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Application of dolochar in the removal of cadmium and hexavalent chromium ions from aqueous solutions

L. Panda, B. Das*, D.S. Rao, B.K. Mishra

Council of Scientific and Industrial Research, Institute of Minerals and Materials Technology, Bhubaneswar 751013, India

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ABSTRACT

Dolochar, a waste material generated in sponge iron industry, is processed and put to test as an adsorbent for removal of Cd(II) and Cr(VI) ions from aqueous solutions. The dolochar samples were characterised to determine the different phases and their distribution by reflection microscopy. The analysis indicated that the sample consists of metallic iron, fused carbon, and Ca–Mg bearing phases (Ca–Mg–silicate-oxide) along with lots of voids and pores. The fixed carbon (FC) content of the material is 13.8% with a Langmuir surface area of 81.6 m^2/g and micropore area of 34.1 m^2/g. Batch adsorption experiments have been conducted to study the sorption behaviour of Cd(II) and Cr(VI) ions on dolochar as a function of particle size, contact time, adsorbent dosages, pH and temperature. It is observed that higher pH and temperature enhances sorption of Cd(II) ions. In contrast, the adsorption for Cr(VI) is found to be better in acidic pH in comparison to alkaline media. The equilibrium adsorption isotherm data are tested by applying both Langmuir and Freundlich isotherm models. It is observed that Langmuir isotherm model fitted better compared to the Freundlich model indicating monolayer adsorption. The thermodynamic parameters such as ΔG°, ΔH° and ΔS° indicate the effectiveness of dolochar to remove Cd(II) and Cr(VI) ions from aqueous solution. The kinetics of adsorption is found to better fit to pseudo second order reaction.

1. Introduction

Large quantities of solid waste materials including coal fines and dolochar are generated during the production of direct reduction of iron (DRI) by rotary kiln. While a part of the coal fines can be used as fuel in coal fired furnaces, the voluminous low calorific dolochar poses serious disposal and environmental problems. For example, a typical 100 tons per day (tpd) DRI plant produces around 40 tpd dolochar resulting in a total generation of 14,600 tons of waste material per annum. India has now emerged as the largest producer of coal based sponge iron in the world. It produces around 32 million tons of sponge iron per annum, which is used as a substitute for imported scrap. However, the utility of wastes generated, particularly the carbonaceous material, dolochar, still remain as an unsolved problem. Only few plants in India have taken the initiative towards utilisation of dolochar by installing atmospheric or circulating fluidized bed combustion (A/CFBC) boilers for captive power generation. These boilers accept dolochar with fixed carbon content of >20% by weight with a gross calorific value of 1800–2000 kcal/kg. However, most of the dolochar that are being produced from sponge iron industries of India contain very low levels of fixed carbon (8–13%) and volatile matter (3–7%). The dolochar samples contain high percentage of ash (∼70–80%) due to which it cannot be reused as a substitute for fuel. In the recent years, we had attempted to recover the carbon values present in dolochar through flotation. But due to poor liberation and lack of hydrophobicity of the carbon particles present in dolochar, it could only be beneficiated to 32% fixed carbon [1]. However in order to find some utility of dolochar as an adsorbent and taking into account its carbon content and inherent porosity, adsorption studies with regard to some heavy metal ions like Cd(II) and Cr(VI) were attempted.

Cadmium and chromium are toxic metals found in several industrial discharges and effluents [2]. The major ill-effects caused in case of Cd(II) ions in human body are head ache, chest pain, nausea and vomiting, extreme weakness, diarrhea, muscular cramps, skeletal deformation, teeth discolouration, etc. [3,4]. Due to its toxicity, the permissible limit of Cd(II) ions in industrial effluents as per Central Pollution Control Board (CPCB) of India guidelines is set at 0.2 mg/L. Therefore, the Cd(II) and other heavy metals in the effluents need to be removed before discharge into the waste stream [5,6]. Similarly, Cr(VI) is another harmful heavy metal ion which exists primarily as salts of chromic acid and chromate ion that contaminate the surroundings. Exposure to hexavalent chromium causes several health problems, such as it can affect liver and kidney and cause internal haemorrhages, respiratory irritation, skin ulcer, etc. [7,8]. Cr(VI) is also considered to be genotoxic and carcinogenic in nature. The permissible limit of Cr(VI) in industrial effluents is set at 0.5 mg/L by the Ministry of Environment and

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* Corresponding author. Tel.: +91 674 2581635; fax: +91 674 2581637.
E-mail address: bdas@immt.res.in (B. Das).

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Table 1
Proximate and ultimate analysis of dolochar.

Proximate analysis	
Constituents	**%**
Ash	79.7
Moisture	2.7
Volatile matter	3.8
Fixed carbon	13.8

Ultimate analysis	
Constituents	**%**
Carbon	16.8
Hydrogen	0.6
Nitrogen	0.02
Oxygen	82.58

Forests (MoEF), Government of India. But in most of the mining and industrial effluents it is present in much higher concentration than the permissible limit [9]. Several efforts have been made for its removal from industrial wastewater involving textile dyeing, leather tanning, electroplating, mining, etc.

It is clear that the removal of the above two toxic elements from the effluents is of paramount importance that calls for a concerted R&D effort in order to develop low cost adsorbents which can neutralize the harmful effects before discharge into the environment. Several carbon bearing [10–13] and other adsorbents such as zeolite, agricultural by-products [14–16], etc. have been used by a number of researchers for the removal of Cd(II). It is well known that charcoal and many other carbonaceous materials are good adsorbents for inorganic and organic molecules. Active carbon is produced by heating charcoal with steam to approximately 1000 °C in absence of oxygen, which removes residual non-carbon elements and produces a porous internal microstructure having an extremely high surface area, and high degree of surface reactivity. Furthermore, the presence of different surface functional groups on activated carbon, especially carboxylic, carbonyl, lactonic, and phenolic groups [17] leads to the adsorption of heavy metal ions. The dolochar easily mimics the role of activated carbon by adsorbing Cd(II) and Cr(VI) onto itself from waste water.

Dolochar is a carbonaceous material and therefore, it is expected to have high surface area with requisite porosity which makes it ideal for adsorption. We have attempted to remove Cd(II) and Cr(VI) from the aqueous solutions using dolochar. To the best of our knowledge, so far, the adsorption studies for the removal of Cd(II) and Cr(VI) ions using dolochar have not been reported. The main objective of the present study is to find a suitable bulk use of dolochar, which is produced in huge amounts as a by-product of sponge iron industry. The other objective of this study is to explore the possibility of replacing activated carbon and other high cost adsorbents by dolochar.

