Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals

Sevgi Kocaoba

Yildiz Technical University, Faculty of Art & Science, Department of Chemistry, Davutpaşa Cad. No: 127, 34210 Davutpasa, Istanbul, Turkey

Abstract

The presence of heavy metals in the environment is major concern due to their toxicity. Contamination of heavy metals in water supplies has steadily increased over the last years as a result of over population and expansion of industrial activities.

A strong cation-exchange resin, Amberlite IR 120 and a natural zeolite, dolomite were used for the removal of lead(II) and cadmium(II). The optimum conditions were determined in a batch system as concentration range was between 5 and 100 mg/L, pH range between 1 and 8, contact time between 5 and 90 min, and the amount of adsorbent was from 0.1 to 1 g. A constant stirring speed, 2000 rpm, was chosen during all of the experiments. The optimum conditions were found to be a concentration of 20 mg/L, pH of 5, contact time of 60 min and 0.5 g of adsorbent.

Also, for investigation of exchange equilibria different amounts of ion exchange resin and dolomite were contacted with a fixed volume and concentration of a heavy metal bearing solutions. Sorption data have been interpreted in terms of Langmuir and Freundlich equations.

The effect of adsorption temperature on the heavy metals adsorption onto dolomite was investigated at three different temperatures (20, 40 and 60 °C). Thermodynamic parameters were calculated.

The results obtained show that the Amberlite IR 120 strong cation-exchange resin and dolomite performed well for the removal of these heavy metals. As a low cost adsorbent, dolomite can preferable for removal of heavy metals from wastewaters.
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1. Introduction

Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. Pb^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders [1,2]. Pollution by heavy metals is currently of great concern, due to the increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment [3]. The stricter environment regulation on the discharge of heavy metals make it necessary to develop various technologies for the removal. The heavy metal levels in wastewater, drinking water and other water sources that for used for agriculture must be reduced to the maximum permissible concentration [4,5]. The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. In order to solve heavy metal pollution in ecosystem, it is important to bring applicable solutions to the subject. It is possible to clean polluted environment only with long study requiring expensive and complex plants. Therefore, it is important to take effective precautions to prevent water, soil and air pollution [6].

Lead(II) pollution has been recognized as a potential threat to air, water and soil. Lead(II) has been found to be acute toxic to human beings when present in high amounts. The average concentration of lead(II) in the Earth's crust is around 13 µg/g but there is considerable variability in natural concentrations because of inputs from mineralized deposits of lead(II). However, a major feature of the environmental chemistry of lead(II) is the general diffuse pollution in top soils from a range of sources, including mining and smelting, recycling of sewage sludge and from motor vehicle exhausts. Because lead(II) is not biodegradable, once soil has become contaminated it remains a long-term source of lead(II) exposure [7,8]. Cadmium(II) is also released into natural water from metal plating, mining, pigments and alloy

E-mail address: kocaoba@yildiz.edu.tr.

industries as well as from sewage. Cadmium(II) compounds are often found in or attached to small particles present in the air, but it is difficult to tell by smell or taste, as it does not have any recognizable taste or odor. Breathing air with very high levels of cadmium can severely damage the lungs and may cause death [9].

There are several methods to treat the metal contaminated effluent such as precipitation, ion exchange and adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment. Ion exchange and adsorption is one of the more popular methods and has been widely practiced in industrial wastewater treatment processes for the removal of heavy metals from wastewater [10–14]. In the purification process, low cost purificant–adsorbent systems are preferred. For this reason, industrial wastes and metallurgical by-products are used and also natural substances like zeolites particularly clays [15–19]. The clay minerals in soil play an important role in the environment by acting as a natural scavenger of pollutants from water through both ion exchange and adsorption mechanisms. The high specific surface area, chemical and mechanical stability, layered structure, high cation-exchange capacity, etc., have made the clays excellent adsorbent materials [9]. Other low cost adsorbents, such as agricultural wastes, biomass, algae, etc., have been studied less extensively due to their local availability [20–24].

In this study, as a low cost adsorbent, dolomite's performance for removal of lead(II) and cadmium(II) was investigated against a strongly cationic resin Amberlite IR 120. Dolomite usage is increasingly important in different branches of industry such as the food and pharmaceutical industries and the production of fertilizers, glass and building materials [25].

The Pb(II), Cd(II)–dolomite system was chosen for this study for some reasons. First, lead(II) and cadmium(II) are common pollutants found in industrial wastewater discharges and contaminated groundwater systems. Second, dolomite is a major constituent in many shallow groundwater aquifers that serve as a drinking water source and in deep geological formations that are used for underground injection of wastewater and spent brines. Also, there is not enough study in this system.

