

Removal of Cadmium and Lead from Aqueous Solution by Calcite

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Abstract

The removal of toxic cadmium(II) and lead(II) from aqueous solutions was investigated using calcite, which is inexpensive and widespread over the globe, as the effective inorganic adsorbent. The experimental data of the removal equilibrium were correlated by either the Langmuir or Freundlich equations. Results indicate that the Langmuir model gave a better fit to the experimental data than the Freundlich equation. Maximum adsorption capacities were determined as 18.52 mg/g Cd and 19.92 mg/g Pb for natural calcite at 25°C, respectively.

Keywords: cadmium, lead, removal, adsorption, calcite

Introduction

Industrial wastewater effluents from metal-finishing and mining/metallurgical sectors often contain elevated levels of heavy metals and cause serious environmental pollution problems.

Water pollution due to heavy metals such as cadmium and lead are serious global problems.

Toxicological effects of acute cadmium poisoning are manifested in a variety of symptoms, including high blood pressure, kidney damage, and destruction of red blood cells. Cadmium is used in a wide variety of industries such as the electroplating industry, nickel-cadmium batteries, pigments, plastics, pesticides, dyes and textile operation. Lead is known to damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damage [1]. The main sources of human exposure to lead include the uses of leaded gasoline, industrial sources such as lead mining, smelting and coal combustion, the use of lead-based paint and

lead containing pipes in water supply systems.

Therefore, a systematic study of the removal of cadmium and lead from wastewater is of considerable significance from an environmental point of view. There are several methods to treat 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.

Adsorption is one of the methods for the removal of heavy metals from wastewater. Much work has been done on the removal of lead and cadmium by clays [1-5], minerals such as goethite [6], hydroxyapatite [7] and calcite [8-11], calcareous soils [12-13] some industrial by product and waste materials such as slags, sludges [14], modified asphaltite ashes [15], bark, fly ash [16], chitosan, dead biomass, modified wool, moss, peat, seaweed, zeolite, humic acid [17], sesquioxides (iron, aluminium, or manganese oxides) [18] and others. Some of the highest adsorption capacities reported for some heavy metals are: 48.78 mg Cd/g hydroxyapatite [5], 6 mg Pb/g natural bentonite [14], 4.11 mg Cd/g acid treated bentonite, 16.50 mg Cd/g heat treated bentonite [2], and 0.57 mmol (64 mg) Cd/g bone char [19], 1.02 and 64.93 mg Cd/g for natural and thermally activated dolomite, respectively [20].

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Calcite is an important mineral that is ubiquitous in soils, shallow ground water aquifers and marine sediments. Calcite may be the dominant sorbent for a variety of metals in carbonate aquifers [8, 11, 21].

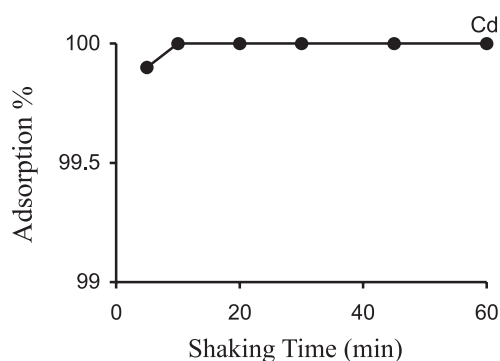
In this paper, systematic laboratory investigations on the removal of Cd(II) and Pb(II) from an aqueous solution using natural calcite by a batch operation technique have been reported.

Materials and Methods

Natural calcite used as an adsorbent in the experiments was received from Cermik-Diyarbakir, Turkey. It was crushed, ground, sieved below 100 mesh size and dried at 105°C in an oven for 2 h before use. Chemical analysis of the calcite was performed by atomic absorption spectrophotometer (Unicam model Solar-929) and a flame photometer (JENWAY PFP 7 Model) and results were given in Table 1. Chemicals used were of analytical grade.

Table 1. Chemical composition of natural calcite.