2. Materials and methods

2.1. Adsorbent

Dolochar sample was collected from one of the sponge iron plants of Orissa, India. The material was washed several times with deionised water to remove contaminant and dried at 50 °C for a few hours. The material was then subjected to fine grinding using laboratory ball mill with required ball to particle ratio. The proximate and ultimate analysis of this sample is given in Table 1. The proximate analysis was carried out following the standard method for coal samples while the ultimate analysis was carried out using Truspec-CHN analyser, Leco Corporation, USA. The chemical composition of the carbon free dolochar ash sample was analysed by wet chemical and AAS techniques and the results are shown in Table 2. The ground particle confirmed to a d_{80} size of 45 μm.

Table 2
Chemical composition of dolochar (ash).

Constituents	%
Fe	9.8
Fe_2O_3	14.0
CaO	4.1
MgO	4.2
Al_2O_3	16.1
SiO_2	61.2

2.2. Adsorbate

Anhydrous cadmium chloride and potassium dichromate (Analytical grade) were used without any purification. Stock solutions of Cd(II) and Cr(VI) (1000 mg/L) were prepared by dissolving the required amounts of the compound in distilled water. Different concentrations of these two solutions were then prepared by progressive dilution of the stock solution. The pH of the solution was adjusted to the required value by adding either dilute H_2SO_4 or NaOH solutions.

2.3. Adsorption method

The batch adsorption experiments were carried out in 250 mL conical flasks in a solution of Cd(II) and Cr(VI) in various concentrations (10–50 mg/L). Dolochar samples (5–65 g/L) with different particle sizes (50–500 μm) were added to 100 and 200 mL of Cd(II) and Cr(VI) solutions, respectively. pH of different stock solutions was adjusted (1.5–8.5) and transferred into the flasks. The solutions were agitated in a magnetic stirrer for the desired time period (5–90 min). At each time interval, the solutions were filtered and collected in a volumetric flask. The pH of the final solution was measured at the end of the experiment. Further, experiments were carried out by varying different variables such as agitation time, metal ion concentration, pH, adsorbent dosages, temperature, etc. Kinetic studies were performed for an initial concentration of 10–50 mg/L at 300, 318 and 338 K. The resultant filtrates collected at the end of the predetermined time intervals were subjected to chemical analysis by atomic absorption spectrophotometer (AAS) and UV visible spectrophotometer.

2.4. Analytical method

The cadmium concentrations of the solution at equilibrium were analysed using Perkin Elmer-2380 AAS. The pH of the solution was measured by Eutech pH meter. A UV–Visible spectrophotometer (Shimadzu UV-2450) was used for the estimation of hexavalent chromium by complexing with 1,5-diphenyl carbazide in acid solution. The purple-violet colour developed due to complexation with hexavalent (and not trivalent) chromium at low pH was measured at 540 nm. The complex was ascertained to have the following structure (Fig. 1). X-ray diffraction studies were carried out by using X-ray powder diffractometer (PANalytical, X'pert) equipped with Cu-Kα radiation operated at 40 kV and 30 mA. FTIR spectra of the samples were recorded on a Shimadzu FTIR by using KBr as reference.

2.5. Desorption studies of cadmium and chromium

In these experiments, desorption of both Cd(II) and Cr(VI) from loaded dolochar was performed using water and two concentrations of HCl and NaOH solution. Studies were conducted by exposing dolochar containing Cd(II) and Cr(VI) solutions separately

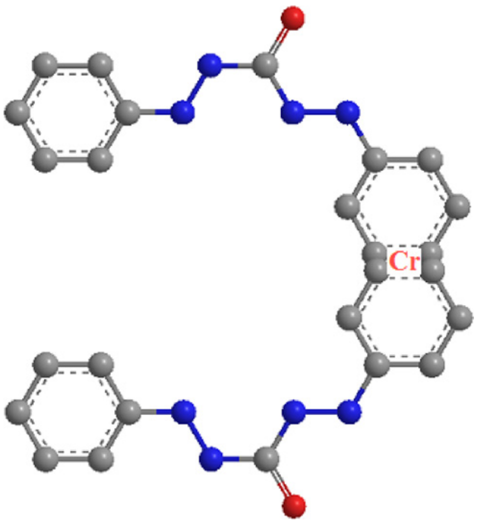
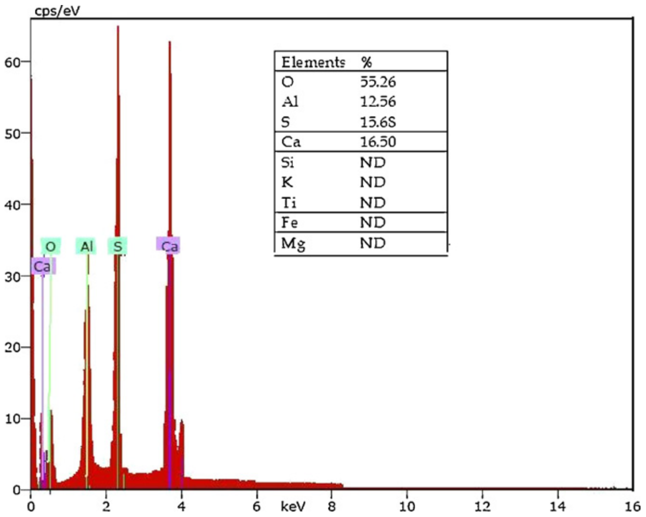


Fig. 1. Complex structure of chromium with 1,5-diphenyl carbazide.



Elements	%
O	55.26
Al	12.56
S	15.68
Ca	16.50
Si	ND
K	ND
Ti	ND
Fe	ND
Mg	ND

Fig. 3. Energy Dispersive Spectrum (EDS) of dolochar sample.

to 100 mL solution of 0.1 and 0.2 M HCl or NaOH. The mixture was agitated at 500 rpm for 90 min. After desorption, the dolochar samples were separated by decantation and filtration and cadmium and chromium concentrations were measured in the filtrate.