2. Materials and methods

2.1. Materials

A strong cation-exchange resin, Amberlite IR 120 (Rohm & Haas Company) in hydrogen form and a natural zeolite, dolomite [$CaMg(CO_3)_2$] were used for the removal of lead(II) and cadmium(II). For conditioning of resin, after three preliminary recycling of the resin in column system with 1 M HCl and NaOH solutions to remove eventual chemicals residues (solvents, functionalizing agents) trapped in the resins' matrixes during their preparation, the samples were finally converted in hydrogen forms by 1 M HCl. The properties of Amberlite IR 120 are given in Table 1.

Dolomite is a kind of primary sediment mineral and has a widespread geological distribution. Its chemical formula is written as $CaMg(CO_3)_2$, with chemical composition in oxide (wt.%)

Table 1
Properties of Amberlite IR 120

Data	Amberlite IR 120
Matrix	Styrene
Functional group	Sulphonic acid
Particle size (mm)	0.3–1.2
Maximum temperature (°C)	120
pH range	0–14
Total capacity (equiv./L)	1.8

CaO 29.46%, MgO 20.65% and loss of ignition 38.45% used in this study. Chemical composition of the dolomite sample was first identified by X-ray diffraction, differential thermal and IR spectrophotometric analysis. Chemical analysis of the sample was carried out on GE-SPG 7, X-ray fluorescence spectrophotometer. The results are summarized in Table 2. Dolomite was washed thoroughly with double distilled water to remove the dirt and other foreign matter and dried at 40 °C for a period 4–5 h. The samples were 200 mesh particle size.

2.2. Chemicals

Analytical reagent grade $Pb(NO_3)_2$, $Cd(NO_3)_2$, HCl, NaOH, chemicals from Merck, Germany were used. Freshly prepared solutions were used throughout the experiments. Water was deionized and purified further with a Milli-Q water purification system (Millipore, USA).

2.3. Methods

2.3.1. Determination of optimum conditions

The adsorption of Pb(II) and Cd(II) on dolomite samples was studied by a batch technique. The optimum conditions were pH, adsorbent amount, contact time and concentration. The batch adsorption experiments were carried out by shaking known amounts of dolomite with 100 mL aqueous metal solutions of 5–100 mg/L concentration at various pHs (1–8) and at room temperature (20 ± 2 °C) in several stoppered bottles for retention times varying from 5 to 90 min. The study of adsorbent doses was carried out by varying the amount of adsorbent (0.1–1 g). The batch adsorption experiments were also conducted at different pH levels (pH 1–8) and solution pHs were

Table 2
Chemical analysis of natural dolomite

Component	%
SiO_2	0.32
Al_2O_3	0.25
Fe_2O_3	0.16
CaO	29.46
MgO	20.65
Na_2O	0.9
K_2O	2.3
MnO	0.03
P_2O_5	0.16
LOI[*]	38.45

[*] LOI, loss of ignition.

adjusted by adding 0.1N NaOH and HCl solutions. The pHs of the solutions were adjusted before adding ion exchange resin and dolomite. The stirring speed was 2000 rpm during all of the batch experiments. Dolomite samples were well dispersed in aqueous metal solutions. At the end of the pre-determined time interval, the adsorbent was removed by the filtration (the supernatant solution was filtered through 0.45 μm microporous membrane filter) and the final concentration was determined in the filtrate by atomic absorption spectrophotometry using an air–acetylene flame (Varian Spect AA 220). Optimum conditions were determined for both metals.

2.3.2. Equilibrium experiments

For investigation of the equilibrium 0.5, 1, 1.5, 2, 3 g ion exchange resin and dolomite samples were weighed into Erlenmeyer flasks. They were contacted with 200 mL of lead(II) and cadmium(II) bearing solutions containing a constant concentration values (100 mg/L) at room temperature (20 ± 1 °C) for 5 days in a shaker. The stirring speed was at 200 rpm to maintain resin and dolomite particles in suspension. Since the state of equilibrium is mainly dominated by the pH of the liquid phase the pH value was varied in each series of experiments. The initial and equilibrium pH values were measured with an electrode and pH meter.

The amount of metal adsorbed per unit mass was calculated as

$$Q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations (mequiv./L); m the mass of the adsorbent (g); V is the volume of the solution (L).

2.3.3. Adsorption isotherms

Many models have been proposed to explain adsorption equilibria, but the most important factor is to have applicability over the entire range of process conditions. The Freundlich and Langmuir isotherms are used most commonly to describe the adsorption characteristics of adsorbent used in water and wastewater treatment [7–9,26].