Element	%
CaO	56.0
MgO	17.0
Fe ₂ O ₃	0.14
loss of ignition	27.9



The pH of the solutions was measured with a pH meter (NEL 890) pH of cadmium(II) and lead(II) solutions are 5-6 and 7-8 before and after adsorption experiments. A water bath with shaker model (NUVE ST 400) was used for shaking the adsorption batches.

Adsorption measurements were made by batch technique at room temperature ($25 \pm 1^\circ\text{C}$). A known amount of calcite was placed in 100 ml reagent bottles containing 10 ml cadmium and lead solution and shaken for a given time period. Then, calcite was separated using a centrifugation step (4500 rpm) over 15 min. Metal concentrations in the supernatant were determined by atomic absorption spectrometry.

Results and Discussion

Various adsorption parameters for the effective removal of cadmium and lead using calcite as an adsorbent from aqueous solution were studied and optimized.

Effect of Shaking Time

The time-dependent behaviours of Cd(II) and Pb(II) adsorption were measured by varying the equilibrium time between adsorbate and adsorbent in the range of 5-60 min. The concentration of Cd(II) and Pb(II) were kept as 10 µg/ml while the amount of calcite added was 0.1 g. The percentage adsorption of Cd(II) and Pb(II) plotted in Fig 1 as a function of contact time indicates that the equilibrium between the Cd(II) and Pb(II), and calcite were

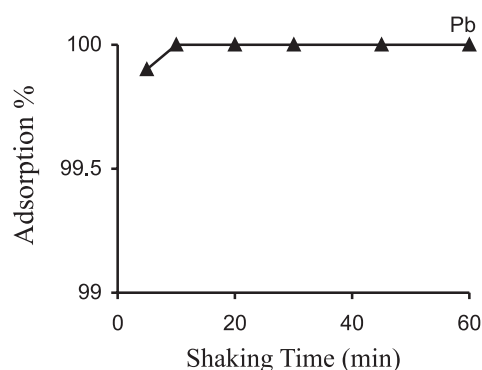


Fig. 1. Effect of shaking time on adsorption of Cd(II) and Pb(II) onto natural calcite. Initial concentration of Cd (II) and Pb(II): 10 µg/ml; amount of calcite: 0.1 g.

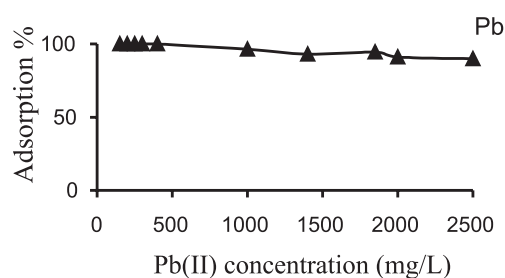
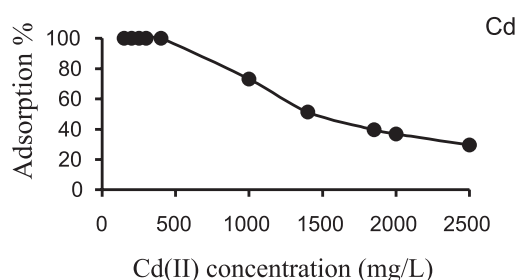


Fig. 2. Effect of initial concentration of Cd (II) and Pb (II) on the adsorption of Cd (II) and Pb (II) onto calcite. Shaking time: 10 min; amount of calcite: 0.1 g.

attained within 10 min. Therefore, a 10 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent measurements.

Effect of Initial Concentration of Cd (II) and Pb (II)

Fig. 2 shows the effect of varying cadmium and lead concentration on the adsorption under optimized conditions of 10 min shaking time and *0.1 g adsorbent in aqueous medium. The concentrations of cadmium and lead were varied from 150 to 2500 µg/ml.

Results show that the adsorption of the cadmium and lead remains constant up to 500 µg/ml and then decreases as the cadmium and lead concentration increases. Also, adsorption isotherms for Cd and Pb on the calcite are presented in Fig 3. These isotherms are generally L and H type according to the Giles classification. Type L (and H) represents the Langmuirian adsorption isotherm, which is characteristic for strong chemical interactions.