3. Mineralogical characterisation of dolochar

Mineralogical characterisation studies were carried out with the help of Leitz petrological stereomicroscope as well as electron microscope. Mineralogical characteristics of the dolochar sample are very important because they tend to influence the sorption capacity, physico-chemical and engineering properties for different applications. The dolochar sample was mostly black in colour due to the presence of fused carbon in it. Some white particles were noticed due to the presence of lime (Ca–Mg–silicate-oxide). Stereomicroscopic study showed that the dolochar particles have voids and pores (Fig. 2a and b) giving rise to the spongy texture. The particles show widely varying shapes and sizes (Fig. 2c and d). The dolochar samples show three distinct phases, viz., white phase (lime bearing), black phase (fused carbon) and the metallic iron phase. The background matrix could be an admixture of iron and sponge iron particles. Generally the white phase is marked around the fused carbon. The layers of white lime material are also observed as banded structures along with fused carbon. Many times the tiny metallic iron particles were found either associated with fused carbon or as isolated stray pieces. Lime is a good adsorbent for the removal of heavy metal ions besides unburnt carbon in dolochar samples. Ca–Mg–silicate-oxide phase as identified by microscopic study will be responsible for adsorption of both Cd(II) and Cr(VI) ions from aqueous solutions.

In order to identify the different elements associated with the dolochar sample, Energy Dispersive X-ray Spectrum (EDS) was recorded to obtain the elemental composition of small objects on the surfaces of dolochar. The spectra along with the corresponding elemental composition of a point surface of dolochar are shown in Fig. 3. It indicates that the point sample contains aluminium,

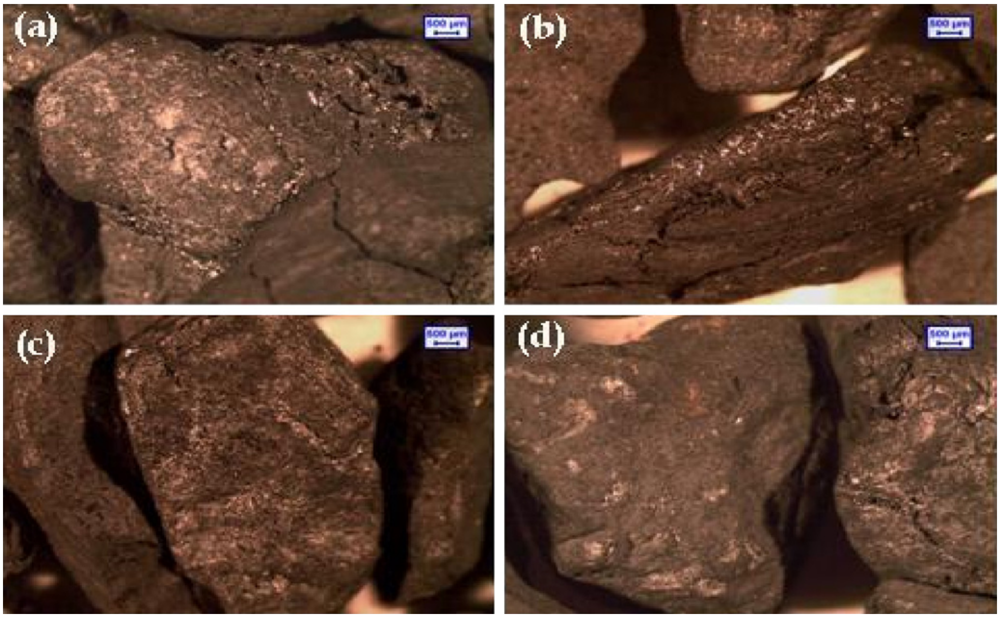


Fig. 2. Stereomicroscopic photographs of dolochar (a) a sub rounded dolochar particles with pores and voids. (b) Dolochar particles with pores, voids and cracks; (c) a flat dolochar particle show pores and voids. (d) Dolochar particles filled with lime and with voids and pores.

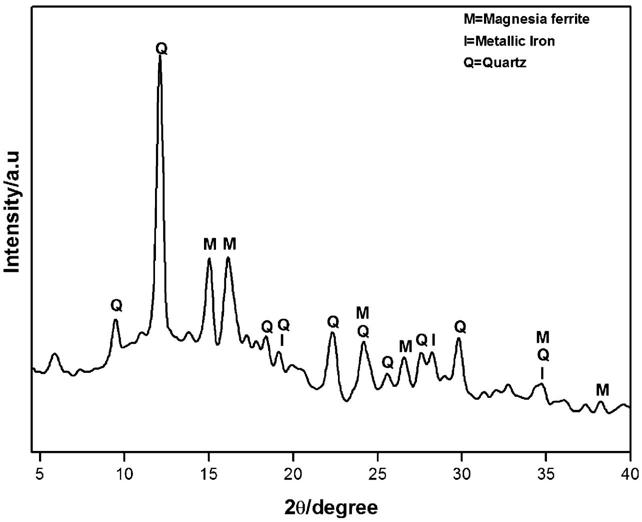


Fig. 4. X-ray diffraction spectra of dolochar ash.

sulphur and calcium as the associated elements in the dolochar. The calcium content was found to be 16.5% which is next to the oxygen (55.3%). The XRD studies (Fig. 4) indicate the presence of quartz, iron and metallic iron phases. The dolochar ash was completely free from carbon after slow heating of the samples for several hours.

4. Textural characteristics of dolochar

The dolochar is known to contain micropores as well as mesopores indicating high adsorption capacity for metal ions [18]. In order to ascertain the adsorption characteristics of the sample, several parameters such as total surface area, pore area, pore volume, pore diameter, pore width, micropore and mesopore volumes of the sample were determined by N_2 adsorption–desorption method using the Micromeritics ASAP 2020 surface area analyser. The Langmuir, BET and single point surface area of the sample used in our study were found to be 81.6, 61.9 and 60.6 m^2/g, respectively. From the data given in Table 3, it is observed that the average pore width (BET) and pore diameter (BJH ads) are 3.7 and 7.5 nm, respectively, which indicate that the sample is prone to adsorption. A typical experimental adsorption/desorption isotherm of N_2 on the dolochar sample is shown in Fig. 5. It shows that the isotherm belongs to type-IV adsorption–desorption isotherm with H_3 type of hysteresis loop indicating the presence of mesoporosity with affinity for adsorption. This is in accordance with BDDT classification [19]. The path dependent adsorption–desorption behaviour leading to hysteresis is an indicator of the porous nature of the sample. The Langmuir surface area plot is shown in Fig. 6. The straight line plot between pressure (*P*) vs. and *P*/*Q* indicates that the material is suitable for chemical adsorption as well as for physical adsorption on dolochar materials.

