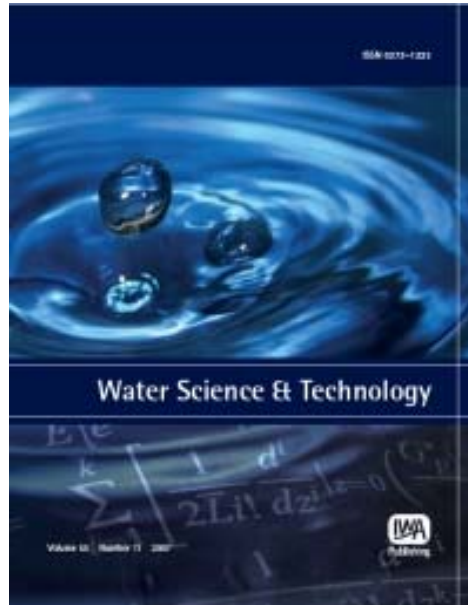


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The sorption of lead, cadmium, copper and zinc ions from aqueous solutions on a raw diatomite from Algeria

Messaouda Safa, Mohammed Larouci, Boumediene Meddah and Pierre Valemens

ABSTRACT

The adsorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions from aqueous solution by Algerian raw diatomite was studied. The influences of different sorption parameters such as contact pH solution, contact time and initial metal ions concentration were studied to optimize the reaction conditions. The metals ions adsorption was strictly pH dependent. The maximum adsorption capacities towards Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} were 0.319, 0.311, 0.18 and 0.096 mmol g^{-1} , respectively. The kinetic data were modelled using the pseudo-first-order and pseudo-second-order kinetic equations. Among the kinetic models studied, the pseudo-second-order equation was the best applicable model to describe the sorption process. Equilibrium isotherm data were analysed using the Langmuir and the Freundlich isotherms; the results showed that the adsorption equilibrium was well described by both model isotherms. The negative value of free energy change ΔG indicates feasible and spontaneous adsorption of four metal ions on raw diatomite. According to these results, the high exchange capacities of different metal ions at high and low concentration levels, and given the low cost of the investigated adsorbent in this work, Algerian diatomite was considered to be an excellent adsorbent.

Key words | adsorption, diatomite, heavy metals, kinetics

Messaouda Safa (corresponding author)
Mohammed Larouci
Boumediene Meddah
Pierre Valemens
The Faculty of Natural and Life Sciences,
Mascara University,
P.O. Box 763,
29000 Mascara,
Algeria
E-mail: hamasafa@hotmail.fr

INTRODUCTION

Industrial development and urban expansion are frequently considered to be sources of water resources pollution with organic and inorganic pollutants, especially heavy metals (Rainbow 1985). Several adverse health effects of heavy metals have been known for a long time. According to an ATSDR/EPA assessment, lead, cadmium and copper are among the top toxics having the most adverse effects on public health based on toxicity and current exposure levels (ATSDR/EPA 2001).

Several techniques have been used for heavy metal removal from wastewater such as coagulation-flocculation and chemical precipitation, ion exchange, membrane filtration, electrodialysis methods, reverse osmosis and solvent extraction (Dabrowski *et al.* 2004; Erdem *et al.* 2004). However, these methods usually involve expensive materials and high operational costs (Kurniawan *et al.* 2006a). The adsorption methods have been considered to be the most effective for removing heavy metals from

water, because of their low cost and simple technique (Jorgensen & Weatherley 2006; Kurniawan *et al.* 2006b). In recent years, numerous studies have focused on the removal of heavy metals from aqueous solutions using low-cost adsorbents with high exchange capacities, which are locally available and accessible. Various materials, including natural and synthetic materials, have been studied for this purpose, such as natural organic and inorganic materials (chitosan, zeolites, clay and clay minerals, etc.) and some waste products from industrial operations (fly ash, coal and oxides) (Babel & Kurniawan 2003; Wang *et al.* 2003).

Diatomite is one of many adsorbents that have been tested for heavy metal adsorption. Šljivić *et al.* (2009) studied the adsorption properties of raw diatomite from Serbia toward Cu^{2+} , and Khraisheh *et al.* (2004) investigated the potential use of raw diatomite from Jordan as adsorbent for Cd^{2+} , Cu^{2+} and Pb^{2+} . Furthermore, diatomite was found to be a promising

agent for immobilization of caesium and cobalt radionuclides (Osmanlioglu 2007), as well as uranium (Aytas *et al.* 1999).