2.3.3.1. Freundlich isotherm.

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [27]. The Freundlich equation may be written as

$$Q_e = K_f C_e^n \quad \text{(non-linear form)} \tag{2}$$

$$\log Q_e = \log K_f + n \log C_e \quad \text{(linear form)} \tag{3}$$

where Q_e is the amount of solute adsorbed per unit weight of adsorbent (mequiv./g); C_e equilibrium concentration of solute in the bulk solution (mequiv./L); K_f constant indicative of the relative adsorption capacity of the adsorbent (mequiv./g); n is the constant indicative of the intensity of the adsorption. Both K_f and n are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively.

2.3.3.2. Langmuir isotherm.

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces [28]. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes. A basic assumption of the Langmuir theory is that sorption takes place at specific homogenous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented by the expression:

$$Q_e = \frac{X}{m} = \frac{Q_0 b C_e}{1 + b C_e} \quad \text{(non-linear form)} \tag{4}$$

where X the initial concentration of solute minus the final concentration of solute in solution at equilibrium (mequiv./L) and m is the concentration of adsorbent (mequiv./L).

A linear form of this equation is

$$\frac{C_e}{Q_e} = \frac{1}{b Q_0} + \frac{C_e}{Q_0} \quad \text{(linear form)} \tag{5}$$

where C_e is the equilibrium concentration of metal in solution; Q_e is the amount of metal ion sorbed onto dolomite and resin, b and Q_0 are Langmuir constants representing the equilibrium constant for the adsorbate–adsorbent equilibrium and the monolayer capacity.

The linear Freundlich and Langmuir plots are obtained by plotting (i) $\log Q_e$ versus $\log C_e$ and (ii) C_e/Q_e versus C_e, respectively, from which the adsorption coefficients could be evaluated. The Langmuir equation is also used to obtain R_L, the dimensionless equilibrium parameter or the separation factor [29] from the expression:

$$R_L = \frac{1}{1 + b C_0} \tag{6}$$

where C_0 is the initial concentration of the adsorptive. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, 1 and 0, respectively describe unfavorable, linear and irreversible adsorption.

2.3.4. Effect of temperature on the metal adsorption onto dolomite

Equilibrium experiments with respect to sorption equilibria were carried out at constant concentrations in the liquid phase and constant quantities of dolomite in each of the samples. For the determination of the sorption equilibrium, samples of material (1 g) was taken in different stoppered bottles containing 300 mL bearing solutions of metals having an initial concentration of 100 mg/L metal concentrations at three different temperatures (20, 40 and 60 °C) and a constant stirring speed of 200 rpm. The bottles were shaken thoroughly in a temperature-controlled shaker for 3 h at desired temperature. The experiments show that equilibrium was attained within this period. Over this period a series of 5 mL solution samples were taken periodically and analyzed for metal ions. The samples

were analyzed for the metal concentrations by means of atomic absorption spectrophotometer.

All pH measurements were made with a pH-meter (Metrohm) and a combination glass electrode.

3. Results and discussion

In this study, adsorption properties of lead(II) and cadmium(II) on dolomite has been studied by using batch technique and the results were compared with Amberlite IR 120, strong cationic resin. Optimum conditions were determined for both metals. The results are given in Figs. 1–8.
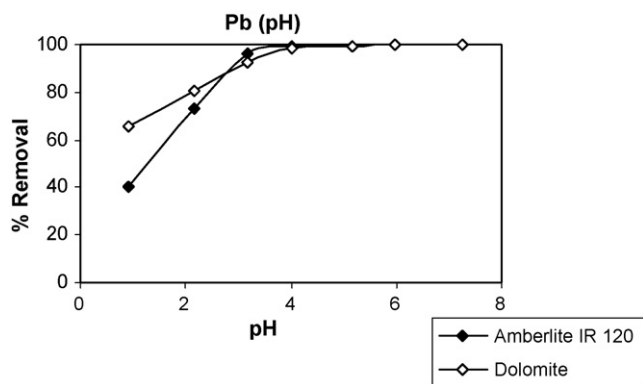

Fig. 1. Effect of pH for removal of lead(II) ions (0.5 g, 60 min, 20 mg/L).
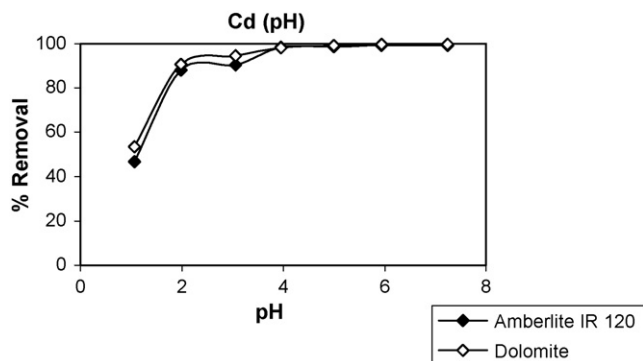
Fig. 2. Effect of pH for removal of cadmium(II) ions (0.5 g, 60 min, 20 mg/L).
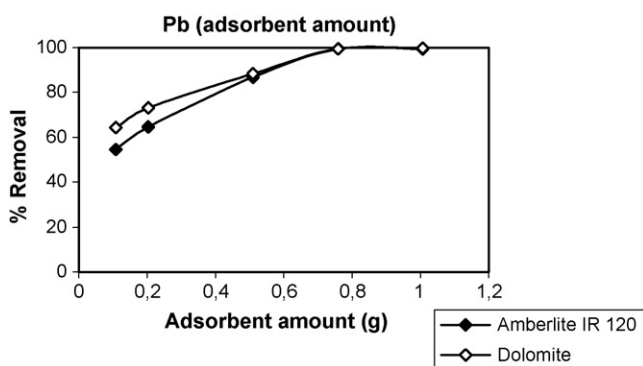