Table 3
Calculated textural parameters of dolochar.

Methods	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Langmuir	81.6	–	–
BET	61.9	–	3.7 (pore width)
Single point, at $P/P_0 = 0.13$	60.6	0.06	–
t-Plot micropore area	34.1	0.01	–
t-Plot external surface area	27.8	–	–
BJH adsorption	22.4	0.04	7.5
BJH desorption	17.7	0.03	7.7
Horvath Kawazoe	–	0.03 at $P/P_0 = 0.15$	0.7 (pore width)

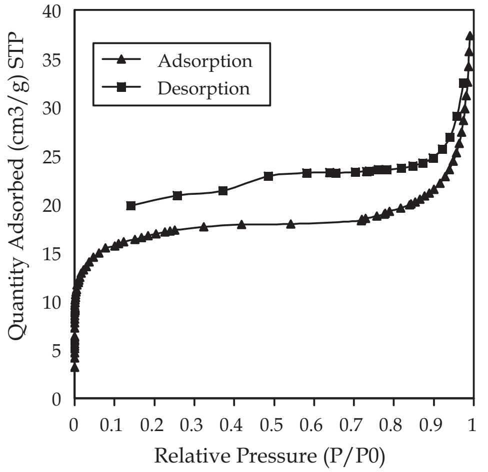


Fig. 5. Nitrogen adsorption–desorption isotherms of dolochar sample.

5. Results and discussion

The proximate analysis of the dolochar sample indicates that it contains 79.7% ash, which comprises of inorganic constituents such as silica, alumina, iron, calcium, magnesium, etc. It contains very low amounts of volatile matter (2.7%) and fixed carbon (13.8%) for which it cannot be used as a fuel in any metallurgical industry. The results of ultimate analysis also indicate that the hydrogen and nitrogen content in the sample is very low. The chemical composition of the dolochar ash indicates that besides carbon, silica, alumina and iron are the major constituents. Other minor constituents such as calcium oxide and magnesium oxide are found to be 4.0% and 4.2%, respectively. Analysis of the sample indicates that both carbon and silica can be considered as a good source of adsorption.

5.1. 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

$$q = \frac{(C_0 - C_t)V}{M} \tag{1}$$

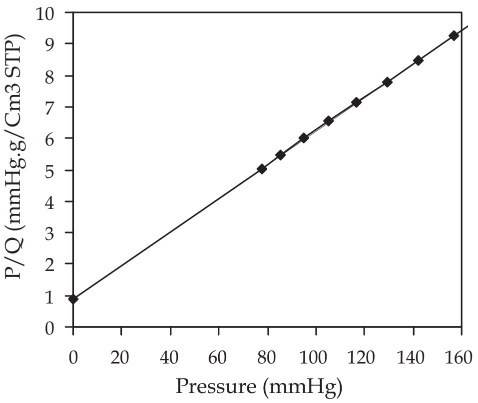


Fig. 6. Langmuir surface area plot of dolochar.

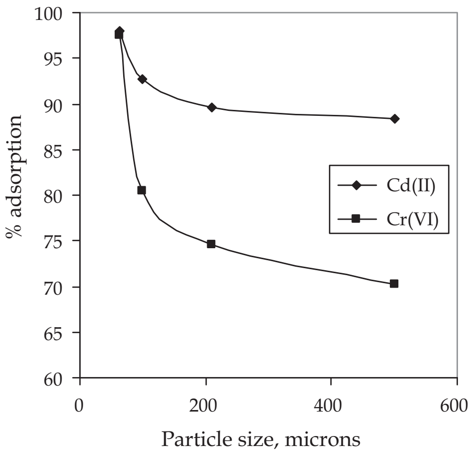


Fig. 7. Effect of particle size on sorption of cadmium and chromium ions (solution 100 mL of 20 mg/L, pH 6.0, dolochar 1 g, temp. 308 K).

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 M (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.

5.1.1. *Effect of particle size*

Batch adsorption experiments were carried out by using 100 mL solutions at initial concentration of 20 mg/L and 1.0 g of dolochar. The particle size of dolochar was varied from 63 to 500 μm. Fig. 7 shows the metal uptake capacity of Cd(II) and Cr(VI) ions at different particle sizes. It was observed that the adsorption capacity of Cd(II) and Cr(VI) ions decreased with increase in particle diameter. It was also observed that the adsorption/uptake of Cr(VI) ions with regard to particle size is less prominent compared to Cd(II). As adsorption is a surface phenomenon, it is very likely that the extent of adsorption is proportional to the surface area. Hence smaller the particle size, greater will be the amount of adsorption as smaller particles have larger surface area. Our result is in conformity with the above assertion as the adsorption of Cd(II) and Cr(VI) is observed to be highest on 63 micron particles. Therefore, for further experimental studies, we kept the particle size less than 63 microns. The cut-off size was selected purely based on practical convenience.

5.1.2. *Effect of contact time*

The time dependent behaviour of Cd(II) and Cr(VI) adsorption was measured by varying the contact time in the range of 5–90 min to determine the metal ion adsorption capacity of the dolochar. The initial concentration of metal ions of 10, 20 and 50 mg/L was taken using 1 g of adsorbent at 308 K. Fig. 8 shows the Cd(II) and Cr(VI) uptake capacity of the dolochar at different time intervals. It was observed that the kinetics of adsorption of metal ions is faster during the initial period followed by a period of slower rate. The initial faster rate of adsorption prevailed for about 20 min followed by the slower rate for about 20–90 min. Beyond 90 min, there was hardly any sorption indicating attainment of equilibrium.

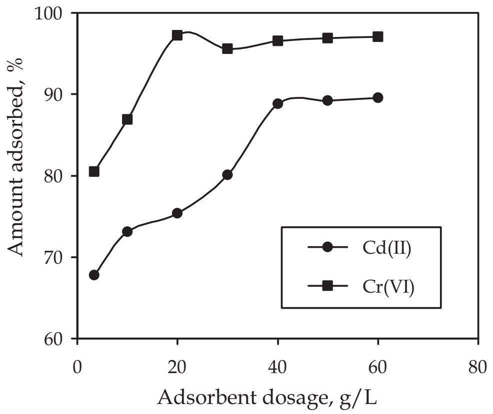


Fig. 9. Effect of amount of adsorbent on Cd(II) and Cr(VI) (contact time 60 min, metal concentration 20 mg/L, pH 4.8 (Cd) & 2.8 (Cr)).