Diatomite or diatomaceous earth is available in large deposits around the world. It is a siliceous sedimentary rock formed from the sedimentation of diatoms (Goren *et al.* 2002). Diatomite's highly porous structure, with low density and high surface area, consists essentially of amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Thus, diatomite can be used in many applications such as water purification, filtration, bleaching of liquors and juices, and for the refining of edible and industrial oils and chemicals (Korunic 1998).

In Algeria, diatomite is widely available but is not exploited as an adsorbent for heavy metals. The aim of this study was to investigate the effectiveness of the natural raw diatomite from Algeria as an adsorbent for the removal of heavy metal ions from a model aqueous solution. Optimization of the adsorption conditions requires a better understanding of controlling environmental parameters; thus, the effects of adsorption time, initial pH values and initial metal ions concentration on adsorption capacity have been investigated. The adsorption data capacities were applied to various isotherm models in order to exploit different important adsorption parameters.

MATERIALS AND METHODS

Preparation and characterization of raw diatomite

Natural raw diatomite samples collected from Enfo Sig, Mascara Region, Algeria, were crushed into aggregate-sized pieces in roller mills, air-dried and gently ground to pass through a $63 \mu\text{m}$ mesh metal sieve.

The physicochemical characterization of raw diatomite was performed using standard procedures. Characterization of the raw diatomite was carried out by chemical composition, surface area analysis and bulk density. The chemical composition of diatomite was determined by X-ray fluorescence; the surface area of diatomite was obtained using the Brunauer, Emmett and Teller (BET) method. Nitrogen adsorption at 77 K is a standard and widely used method for determining surface area, pore volume and pore size distribution of the adsorbent. The cation exchange capacity (CEC) of the investigated adsorbent was tested using the ammonium exchange method. The density of the samples was determined by specific gravity bottle and the structure was studied using X-ray diffractograms (XRDs).

Effect of the pH solution

Stock aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were prepared, by dissolving 15.73, 15.29, 9.39 and 8.86 mmol/L of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively, into deionized water. The heavy metal solutions used in each study were prepared by fresh appropriate dilution of this stock solution.

The initial pHs for each solution were adjusted from ~ 2 to ~ 9 with the addition of NaOH or HCl solution 0.1 mol/L. Accordingly, adsorption is performed by mixing 0.5 g of raw diatomite with 50 mL of each solution (1.573, 1.529, 0.939 and 0.886 mmol/L of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively). The samples were shaken at 150 rpm for 24 h on a rotating box at room temperature. Finally, the samples were filtered and the pH values were measured by pH meter, and the concentrations of heavy metals of supernatants were determined using the atomic absorption spectroscopy (AAS) method.

Influence of contact time

To determine the effect of contact time on the exchanged amount of the heavy metals, batch experiments were carried out by preparing 0.5 g of raw diatomite and 50 mL of metal ion solutions with an initial concentration of 1.573, 1.529, 0.939 and 0.886 mmol/L of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively. The initial pHs of the solutions were maintained at ~ 5.5 by adding 0.01 M NaOH solution. The suspensions were shaken at 150 rpm at room temperature for different time intervals ranging from 10 min to 36 h. Finally, the suspensions were filtered through Whatman filter paper and immediately the concentrations of heavy metal cations in the filtrates were determined using the AAS method.

Isotherm study

The adsorption isotherms of heavy metal cations on raw diatomite were studied in a batch mode. An accurate amount of the diatomite was fixed at 0.5 g/50 mL while the initial heavy metal concentrations (C_0) varied from 0.1573 to 4.72, 0.1529 to 4.58, 0.0939 to 2.81 and 0.0886 to 2.66 mmol/L of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively. The initial pH of each solution was adjusted to ~ 5.5 . Sample bottles were sealed and shaken at room temperature under agitation with rotating rate speed of 150 rpm for 2 h. The suspensions were then filtered and subsequently heavy metal concentrations were determined using the AAS method.

RESULTS AND DISCUSSION

Chemical composition and X-ray diffraction

The chemical composition of diatomite was: SiO₂ (72.10%), Al₂O₃ (5.30%), CaO (7.20%), Fe₂O₃ (3.80%), MgO (2.60%), Na₂O (0.65%), K₂O (0.54%) and TiO₂ (0.37%), as shown in Table 1.