Fig. 3. Effect of adsorbent amount for removal of lead(II) ions (pH 5, 60 min, 20 mg/L).
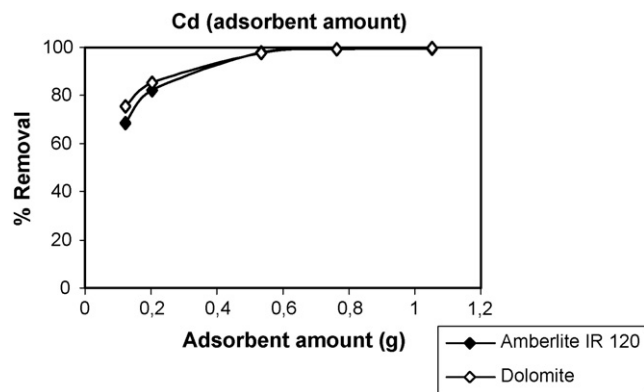

Fig. 4. Effect of adsorbent amount for removal of cadmium(II) ions (pH 5, 60 min, 20 mg/L).
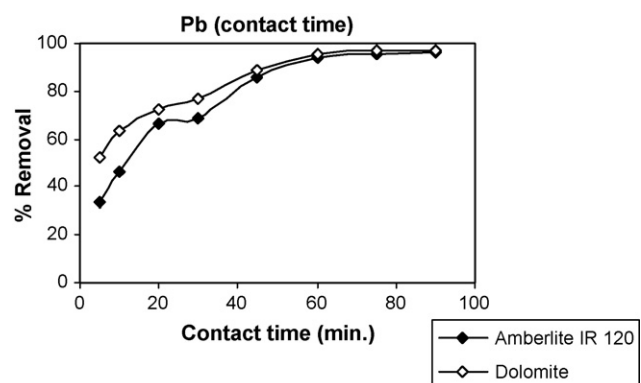

Fig. 5. Effect of contact time for removal of lead(II) ions (pH 5, 0.5 g, 20 mg/L).
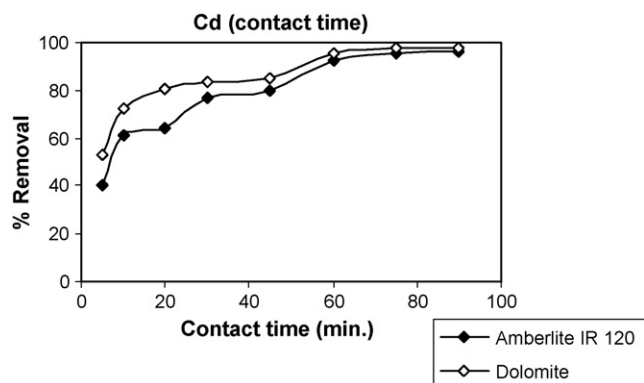

Fig. 6. Effect of contact time for removal of cadmium(II) ions (pH 5, 0.5 g, 20 mg/L).
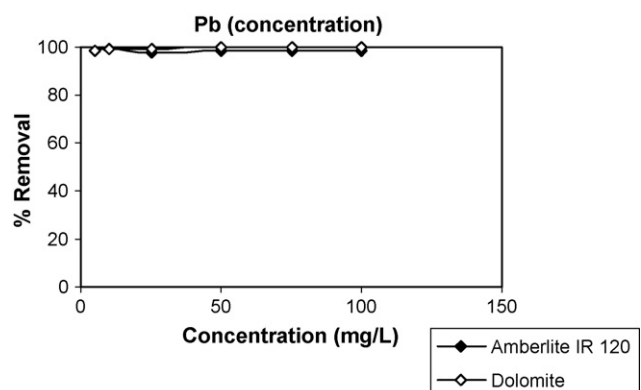