To quantify the adsorption capacity of natural calcite in relation to the cadmium and lead ions, the experimental data were fitted to the Langmuir linear equation:

$$C/X = 1/(bX_m) + C/X_m \quad (1)$$

and Freundlich nonlinear and linear equations:

$$q = K_F C^{1/n} \quad (2)$$

$$\log q = \log K_F + 1/n \log C \quad (3)$$

where: q (mg/g) is the equilibrium concentration of cadmium and lead on calcite, C is in the equilibrium concentration of cadmium and lead remaining in the solution. X is the amount of cadmium and lead retained per gram of calcite. X_m is the maximum amount of cadmium and lead that can be adsorbed in a monolayer (adsorption capacity) and b is a constant related to the energy of adsorption.

Fig. 4 shows the straight lines obtained plotting C/X versus C for cadmium on natural calcite samples studied, correlation coefficients being in both cases greater than 0.99 (all correlations were significant at the 0.001 probability level). X_m and b parameters were calculated from the least squares method applied to the straight lines in Fig 4. The Langmuir characteristics parameters and the degree of correlation of the adsorption data with respect to this equation are given in Table 2.

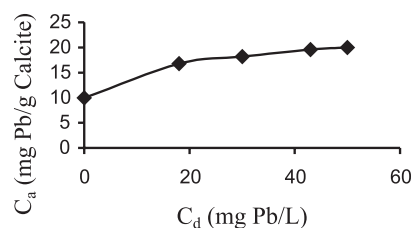
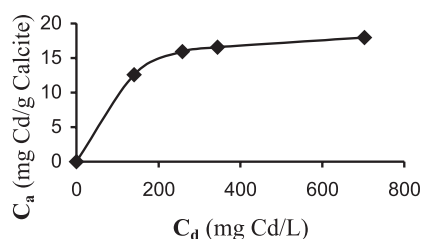


Fig. 3. Adsorption isotherms of Cd(II) and Pb(II) ions on natural calcite.

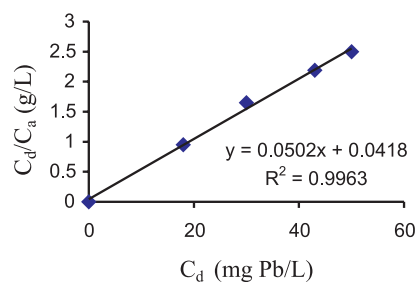
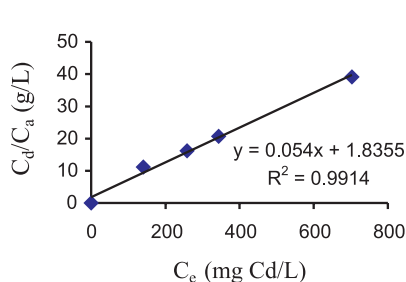


Fig.4. The Langmuir isotherms of Cd(II) and Pb(II) ions on natural calcite.

Table 2. Characteristic, parameters and determination coefficient of the experimental data according to the degree of correlation Langmuir and Freundlich.

Metal	Langmuir parameters			Freundlich parameters		
	X_m (mg/g)	b (L/mg)	r^2	K_F	n	r^2
Cd	18.52	0.029	0.9914	1.483	1.483	0.8698
Pb	19.92	3.461	0.9963	1.482	1.015	0.9161

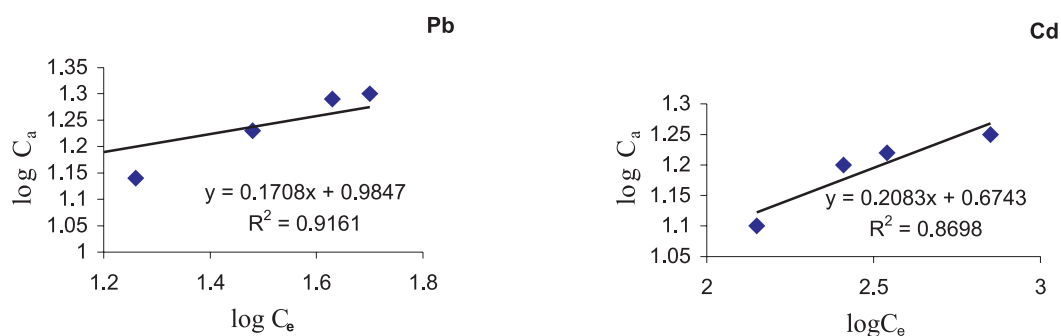


Fig.5. The Freundlich isotherms of Cd(II) and Pb(II) ions on natural calcite.