The N₂ adsorption-desorption isotherms are shown in Figure 1. According to the IUPAC classification, the adsorption-desorption isotherm for the investigated diatomite was of type-IV. The small hysteresis loop in the adsorption-desorption isotherms suggests that our diatomite is a mesoporous material. The results of textural parameters of raw diatomite are shown in Table 2; the BET surface area, total pore volume and average pore diameter are 21 m² g⁻¹, 0.042 cm³/g and 5.86 nm, respectively, and CEC is 2.31 mEq/g.

The crystallographic structure of diatomite was also determined in our study. The XRD pattern in Figure 2 showed typical reflections for amorphous silica (a broad reflection centred at 2θ = 20–25°) and for well-crystallized quartz.

Effect of initial pH

The removal of metal ions from water by an adsorbent is highly dependent on the pH of the solution, which subsequently affects the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate species (Schumi *et al.* 2001). The influence of initial pH on the adsorption amounts of four metal ions is illustrated in Figure 3. Similar curves were obtained for the four metal ions; the adsorption amount (q_e) of metal ions was affected by the initial pH of the solution. The q_e of the four metal

Table 1 | Chemical composition of raw diatomite

Constituent	Per cent by weight (%)
SiO ₂	72.1
Al ₂ O ₃	5.30
CaO	7.20
Fe ₂ O ₃	3.80
MgO	2.60
Na ₂ O	0.65
K ₂ O	0.54
TiO ₂	0.37

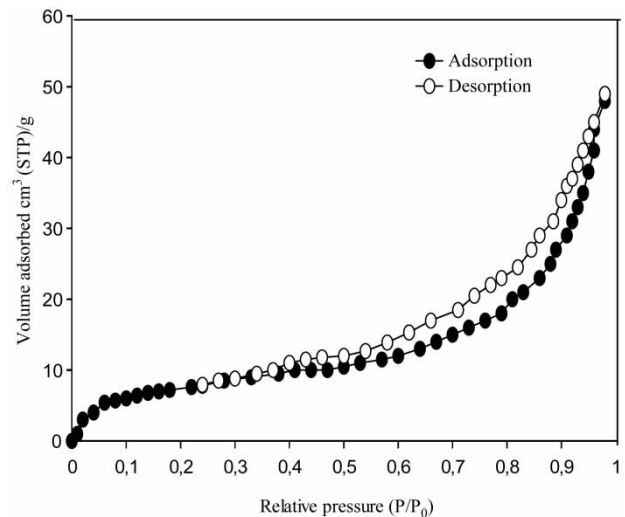


Figure 1 | Nitrogen adsorption-desorption isotherm.

Table 2 | Physicochemical properties of raw diatomite

Surface area (S _{BET}) (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Bulk density (cm ³ /g)	CEC (mEq/g)
21	0.0402	5.86	0.217	2.31

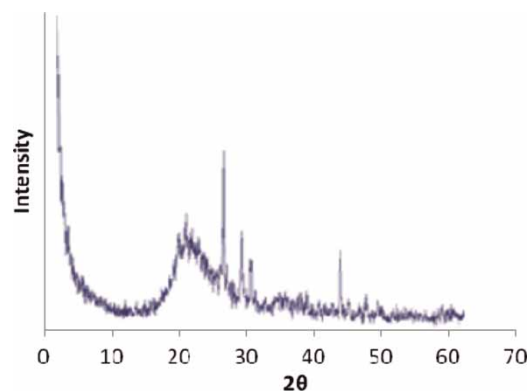


Figure 2 | XRD patterns of the raw diatomite.

ions increases with initial pH between 2 and 5. The maximum uptakes of the four metals were observed for the initial pH ~5; after initial pH 5 the metal ions uptake was almost 100%, regardless of the adsorbent. This may be caused by metal precipitation in alkaline solutions. It has been reported that precipitation of heavy metals starts at pH 8.3 (Cd²⁺), pH 7–8 (Pb²⁺), pH 7–10 (Cu²⁺) and pH 7–8 for Zn²⁺ (Namasivayam & Ranganathan 1995; Zheng & Qui 2009). In general, the precipitation of metal hydroxides into pores or spaces around the particles is barely possible because the sorption process is kinetically