Fig. 7. Effect of concentration for removal of lead(II) ions (pH 5, 0.5 g, 60 min.).
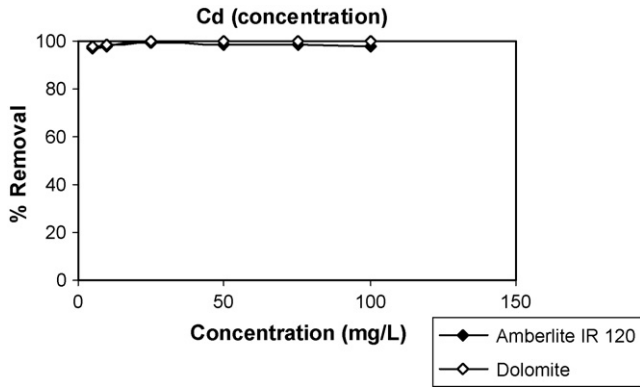
Fig. 8. Effect of concentration for removal of cadmium(II) ions (pH 5, 0.5 g, 60 min).
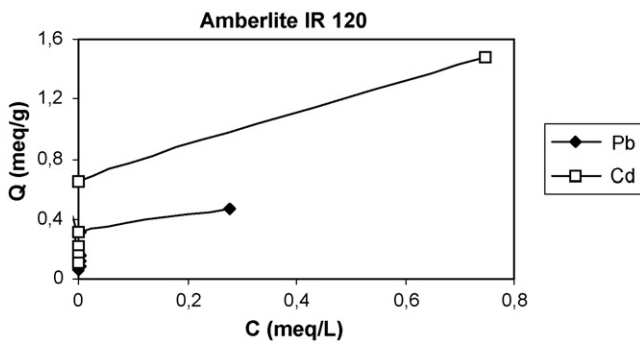

Fig. 11. Freundlich sorption isotherm of lead(II) and cadmium(II) ions by Amberlite IR 120.

Fig. 9. Equilibrium isotherms of lead(II) and cadmium(II) ions by Amberlite IR 120.

Fig. 12. Freundlich sorption isotherm of lead(II) and cadmium(II) ions by dolomite.

Equilibrium experiments were done and adsorption isotherms were obtained and presented in Figs. 9–14. Sorption data have been interpreted in terms of Langmuir and Freundlich equations. The parameters of Langmuir and Freundlich isotherms for sorption of metal ions on dolomite and Amberlite IR 120 are given in Table 3.

The effect of temperature on heavy metal adsorption onto dolomite surface was investigated and the results are given in Figs. 15 and 16. Thermodynamic parameters were calculated and the results are given in Table 4.
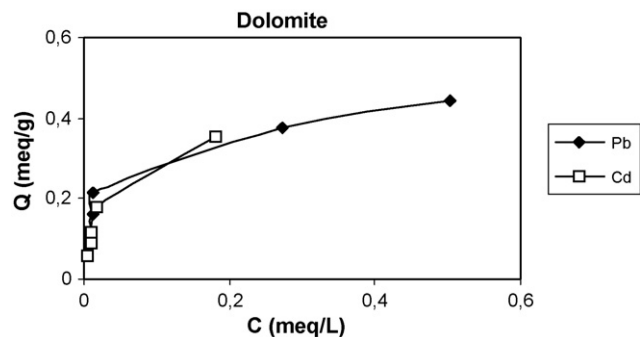

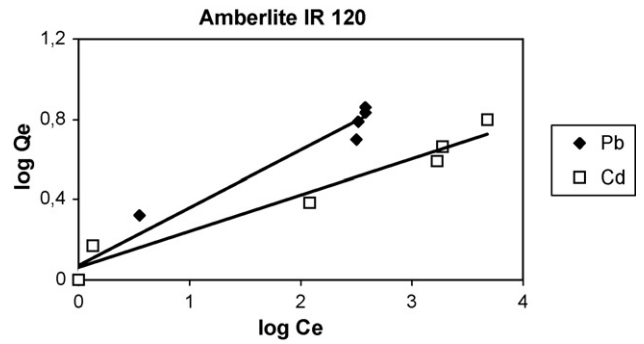Fig. 13. Langmuir sorption isotherm of lead(II) and cadmium(II) ions by Amberlite IR 120.
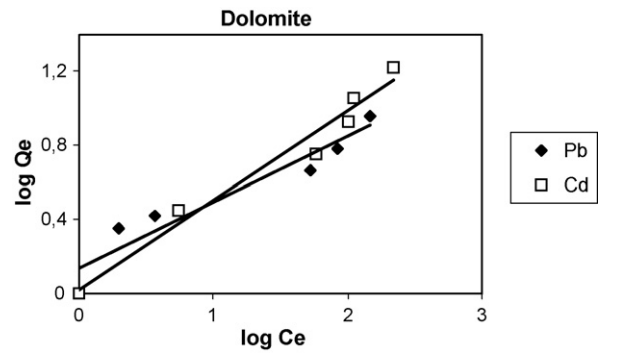