5.1.3. *Effect of adsorbent dosage*

The adsorbent dosage is also an important parameter with respect to the adsorption studies as it determines the potential of material to adsorb metal ions for a given initial concentration of the sorbent. The effect of amount of dolochar sample on Cr(VI) and Cd(II) uptake is shown in Fig. 9. Removal of Cd(II) and Cr(VI) by dolochar was studied at different adsorbent dosages for 20 mg/L at 308 K. 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 ion concentration. Similar findings were observed for the uptake of heavy metals ions onto activated carbon, eucalyptus globule, bark, bambusa glaucescens dust and clay as observed by different investigators [20–22].

5.1.4. *Effect of pH*

pH of the solution plays an important role in the adsorption process as the adsorbent surface acquires positive or negative charge in response to change in pH. The effect of pH on the adsorption of Cd(II) and Cr(VI) was investigated by varying the pH from 1 to 8. The

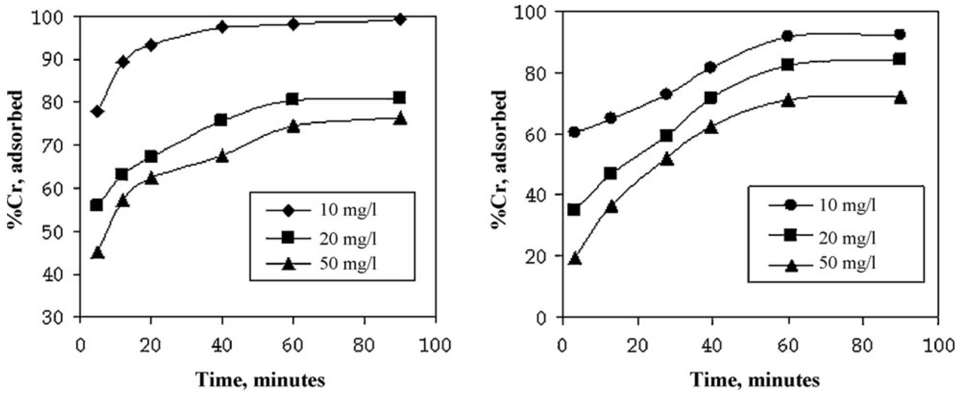


Fig. 8. Effect of contact time on sorption of cadmium and chromium (pH 6.0, dolochar 1 g, temp. 308 K).

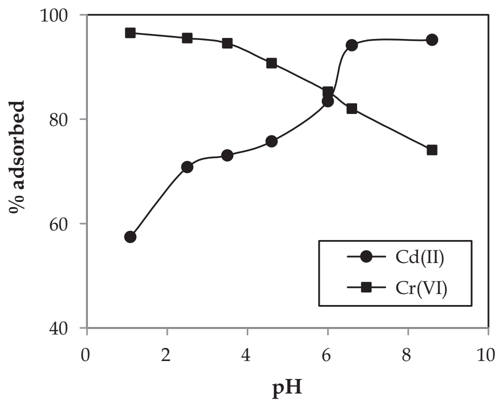


Fig. 10. Effect of pH on removal of Cd(II) and Cr(VI) (contact time 60 min, conc 20 mg/L, temp. 308 K, particle size 63 μm, sample 2.0 g/200 mL).

effect of pH on the uptake capacity of Cd(II) and Cr(VI) is shown in Fig. 10. In case of Cd(II), the adsorption increases from 57.4 to 97.4% with increase in pH from 1 to 8, but in case of Cr(VI), the reverse order was observed. The optimum pH for removal of Cd(II) ions is found to be at pH 6.6. The near neutral pH is found to be favourable for adsorption. It was also found that during the process of adsorption, the pH value of the adsorbing solution slightly decreases to the extent of 0.3–0.5 units. It suggests that the functional species containing H^+ ions attached with dolochar are released bringing the pH down. The solution pH also plays an important role in the adsorption of Cd(II) ions, which is mainly due to formation of surface species such as Cd^{2+}, $Cd(OH)^+$ and $Cd(OH)_2$ [23]. It was also pointed out that no change in rate of adsorption occurs at higher (alkaline) pH due to precipitation of Cd ions as $Cd(OH)_2$. It was observed that Cd(II) starts precipitating at pH 9 and above and at pH 8, the distribution of Cd species is approximately 90% as Cd(II) and 10% $Cd(OH)_2$ [24,25].

Removal of hexavalent chromium by dolochar at different pH values indicated that the amount of adsorbed Cr(VI) increases from 75 to 96% as the pH decreases from 8 to 1. This indicates that the adsorption is better at acidic pH in comparison to alkaline pH. The highest adsorption was observed at pH 1 as it provides a favourable adsorbent surface charge for the adsorption of Cr(VI) ions. It is also known that Cr(VI) ions in solutions exist mostly in two oxidation states which are Cr(VI) and Cr(III) and the stability of these forms is dependent on the pH of the solution [26,27]. It is assumed that at acidic pH, during interaction of dolochar with Cr(VI), the hexavalent Cr(VI) is reduced to Cr (III) and this metal ion binds with C-skeleton of dolochar sample [28,29]. In an aqueous solution, the chromate ion ($CrO_4{}^{2-}$) can be converted to the dichromate ion, ($Cr_2O_7{}^{2-}$), and vice versa. The extent to which these reactions occur is dependent upon the concentration of the hydrogen ion in the solution [30]. The reactions at low and moderate pH can be expected as follows.

$$\text{AtlowpH,}\quad Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr3^+ + 7H_2O \qquad (2)$$

$$\text{AtmoderatepH,}\quad HCrO_4{}^- + 7H^+ \rightarrow Cr3^+ + 4H_2O \qquad (3)$$

5.1.5. *Effect of temperature*

The temperature dependence of Cd(II) and Cr(VI) adsorption by dolochar was studied with a constant initial metal ion concentration of 20 mg/L for different temperatures (308, 323 and 343 K). The results of the studies are shown in Figs. 11 and 12 for Cd and Cr, respectively. From the figures, it is observed that the adsorption density (%) increases with increase in temperature in both the cases i.e. Cd(II) and Cr(VI), indicating involvement of chemisorption.

