorption isotherms

The relative parameters of two adsorption isotherm models, Langmuir and Freundlich were determined at three different temperatures and shown in Table 1. Both the isotherm plots showed a linear pattern, The best-fit equilibrium model was determined on the basis of regression correlation coefficient R^2 and as shown in the Table1. It follows Freundlich model closely.

3.8. Kinetics of adsorption

The pseudo-first order and second order kinetic models were used for evaluating the adsorption kinetics of Pb(II) and Cr(VI). It was observed that the sorption process follows the pseudo second-order kinetic, which agrees with chemisorptions as the rate-limiting mechanism. Figs. 11 and 12 show the pseudo second order plot for chromium and lead respectively. Kinetic parameters and correlation coefficients of different models are given in Table 2. The correlation coefficients of pseudo second-order kinetic model were observed to be highest and almost equal to 1 (Ho and McKay 2000; Cheung et al., 2001; Mohapatra et al., 2009; Namasivayam and Yamuna 1995) which is the best fitted model in most of the cases as compared to pseudo first order kinetic model or other models (Souundarrajan et al., 2012; Kumar et al., 2013; Li et al., 2012; Jabeen et al., 2011; Ju et al., 2010; Babu and Gupta 2008; Zhu et al., 2012). This is confirmed by the results observed in the present study**.**

3.9. Mass transfer parameter

3.91. Boyd model

In order to distinguish between film diffusion and particle diffusion, Boyd kinetic equation was employed. The values of Bt were plotted versus time and the linearity was employed to distinguish between the film diffusion and particle diffusion controlled adsorption. As seen from Fig. 13 and 14) for both the metal ions, viz., Cr(VI) and Pb(II) at 10, 25 and 50 mg/l initial concentration, the Bt versus time plots do not pass though the origin indicating the rate-controlling step to be governed by film diffusion. The effective diffusion coefficients Di were calculated from the slope of these plots and are presented in Table 3.

3.9.2. Film diffusion parameter

Figs. 15 and 16 are the plots of C/C_0 versus time which demonstrate the effect of initial metal ion concentration on the external diffusion rate. It may be was seen from the figures that the concentration of metal ion falls rapidly during initial uptake before intraparticle diffusion could start to control the adsorption kinetics for all the cases. The kinetic data were fitted to the equation for the initial uptake phase. Table 4 presents the external mass transfer coefficients determined from the slope at time tends to zero.

3.10. Thermodynamic parameters

Figs. 17 and 18 show linear plot of log Kc vs. 1/T for both metal ions. Table 5 shows the values of $\Delta H\circ$ and $\Delta S\circ$ determined from the slope and intercept of the figures. Both $\Delta H\circ$ and $\Delta S\circ$ values are found to be positive suggesting chemisorption. The irreversible and stability of the adsorption process is confirmed from the positive value of entropy

(Malkoc andd Nuhoglu 2007; Suksabyea et al., 2009; Erdem et al., 2004 ; Srivastava et al., 1997). Also, as seen in Table 5, the ΔG° value is found to be negative indicating the adsorption process to be feasible and spontaneous.

3.11. 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 ± 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 versus time at bed depths 10 cm are shown in Fig. 19 and Fig. 20 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 spectrophotometer. The volume of metal effluent treated and the requirement of dolochar upto breakthrough point have been shown in Table 6.

3.12. Column Regeneration and Reuse Studies

The eluting solution must be low in volume and high in concentration for easy handling and recovery of the metals. 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 1M 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, i.e. 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 as is shown in Fig. 21 and Fig. 22. It was observed that desorption cycle took approximately 1 hr, after which there was hardly any desorption. The total volume of this eluent at 1 hr 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.

4. Conclusions

The preset 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 adsorbents 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 Freundilch 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 0.2N HNO_3 for lead-dolochar system and 0.5M NaOH for chromium-dolochar system.

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