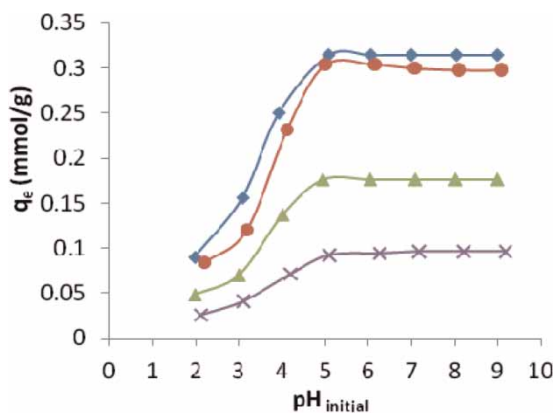


Figure 3 | Effect of pH on adsorption amount of Cd^{2+} (▲), Zn^{2+} (●), Cu^{2+} (■) and Pb^{2+} (×).

faster than the precipitation (Morel & Hering 1993; Dimitrova & Mehandgiev 1998). At low pH values, H^+ ion concentration is high and therefore protons can compete with the metal cations for surface sites. When the pH was increased, the competing effect of H_3O^+ decreased and the positively charged metal ions took up the free binding sites and hence the metal uptake capacity was increased (Matheickal *et al.* 1999).

Figure 4 represents the changes of final pH as a function of the initial pH. In the initial pH range 2–4, final pH increased with the initial pH for the four metal ions, where the plateaus began. The equilibrium final pHs for each metal ion were different; this finding can be explained considering the properties of metals and the relative amounts adsorbed for each metal.

Effect of contact time

The effect of contact time on metal ion sorption is a very important parameter for establishing the sorption systems

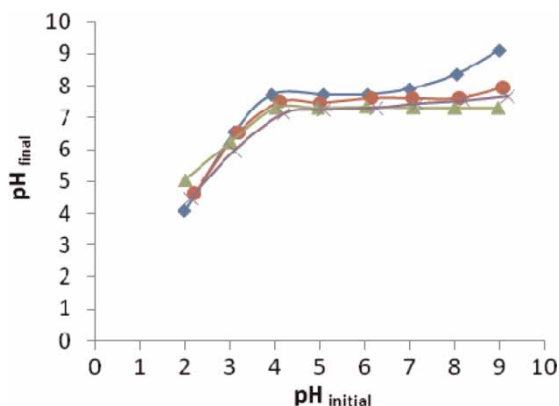


Figure 4 | Initial and final pH values Cd^{2+} (▲), Zn^{2+} (●), Cu^{2+} (■) and Pb^{2+} (×).

and selecting the optimum operating conditions for maximum batch metal removal process. The effect of contact time on the batch adsorption of a metal solution containing 1.573, 1.529, 0.939 and 0.886 mmol/L of Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively, at ambient temperature and initial pH value 6 is shown in Figure 5. The amount of Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} adsorption increased slowly with increase in contact time and then became almost stable, denoting attainment of equilibrium. It was shown that 120 min is enough to reach a maximum adsorption and to reach adsorption equilibrium for the four metal ions. The quick equilibrium time is due to the particle size. The effective surface area is high for small particles. The observed rapid kinetics has significant practical importance, as it will facilitate the scale-up of the process to smaller reactor volumes, ensuring efficiency and economy (Aksu 2002). A contact time of 120 min was selected as the optimum operating time for all the subsequent sorption experiments. Low reach adsorption equilibrium for Pb^{2+} (90 min) and high reach adsorption equilibrium for Cu^{2+} (240 min) were reported for raw diatomite from Jordan (Majeda *et al.* 2004) and from Serbia (Šljivić *et al.* 2009), respectively.

Sorption kinetics

A batch adsorption process was analysed by using two kinetics models that are based on adsorption equilibrium capacity: the Lagergren pseudo-first-order model (Lagergren 1898) and Ho's linear form (Ho 1995; Ho & McKay 2000) of the pseudo-second-order model, developed by Blanchard *et al.* (1984).