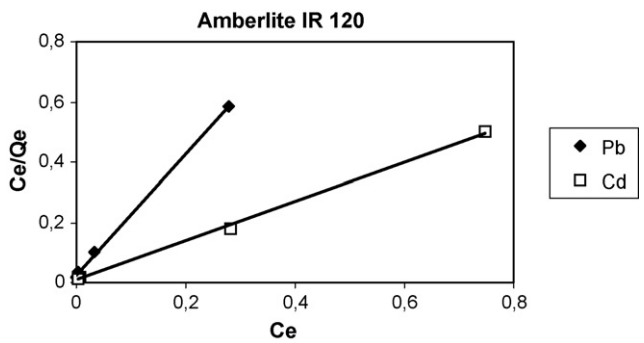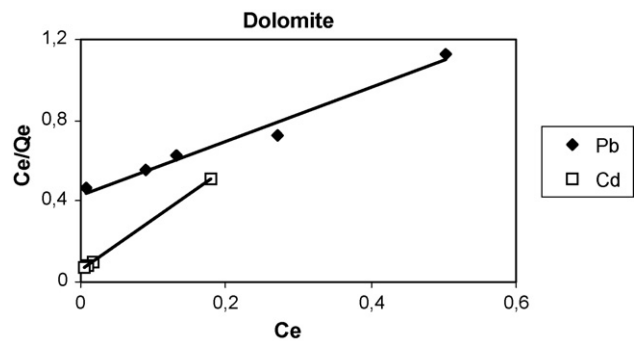Fig. 10. Equilibrium isotherms of lead(II) and cadmium(II) ions by dolomite.

Fig. 14. Langmuir sorption isotherm of lead(II) and cadmium(II) ions by dolomite.

Table 3
Parameters of Langmuir and Freundlich isotherms for sorption of metal ions on dolomite and Amberlite IR 120

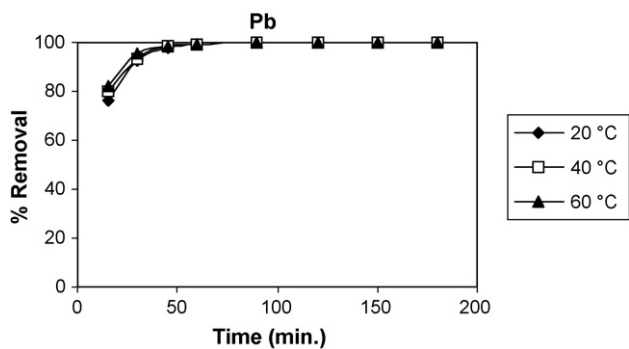| Metal ion	Langmuir isotherm method				Freundlich isotherm method		
	b	Q_0	R^2	R_L	K_f	n	R^2
Pb^{2+}(dolomite)	1.3210	0.4334	0.9768	0.457	0.3547	0.1376	0.9173
Cd^{2+}(dolomite)	2.5092	0.0579	0.9995	0.191	0.4606	0.0616	0.9145
Pb^{2+}(Amberlite IR 120)	2.0239	0.0236	0.9984	0.360	0.2871	0.0701	0.9596
Cd^{2+}(Amberlite IR 120)	0.6513	0.0104	0.9983	0.480	0.1827	0.0582	0.9547

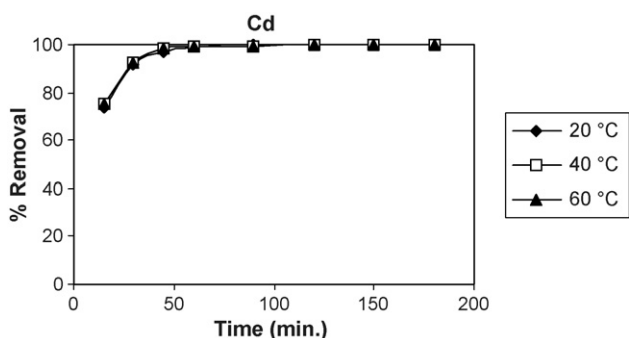Fig. 15. Effect of temperature for removal of lead(II) ions (pH 5, 100 mg/L, 1 g dolomite).

Fig. 16. Effect of temperature for removal of lead (II) ions (pH 5, 100 mg/L, 1 g dolomite).