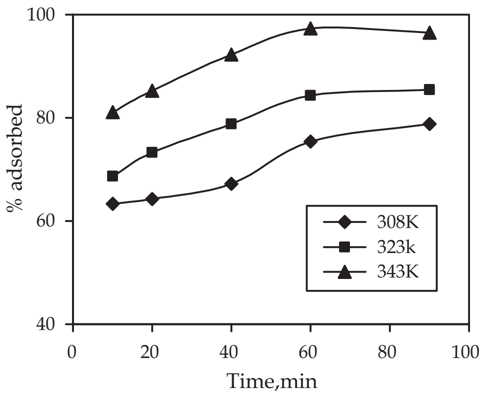


Fig. 11. Effect of temperature on Cd(II), particle size 63 μm, pH 4.6.

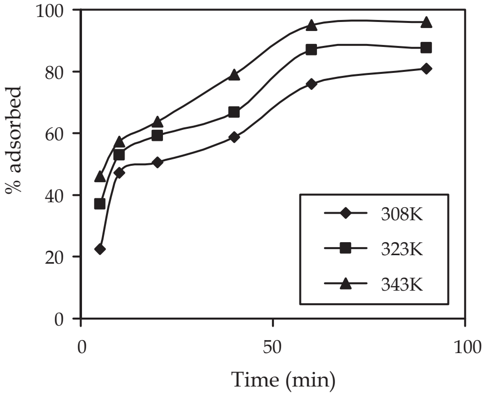


Fig. 12. Effect of temperature, Cr(VI), particle size 63 μm, pH 2.8.

Table 4
Langmuir isothermic parameters for cadmium and chromium metal ions.

	Temperature					
	Cadmium			Chromium		
	308 K	323 K	343 K	308 K	323 K	343 K
Q_0 (mg/g)	2.02	1.78	1.42	5.21	2.83	2.17
b (L/mg)	0.33	0.53	2.82	0.05	0.18	0.45
R^2	0.98	0.99	0.99	0.82	0.91	0.96
R_L	0.13	0.09	0.02	0.49	0.22	0.10

5.2. *Adsorption isotherms*

The equilibrium adsorption isotherm is one of the most important criteria to understand the mechanism of the adsorption. The equilibrium data for Cd(II) and Cr(VI) adsorption using dolochar were applied to two adsorption isotherm models, Langmuir and Freundlich to fit the experimental results. The relative parameters of both models were determined at three different temperatures

Table 5
Freundlich isothermic parameters for cadmium and chromium metal ions.

	Temperature					
	Cadmium			Chromium		
	308 K	323 K	343 K	308 K	323 K	343 K
$1/n$	0.24	0.14	0.10	0.11	0.02	0.12
K_F	1.42	1.32	1.1	1.51	1.32	1.22
R^2	0.95	0.96	0.85	0.69	0.79	0.82

Table 6
Kinetic parameter for cadmium adsorption.

Temperature (K)	$q_{e,\text{exp}}$ (mg/g)	First-order kinetic model			Second order kinetic model		
		K_1	$q_{e,\text{cal}}$ (mg/g)	R^2	K_2	$q_{e,\text{cal}}$ (mg/g)	R^2
308	0.86	3.9×10^{-3}	1.01	0.89	0.30	0.69	0.98
323	0.89	3.85×10^{-3}	1.03	0.98	0.23	0.99	0.99
343	0.99	2.83×10^{-3}	1.06	0.99	0.35	1.01	0.99

Table 7
Kinetic parameter for chromium adsorption.

Temperature (K)	$q_{e,\text{exp}}$ (mg/g)	First-order kinetic model			Second order kinetic model		
		K_1	$q_{e,\text{cal}}$ (mg/g)	R^2	K_2	$q_{e,\text{cal}}$ (mg/g)	R^2
308	0.95	7.8×10^{-4}	1.03	0.94	4.49×10^{-2}	1.13	0.98
323	0.96	9.8×10^{-4}	1.03	0.91	6.85×10^{-2}	1.08	0.98
343	0.98	7.7×10^{-4}	1.04	0.91	8.9×10^{-2}	1.08	0.99

and shown in Tables 4 and 5, respectively. The linear form of Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{4}$$

where q_e (mg/g) is the amount adsorbed at equilibrium and C_e (mg/L) is the equilibrium concentration. The linear plot of C_e/q_e against C_e represents adsorption obeying Langmuir model. The maximum amount of adsorption capacity Q_0 and energy of adsorption b were determined from the slope and intercept. The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless constant or separation factor R_L, which is given by $1/(1+bC_0)$. The R_L values between 0.1 and 1 indicate favourable adsorption of Cd(II) and Cr(VI) on dolochar sample [31].

The linear form of Freundlich isotherm is

$$\log q_e = \log K_F + \frac{1}{n \log C_e} \tag{5}$$

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 $\ln q_e$. The best-fit equilibrium model was determined on the basis of regression correlation coefficient R and as shown in the Tables 4 and 5. It follows Langmuir isotherm more closely.

5.3. Kinetics of adsorption

For evaluating the adsorption kinetics of Cd(II) and Cr(VI), pseudo-first order and second order kinetic models were used to fit the experimental data obtained for three different temperatures 308, 323 and 343 K.

$$\text{Ist order kinetics} \quad \log(q_e - q_t) = \frac{\log q_e - K_{ad}t}{2.303} \tag{6}$$

$$\text{2nd order kinetics} \quad \frac{t}{q_t} = \frac{1}{K_2 qe^{2+}} + \frac{1}{q_e}t \tag{7}$$

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 data were first interpreted according to the first order expression. The kinetic parameters for both Cd(II) and Cr(VI) are given in Tables 6 and 7, respectively. It is observed that the plot of log $(q_e - q_t)$ vs. time are linear with R^2 value varying from 0.897 to 0.990 for Cd(II) and from 0.948 to 0.918 for Cr(VI). However the theoretical and experimental equilibrium adsorption capacity q_e obtained from these plots varied widely. This indicates that this equation cannot provide an accurate fit of the experimental data. The data were then treated to pseudo second order kinetic plot (Eq. (7)). The plots of t/q_t vs. t are shown in Figs. 13 and 14 for the two metal ions respectively at three different temperatures. The adsorption data for both the metal are found to fit well to pseudo 2nd order kinetics as the regression coefficients, R^2, for both Cd(II) and Cr(VI) plot were nearly equal to one [32]. The theoretical and as well as experimental q_e value is nearly equal and with increase in temperature resulted in increase of q_e which is a chemisorptions nature of adsorption [33,34].