A simple kinetic analysis of sorption can be performed with a pseudo-first-order equation, proposed by Lagergren (1898). A pseudo first-order equation relates the adsorption

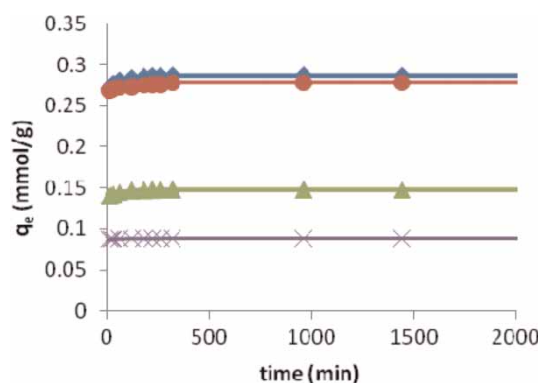


Figure 5 | Effect of contact time on adsorption amount of Cd^{2+} (▲), Zn^{2+} (●), Cu^{2+} (■) and Pb^{2+} (×) on diatomite.

rate to the metal adsorbed amount at time t as:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (1)$$

where k_1 (min^{-1}) is the pseudo-first-order sorption constant, q_e (mmol g^{-1}) is the adsorbed amount of metal on the sorbent surface at equilibrium and q (mmol g^{-1}) is the adsorbed amount of metal at any time t (min). Equation (1) can be integrated to the lineal form:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2)$$

Since $q = 0$ at $t = 0$, the initial rate of sorption h_1 , h_2 ($\text{mmol g}^{-1} \text{min}^{-1}$) can be calculated from Equation (3) as follows:

$$h_1 = k_1 q_e \quad (3)$$

The values of k_1 and q_e can be determined by the Lagergren pseudo-first-order equation from plots of $\ln(q_e - q_t)$ versus t (Figure 6(a)). The parameters of the pseudo-first-order model are summarized in Table 3. The values of determination coefficient for the plots were in the range 0.9481–0.9863. However, the calculated sorption capacity values obtained from this kinetic model do not give logical values and were very low for all metal ions compared with experimental sorption capacity. This finding suggested that the pseudo-first-order sorption rate expression of Lagergren is not appropriate to illustrate the kinetic profile.

The pseudo-second-order rate, which relates the solid adsorption capacity, has been presented by Blanchard et al. (1984), and is represented in the form:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (4)$$

where k_2 is the pseudo-second-order constant ($\text{g mmol}^{-1} \text{min}^{-1}$), q_e is the amount of metal sorbed at equilibrium (mmol g^{-1}) and q is the amount of metal ions on the surface of the sorbent at any time t (mmol g^{-1}). Integrating Equation (5) and transforming in its linear form (Ho 1995; Ho & McKay 2000):

$$t/q = 1/(k_2 q_e^2) + 1/q_e t \quad (5)$$

The initial sorption rate h_2 ($\text{mmol g}^{-1} \text{min}^{-1}$) is given by the following equation:

$$h_2 = k_2 q_e^2 \quad (6)$$

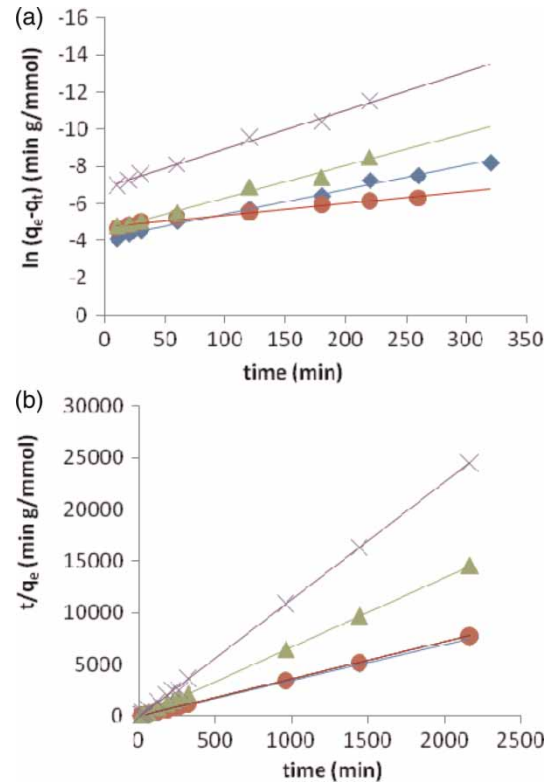


Figure 6 | Modelling of Cd^{2+} (▲), Zn^{2+} (●), Cu^{2+} (■) and Pb^{2+} (×) adsorption kinetics on raw diatomite. Linear plots of (a) pseudo-first-order model; (b) pseudo-second-order model.