3.1. Determination of optimum conditions

3.1.1. Effect of pH

The pH of the aqueous solution is an important variable which controls the adsorption of the metal at the clay–water interfaces. To determine the pH effect on adsorption capacity of materials, solutions were prepared at different pH levels from 1 to 8 before adding Amberlite IR 120 resin and dolomite. The effect of pH on metal adsorption was determined in batch experiments and the results are given in Figs. 1 and 2. The adsorption

values were increased with increasing pH values for both metals. The adsorption efficiency of Cd(II) increases from 46.53 to 99.32% for Amberlite IR 120 resin and increases from 53.48 to 99.32% for dolomite with an increase in pH of solution from 1 to 8. Also, the adsorption efficiency of Pb(II) were increased from 40.64 to 99.9% for Amberlite IR 120 resin and 65.48 to 99.9% for dolomite. At lower pH, the amount of adsorbed was found to decrease because the surface area of the adsorbent was more protonated and competitive adsorption occurred between H^+ protons and free metal ions towards the fixation sites [30]. Therefore, H^+ ions react with anionic functional groups on the surface of the adsorbent and result in restriction of the number of binding sites favorable for the adsorption of metal ions. For avoiding precipitation of metals high pH values were not preferable and the optimum pH was chosen as pH 5 for both metals.

3.1.2. The effect of adsorbent dose

The adsorbent amount is also important parameter to obtain the quantitative uptake of metal ion. The retention of metals was examined in the relation to the amount of adsorbent. The results of the dependence of Pb(II) and Cd(II) adsorption on the amount of resin and dolomite are shown in Figs. 3 and 4. For this purpose, the concentration of metals and stirring time were fixed at 100 mg/L and 60 min, respectively, while the amount of resin and dolomite were varied from 0.1 to 1 g. The percentage adsorption values were increased with increasing amount of adsorbents up to 0.5 g for Cd(II). It was increased up to 0.75 g for Pb(II). These results were expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area and sorption sites [31]. It is readily understood that the number of available sorption sites increases by increasing adsorbent amount. Optimum adsorbent amount was chosen as 0.5 g for both metals.

3.1.3. The effect of contact time

The effect of contact time was studied using a constant concentration of metal ions solution at room temperature. The adsorption of metal ions by Amberlite IR 120 resin and dolomite were studied by taking 0.5 g adsorbents with 100 mL of metal solutions in different stoppered bottles. The bottles were shaken for different time intervals in a shaker. The results are given in Figs. 5 and 6. The concentrations of Cd(II) and Pb(II) were kept as 100 mg/L while the amount of adsorbents added were 0.5 g. As can be seen from these figures, in the beginning of experimental run adsorption values were not high but the percentage of metal ion adsorption increased with increasing time. On the

Table 4
Thermodynamic parameters for the adsorption of metal ions on dolomite

Metal	ΔH° (kJ/mol)	ΔS° (kJ/$^\circ$K mol)	ΔG° (kJ/$^\circ$K mol)		
			293 $^\circ$K	313 $^\circ$K	333 $^\circ$K
Pb^{2+}	49.39	0.41	−62.45	−61.17	−60.26
Cd^{2+}	48.72	0.36	−60.78	−59.45	−58.60

basis of these results a 60 min shaking period was selected for all further studies.

3.1.4. The effect of initial metal ion concentration

Stock solutions of 1000 mg/L each of the standardized Pb(II) and Cd(II) were prepared from their nitrates using double distilled deionized water. Figs. 7 and 8 shows the effect of varying metal concentrations on the adsorption under the optimized conditions of 60 min contact time and 0.5 g of adsorbent in aqueous medium. Lead(II) and cadmium(II) concentrations were selected in the range of 5–100 mg/L. It was found that the metal amounts retained were almost stable in this concentration range for both metals. The maximum adsorption efficiency was obtained as 97.42% (Amberlite IR 120) and 99.82% (dolomite) for cadmium(II) and 98.55% (Amberlite IR 120) and 99.82% (dolomite) for lead(II). So that the optimum concentration was chosen as 20 mg/L in these experiments.

3.2. Adsorption isotherms

The sorption data have been subjected to different sorption isotherms, namely, Freundlich and Langmuir. The results are given in Figs. 9–14.

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. The isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the sorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface [32]. As can be seen in Figs. 11 and 12, $\log Q_e$ versus $\log C_e$ curves give straight lines according to the Freundlich isotherm equation. Both K_f and n are empirical constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively. For favorable adsorption, $0 < n < 1$. Since the degree of favorability increases as n approaches zero all samples shows a very high affinity for studying heavy metals. The adsorption intensity given by the Freundlich coefficient, n, is <1 in all cases, the values lying between 0.058 and 0.137. A greater value of the intercept K_f indicates a higher capacity for adsorption than a smaller value. The Freundlich adsorption capacity (K_f) lies between 0.18 and 0.46.

In order to ascertain whether the adsorption is chemisorptive in nature with chemical forces binding Pb(II) and Cd(II) ions to the surface of the clay adsorbents, the experimental data are also tested with respect to Langmuir isotherm. As seen in Figs. 13 and 14 from the linear relation between C_e/Q_e and C_e, the adsorption equilibrium constant b and maximum adsorption capacity Q_0 of adsorbents were calculated and these are also shown in Table 3. The adsorption isotherm of Pb^{2+} and Cd^{2+} exhibit Langmuir behavior, which indicates a monolayer adsorption.