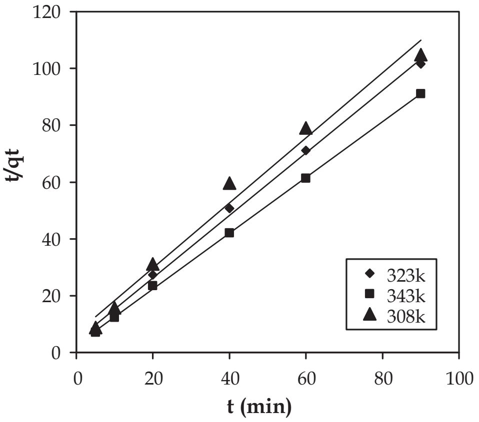


Fig. 13. 2nd order plot of t/q_t vs. t for Cd(II), sample 1.0 g, conditioning time 60 min, particle size 63 μm.

The adsorption capacity of dolochar for both Cd(II) and Cr(VI) was compared with the reported values [35–41] for waste materials and shown in Table 8. From the results, it is evident that dolochar is comparable to many adsorbents for treating wastewater containing Cd(II) and Cr(VI) metal ions.

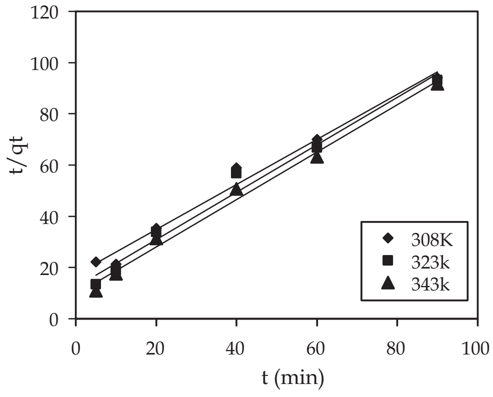


Fig. 14. 2nd order plot of t/q_t vs. t for Cr(VI).

Table 8
Comparison of adsorption capacities of various adsorbents for cadmium and chromium adsorption.

Adsorbents	Adsorption capacity (mg/g)		Reference
	Cadmium	Chromium	
Exhausted coffee	1.4	1.4	[35]
Activated clay	8.7		[36]
Metal sludge	40		[37]
Biomass residual slurry		5.8	[38]
Sawdust		3.3	[39]
Red mud	–	1.6	[40]
Bauxite		0.5	[41]
Blast furnace slag		1.4	[35]
Dolochar	1.9	2.1	Present study

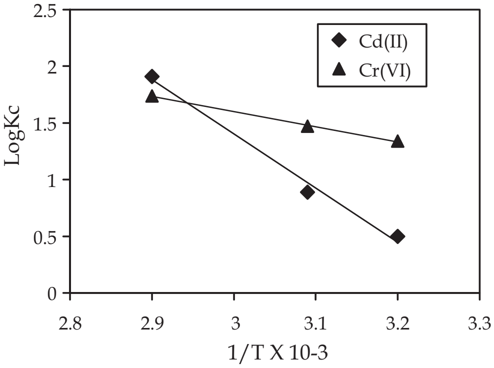


Fig. 15. Van't Hoff plot, $1/T$ vs. $\log K_c$.

5.4. 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

$$\log K_c = \frac{\Delta S^\circ}{2.303} - \frac{\Delta H^\circ}{2.303RT} \tag{8}$$

The ΔG° value was calculated by using the equation

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

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

$$K_c = \frac{C_A}{C_e} \tag{10}$$

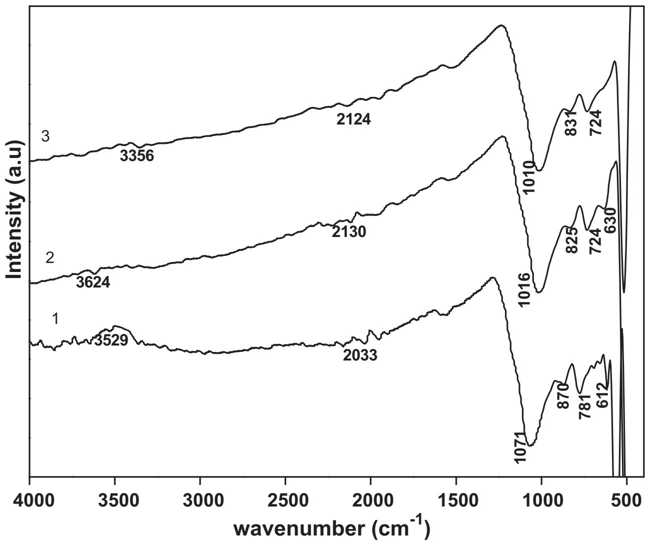


Fig. 16. FTIR spectra of dolochar, and adsorbed with Cd & Cr (1-dolochar, 2-Cd(II), 3-Cr(VI) adsorbed with dolochar).

Table 10
FTIR spectral band position and their assignment for dolochar, Cd(II) and Cr(VI) adsorbed sample.

Band position (cm^{-1})	Assignments
3100–3500	–OH and NH stretching band
2140–2100	C≡C or C≡N
1000–1100	Si–O of stretching
995–665	Aromatic, C–H band
840–600	Heavier atom, S═O, Quartz

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 (g/L). A plot of $\log K_c$ vs. $1/T$ for both Cd(II) and Cr(VI) is found to be linear (Fig. 15) and ΔH° and ΔS° determined from the slope and intercept of the plot are given in Table 9. Both ΔH° and ΔS° values are found to be positive suggesting a chemisorptions process. During chemisorptions, desolvation may be involved leading to a net positive entropy change and a slightly positive enthalpy of adsorption. The positive value of entropy indicates the irreversible and stability of the adsorption process [35,42]. Also, as seen in Table 9, the ΔG° value is found to be negative indicating the process to be feasible and adsorption to be spontaneous.