Table 3 | Predicted kinetic constants for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} adsorption on raw diatomite

	Metals			
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Pseudo-first-order kinetics				
q_1 (mmol g^{-1})	0.0087	0.015	0.010	0.001
k_1 (min^{-1})	0.013	0.006	0.017	0.020
h_1 ($\text{mmol g}^{-1} \text{min}^{-1}$)	1.790	2.900	2.290	4.550
R^2	0.976	0.982	0.987	0.988
Pseudo-second-order kinetics				
q_2 (mmol g^{-1})	0.287	0.278	0.148	0.088
k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$)	3.95	3.21	8.62	-2.83
h_2 ($\text{mmol g}^{-1} \text{min}^{-1}$)	0.303	0.248	0.188	-0.021
R^2	0.999	0.998	0.999	0.999

By plotting t/q versus t as represented in Figure 6(b), the constants (k and q_e) can be determined from the curve. It is clear that the plots of t/q versus t give a linear form for all the initial metal concentrations studied. These results confirm the applicability of the pseudo-second-order equation.

The pseudo-second-order kinetics constants for the sorption of Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} on natural Algerian diatomite are given in Table 3. The regression coefficient values obtained from the pseudo-second-order model indicate a high correlation for all metals ($R^2 > 0.99$). The experimental values of sorption capacity were comparable with the calculated sorption capacity values determined from the pseudo-second-order model. The pseudo-second-order kinetic model fits the experimental data better than the pseudo-first-order kinetic model in this study.

Effect of initial heavy metal concentration

To eliminate the precipitation of metals, and to ensure that the amount of metal cations is removed from the solution only by the adsorption mechanisms, an initial solution of pH 5.5 was chosen as being optimal for maximum adsorption capacity determination.

Figure 7 represents the isotherms in which the amount of metal ions adsorbed at equilibrium, q_e (mmol g^{-1}), is plotted as a function of the concentration of ions in the solution at equilibrium C (mmol l^{-1}). It is clear that the adsorption amount of Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} increased with increase in initial concentration and then became almost stable, denoting attainment of saturation. The maximum adsorption capacities of the metals were 0.314, 0.305, 0.177 and 0.095 mmol g^{-1} adsorbent, respectively, for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} .

Table 5 summarizes the comparison of the maximum adsorption capacities for various adsorbents for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} reported in the literature. In fact, the adsorption capacity for heavy metals is highly dependent on the experimental conditions, e.g. solution pH, solution temperature, adsorbent dose, initial metal concentration,

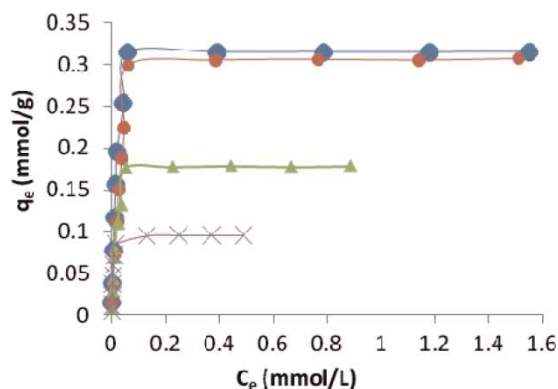


Figure 7 | Isotherms of Cd^{2+} (\blacktriangle), Zn^{2+} (\bullet), Cu^{2+} (\blacksquare) and Pb^{2+} (\times) adsorption on diatomite.

Table 4 | Predicted isothermal constants for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} adsorption on raw diatomite

	Metals			
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Langmuir model				
Q (mmol g^{-1})	0.319	0.311	0.180	0.096
b (L g^{-1})	6.530	4.580	3.410	2.020
R^2	0.990	0.999	0.999	0.990
Freundlich model				
K_F (mmol g^{-1})	3.590	2.390	1.004	3.640
n_1 ($\text{g mmol}^{-1} \text{min}^{-1}$)	1.220	1.290	1.740	1.210
R^2	0.930	0.996	0.993	0.990

contact time, particle size and adsorbent properties. As shown in Table 5, the adsorption capacity of some adsorbents reported in the literature for Pb^{2+} was higher than the investigated diatomite in this work. However, it can be seen that the adsorption capacity of the tested diatomite is superior to many other adsorbents for Cu^{2+} , Zn^{2+} and Cd^{2+} .

Two isothermal equations were applied to evaluate the test results.