The plots have good linearity in both cases (Freundlich plots, $R = 0.91$–0.96, Langmuir plots, $R = 0.97$–0.99) at room temperature. The values of the adsorption coefficients, computed from these plots are given in Table 3. The values of the adsorption

coefficients indicate the favorable nature of adsorption of Pb(II) and Cd(II) on the clay and resin. The Langmuir monolayer adsorption capacity, Q_0, is between 0.01 and 0.43 mequiv./g. The Langmuir equilibrium coefficient, b, has values of 0.65–2.5. The separation factor, R_L, with values of 0.19–0.48, also support favorable adsorption of the metal ions on the dolomite and resin. Strong adsorbate–adsorbent interactions are suggested by the values of the adsorption coefficients.

Also, some other studies showed that Freundlich and Langmuir isotherms correspond well with the experimental results of some heavy metals [1,5,8,19].

3.3. Effect of temperature

To investigate the effect of adsorption temperature on the metal adsorption onto the dolomite surface, experiments were carried out with initial concentrations of lead(II) and cadmium(II) 100 mg/L at 180 min contact time and 1 g adsorbent amount, at three different temperatures (20, 40 and 60 °C) and a constant stirring speed of 200 rpm. A small increase of lead(II) and cadmium(II) sorption is observed by increasing the temperature of the system. The results are given in Figs. 15 and 16. As can be seen from these figures, the adsorption of lead(II) and cadmium(II) onto the surface of dolomite taken place quickly until 30 min and reached adsorption equilibrium at 60 min for three different temperatures. After this period, the adsorption rate exhibits the tendency to be almost constant. Therefore, it can be said that in order to reach adsorption equilibrium, the adsorption time 60 min are sufficient for studying concentrations of these metals.

A small increase in uptake of heavy metal cations with the rise in temperature was observed.

3.4. Thermodynamic studies

The amounts of sorption of single metal ions by natural dolomite are measured in temperature 293–333 °K. Thermodynamic parameters were calculated for this system by using the equation [33]:

$$\ln K_D = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{RT} \right) \tag{7}$$

where K_D is the distribution coefficient; ΔH, ΔS, and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant. The values of enthalpy (ΔH) and entropy (ΔS) were obtained from the slope and intercept of $\ln K_D$ versus $1/T$ plots, which were calculated by a curve-fitting program. Gibbs free energy (ΔG) was calculated using the well-known equation:

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

All these relations are valid when the enthalpy change remains constant in the temperature range. The values of the thermodynamic parameters for the sorption of metal ions on dolomite are given in Table 4.

The positive values of enthalpy changes ΔH, show that the adsorption of metal ions is endothermic. One possible explana-

tion of endothermicity of heats of adsorption is that the metal ions are well solvated. In order for the metal ions to be adsorbed, they have to lose part of their hydration sheath. This dehydration process of the ions requires energy. This energy of dehydration supersedes the exothermicity of the ions getting attached to the surface. We can say that the removal of water from the ions is essentially an endothermic process and it appears that endothermicity of desolvation process exceeds that of the heat of adsorption to a considerable extent. The positive value of adsorption entropy indicates that the adsorption process is irreversible. Also, the positive entropy favors complexation and stability of sorption. The resultant effect of complex bonding and steric hindrance of the sorbed species eventually increases the enthalpy and entropy of the system. The values of free energy change ΔG are negative as expected for a spontaneous adsorption process. The same type of behavior has been reported earlier [7,34].

The thermodynamic parameters show the dolomite–metals interactions to be thermodynamically favorable without requiring large activation energies.

4. Conclusion

In this study, the effects of parameters such as pH, amount of adsorbent, contact time and concentration on removal of lead and cadmium metal ions from aqueous solutions. According to these experimental results and all previous works with cationic resins and natural zeolites [11,12,17,35], it was demonstrated that Amberlite IR 120 is a strong cation-exchange resin and dolomite have good capability and efficiency for the removal of these heavy metals from aqueous medium. Optimum conditions were found at a concentration of 20 mg/L, pH 5, contact time 60 min, and amount of adsorbent 0.5 g.

The adsorption is supported by Freundlich and Langmuir isotherms and the adsorption coefficients indicate favorable adsorption.

Adsorption of Pb(II) and Cd(II) on the clay adsorbent (dolomite) take place through sufficiently strong endothermic interactions accompanied by thermodynamically favorable entropy and Gibbs energy changes.

As a low cost adsorbent, dolomite can be preferable for removal of heavy metals from water and wastewaters.

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