5.5. Mechanism of adsorption

Fourier transform infrared (FTIR) spectra coupled with X-ray diffraction (XRD) were carried out to provide some information on the mechanism of adsorption. FTIR studies were undertaken to investigate variations in the functional groups of dolochar sample due to adsorption with metal ions. The spectrum of dolochar and after adsorption with Cd(II) and Cr(VI) ions is shown in Fig. 16 and their spectral assignments in Table 10. The study indicates that the entire spectrum has more or less similar broad characteristic absorption bands. The change in band position and frequency in the spectrum peaks shows that the adsorption of metal ions affects the functional group positions of dolochar sample. It was also observed that the peaks were slightly diminished in case of Cd(II) and Cr(VI) adsorbed samples (2 and 3) compared to dolochar [43,44]. The XRD studies of dolochar and adsorbed with Cd and Cr ions are shown in Fig. 17. Only the prominent mineral peaks of quartz were observed

Table 9
Thermodynamic parameters of cadmium and chromium adsorption on dolochar.

	Temperature					
	Cadmium			Chromium		
	308 K	323 K	343 K	308 K	323 K	343 K
ΔG° (kJ mol^{-1})	−12.75	−23.92	−54.46	−34.31	−39.47	−49.61
ΔS° (J mol^{-1})	301.35			107.81		
ΔH° (kJ mol^{-1} K^{-1})	28.18			79.20		

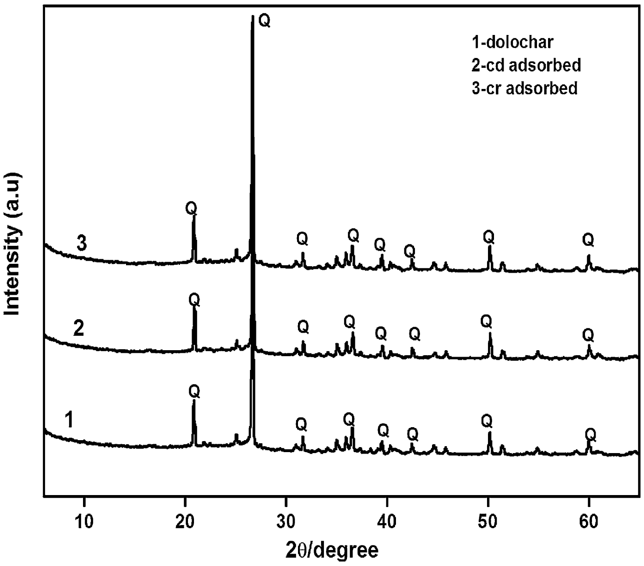


Fig. 17. XRD spectra of dolochar, Cd and Cr adsorbed samples.

in all the three samples. It was observed that the diffraction pattern of dolochar and the adsorbed samples are identical. However careful observation although not conclusive could reveal that the peak intensity of some quartz peaks in the adsorbed samples has been enhanced slightly. Thus the FTIR and XRD results point to the fact that, adsorption of Cd and Cr ions has takes place into the dolochar system.

5.6. Desorption of Cd and Cr ions

It is not advisable to discard Cd(II)/Cr(VI) loaded dolochar material into the environment as the same will slowly release into the environment leading to recontamination of soil and water systems. Besides that dolochar material will create more toxic due to the presence of these elements. It is therefore required to regenerate both the metal ions and the adsorbent by a cheaper desorption method. Desorption study of Cd/Cr loaded dolochar not only helps to recover the metal ions, but also helps to reuse of dolochar for another loading cycle. It was found from the effect of pH studies that adsorption of both the metal ions is highly dependent on pH. Therefore, desorption of metal ions can be achieved by altering the pH of the aqueous solutions. The results of the desorption studies of Cr and Cd ions are shown in Figs. 18 and 19, respectively. These studies showed that Cr(VI) could be desorbed from dolochar at basic pH values while that of Cd(II) takes place only in acidic pH. The desorption efficiency increased with the increase in either alkali or acid concentration. It was also observed that very insignificant desorption was achieved only with water. The maximum desorption of Cr(VI) and Cd(II) was 81% and 61%, respectively at 0.2 M alkali or acid solutions. This indicates that the adsorption of metal ions onto dolochar sorbents is reversible. The result thus suggests that bonding between dolochar sites and metal ions is not strong.

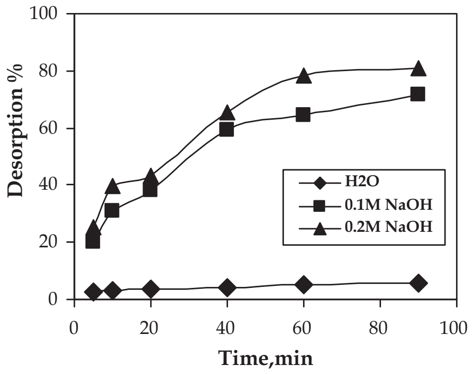


Fig. 18. Desorption study of chromium (particle size 63 μm, pH 7.1–7.8).

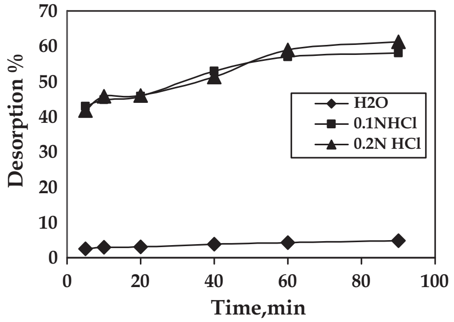


Fig. 19. Desorption of cadmium (particle size 63 μm, pH = 1.4–1.9).

6. Conclusions

The adsorption studies indicate that removal of Cd(II) and Cr(VI) ions from aqueous solution is possible using abundantly available low-cost dolochar as adsorbent. Dolochar was found to be effective, as the removal of Cr(VI) reached 96% and that of Cd(II) 99% at normal temperature. It was also observed that the process of adsorption is strongly affected by the experimental parameters such as adsorbent dosages, particle size, agitation time, metal ion concentration and solution pH. Adsorption of Cr(VI) is highly pH-dependent. The dolochar sample showed very large surface area and microspore as well as mesopore volumes, which makes it suitable as adsorbent of metal ions.

The kinetics of the Cr(VI) adsorption on different adsorbents was found to follow a pseudo second-order rate equation. The negative value of free energy indicates that the process is spontaneous and the positive values of entropy as well as enthalpy indicate higher affinity of the material for Cd(II) and Cr(VI). The adsorption process is determined to be endothermic. The adsorption data fitted well to Langmuir isotherm model.

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