The Langmuir equation is based on a kinetic approach and assumes a uniform surface and a single-layer adsorbed material at constant temperature. The Langmuir isotherm can be written as (Do 1998):

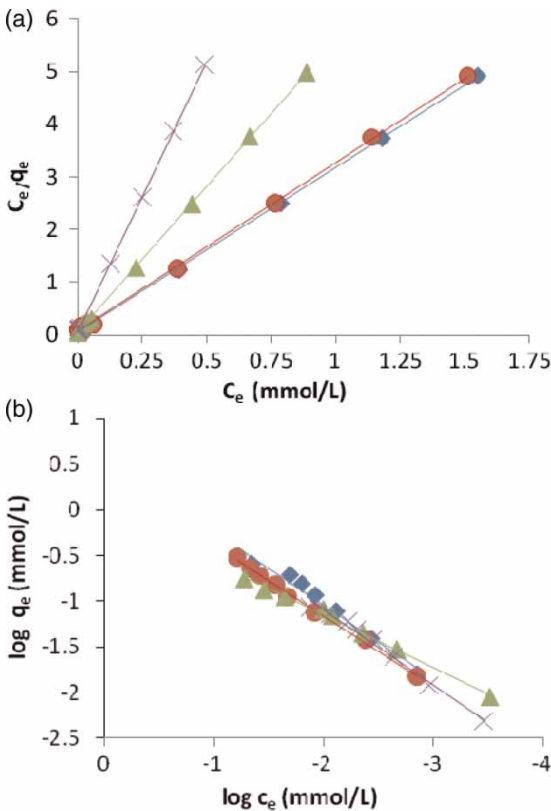
$$\frac{C_e}{q_e} = \frac{1}{bQ} + \frac{C_e}{Q} \quad (7)$$

where C_e is the equilibrium concentration of solute solution (mmol l^{-1}), Q is the maximum adsorption capacity (mmol g^{-1}) and b is the Langmuir constant related to sorption energy (L g^{-1}).

The isotherm simulations from the Langmuir model for diatomite are shown in Figure 8(a). Langmuir provided a good fit with R^2 value of 0.999. The maximum adsorption capacities were 0.319, 0.311, 0.18 and 0.096 mmol g^{-1} , respectively, for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} . The results are generally in high agreement with the experimental data. A high value of Langmuir parameter b indicates a steep desirable beginning of the isotherm, which reflects the high affinity of the adsorption for the sorbate (Davis et al. 2000). Thus the Langmuir constants b for our results were 6.53, 4.58, 3.41 and 2.02 L mmol^{-1} for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} , respectively, indicating that Cu^{2+} has a high affinity for the adsorbent compared with Zn^{2+} , Cd^{2+}

Table 5 | Comparison of the maximum adsorption capacity for Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} on different adsorbents

Metal	Adsorbents	Adsorption capacities (mmol g^{-1})	Literature
Pb^{2+}	Jordanian diatomite	0.230	Majeda <i>et al.</i> (2004)
	Natural clinoptilolite	0.420	Shawabkeh <i>et al.</i> (2004)
	Active carbon powders	0.310	Shu-Huei & Jao-Jia (2007)
	Carbon nanotubes	0.100	
Cu^{2+}	Jordanian diatomite	0.430	Majeda <i>et al.</i> (2004)
	Natural clinoptilolite	0.140	Kurniawan <i>et al.</i> (2006a, b)
	Active carbon powders	0.180	Shu-Huei & Jao-Jia (2007)
	Carbon nanotubes	0.110	
Zn^{2+}	Jordanian diatomite	0.090	Ayşe <i>et al.</i> (2008)
	Natural clinoptilolite	0.210	Shawabkeh <i>et al.</i> (2004)
	Active carbon powders	0.200	Chungsyng & Huantsung (2006)
	Carbon nanotubes	0.160	
Cd^{2+}	Jordanian diatomite	0.140	Majeda <i>et al.</i> (2004)
	Natural clinoptilolite	0.750	Leppert (1990)
	Active carbon powders	0.050	Shu-Huei & Jao-Jia (2007)
	Carbon nanotubes	0.055	

**Figure 8** | Linear fit of adsorption isotherms with (a) Langmuir and (b) Freundlich model Cd^{2+} (\blacktriangle), Zn^{2+} (\bullet), Cu^{2+} (\blacksquare) and Pb^{2+} (\times).

and Pb^{2+} . The values of the isotherm constants Q and b with the correlation coefficients resulting from equilibrium uptake studies are listed in Table 4.