Table 3. Ionic radius of some metals [11].

Metal	Ionic radii (Å°)
Ba	1.34
Sr	1.12
Ca	0.99
Cd	0.97
Mn	0.80
Zn	0.74
Co	0.72
Ni	0.69

Fig. 5 shows a linear relationship $\log q$ versus $\log C$. The parameters K_F and n for cadmium and lead have been calculated from experimental data using the least squares method and results obtained are given in Table 2, which shows correlation coefficient (0.8698. and 0.9161 for Cd and Pb respectively). The magnitude of exponent n gives an indication of favorability and capacity adsorbent/adsorbate. It is generally stated that the value of n in the range 1-10 represents good adsorption.

The incorporation of Pb in bulk calcite is prohibited by the large ionic radius of divalent Pb (1.20 Å°) relative to that of Ca (0.99 Å°) are given Table 3 [11, 23].

Although seemingly paradoxical, there are good thermodynamic arguments indicating that calcite should have a high affinity for Pb. A linear correlation exists between the standard Gibbs free energies of formation of rhombohedral carbonates and the standard Gibbs free energies of their aqueous divalent cations [23]. This correlation allows prediction of the thermodynamic equilibrium constant for the distribution of divalent cations between calcite and aqueous solution. This free energy relationship predicts a relatively large value distribution coefficient $D_{Pb, calcite}$ that can be evaluated experimentally for Pb between calcite and solution,



The equilibrium constants for Eqn. 4 and Eqn. 5 may be called a distribution ratio D :

$$D_{Pb, calcite} = (X_{Pb} / X_{Ca})_{calcite} (\alpha_{Ca^{2+}} / \alpha_{Pb^{2+}})_{aqueous} \quad (6)$$

where X is the solid mole fraction and α is aqueous activity.

The thermodynamic equilibrium constant for Pb distribution between calcite and aqueous solution can also be approximated by the ratio of the equilibrium solubility product K_{sp} for calcite and cerrusite,

$$K_{Pb, calcite} = (K_{sp} CaCO_3) / (K_{sp} PbCO_3) \quad (7)$$

assuming an ideal solid-solution. Thus, with $\log K_{sp}$ values of -8.48 for calcite and -12.9 for cerrusite, a $\log K_{Pb, calcite}$ value of 4.4 is predicted. In the case of an ideal solid solution, from $D_{Pb, calcite}$ from Eqn. 6 and $K_{Pb, calcite}$ from Eqn. 7 would be equal.

Conclusion

The objective of this work was to study the dependence of heavy metals such as lead cadmium on calcite. Conclusions from the present study are as follows:

1. Adsorption of lead(II) and cadmium(II) on calcite followed the Langmuir adsorption isotherm model.
2. Removal of lead(II) and cadmium(II) onto calcite depends on initial concentration.
3. Maximum adsorption capacities of cadmium and lead were determined as 18.52 mg/g and 19.92 mg/g for cadmium and lead ions at 25°C, respectively. Calcite adsorbed more lead ions than cadmium ions because solubility of lead is less than cadmium.
4. Natural calcite, which is inexpensive (about \$ 3-5 per ton of calcite ore) and widespread over the globe, is cheaper when compared with other adsorbents such as kaolinite (\$28-35 per ton of kaolinite ore), clays(\$ 24-39 per ton of clay ore) and activated carbon (about \$ 10 per kg activated carbon).

5. Natural calcite is effective in removing cadmium and lead ions from aqueous solutions, in the range of concentrations used in our experiments. Therefore, natural calcite can be used for a cost-effective treatment to purify wastewater. Removal efficiency could be made better by increasing the amount of the calcite used.

Acknowledgements

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