We can calculate the dimensionless separation factors R_L from the Langmuir constants:

$$R_L = (1 + C_0 b)^{-1} \quad (8)$$

R_L is related to the nature of interaction between the adsorbent and the adsorbate and isotherm type: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Al-Degs *et al.* 2001). The calculated R_L values for various initial metal ions concentrations were $0.046 < R_L < 0.493$ for Cu^{2+} , $0.066 < R_L < 0.598$ for Zn^{2+} , $0.141 < R_L < 0.761$ for Cd^{2+} and $0.330 < R_L < 0.911$ for Pb^{2+} . Thus, the adsorption processes in four metals were favourable. The R_L values were comparable with the results reported for Cu^{2+} adsorption on natural diatomite from Serbia ($0.0144 < R_L < 0.421$) (Šljivić *et al.* 2009).

The Freundlich isotherm can be expressed by the following equation (Do 1998):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where K_F is the Freundlich constant (mmol g^{-1}) indicating the adsorption capacity and strength of the intensity of adsorption and n is the heterogeneity factor. The isotherm constants were determined from the linear isotherm graphs. Figure 8 (a) and (b) are given with correlation coefficients in Table 4. The linearity of these plots with R^2 values ranging from 0.973 to 0.996 indicates the applicability of this model. The K_F values calculated for Cu^{2+} , Zn^{2+} , Cd^{2+} and

Pb^{2+} are 3.59, 2.39, 1.004 and 3.64 mmol g^{-1} , respectively, while their respective n values, 1.24, 1.29, 1.74 and 1.21, are within the range between 1 and 10 showing beneficial adsorptions (Ahalya *et al.* 2005). In our results the values of $0 < \frac{1}{n} < 1$ indicate an adsorption process that is only slightly suppressed at lower equilibrium concentrations (Erdem *et al.* 2004) and is attributed to the heterogeneous nature of the adsorbent's surface without any interaction between adsorbed atoms, molecules or ions (Milonjic *et al.* 2007).

From the Freundlich constants, the free energy change ΔG can be calculated from:

$$\Delta G = -RT \ln(KF \times 1000) \quad (10)$$

where R is the universal gas constant (0.00831447 kJ mol^{-1} K) and T is the absolute temperature (293 K). $\Delta G = -19.94$ kJ mol^{-1} (Cu^{2+}), -18.49 kJ mol^{-1} (Zn^{2+}), -16.83 kJ mol^{-1} (Cd^{2+}) and -19.97 kJ mol^{-1} (Pb^{2+}). The negative free energy values indicate the feasibility of the process and the spontaneous nature of adsorption. The ΔG values were comparable with the results reported for Cu^{2+} adsorption on natural diatomite from Serbia (-23.209 kJ mol^{-1}) (Šljivić *et al.* 2009).

CONCLUSIONS

The present study shows that raw diatomite from Algeria can be used as a readily available ion exchanger for heavy metal removal from water. The batch adsorption experiments for the removal of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} have been examined at different pH values, initial metal ion concentrations and contact time. The adsorbed amount of four metal ions was strongly pH-dependent; in the beginning, low adsorbed amounts were shown at pH <4, which was due to competitive adsorption of H^+ ions. The increase in the adsorbed amount of metal ions at pH >4 was due to precipitation of hydroxyl species. The Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} adsorption amounts on raw diatomite increase steadily with increasing initial concentration and contact time. The kinetics of adsorption of metal ions onto raw diatomite was studied by using pseudo-first- and pseudo-second-order equations. Modelling of sorption kinetics showed good agreement of experimental data with the pseudo-second-order kinetic equation for different initial metal concentrations compared to the pseudo-first-order kinetic equation. The equilibrium data have been analysed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and

related correlation coefficients have been determined. Both isotherms were demonstrated to provide the best correlation for the adsorption of four metal ions onto raw diatomite from Algeria. The R_L values showed that diatomite was favourable for the sorption of the four metal ions; also the calculated values of free energy changes ΔG indicated that the adsorption processes were favourable, feasible, spontaneous and endothermic.

This study indicated the suitability of raw diatomite from Algeria; it was found to be most efficient for metal ions adsorption and for wastewater treatment application.

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