Equilibrium study of adsorption of Pb^{2+} from aqueous solution onto Algerian bentonite clay

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ABSTRACT

The adsorption of Pb(II) onto Algerian bentonite clay (Mostaganem region) was examined with respect to adsorbent dosage, solution pH, shaking time and initial concentration of metal. The results showed that the removal efficiency of Pb^{+2} by Algerian bentonite clay could reach 92% when the initial concentration of metal ions was 10 mg/L and shaking time 2 h. Two isotherm equations, the Freundlich and Langmuir models, were applied to describe equilibrium isotherms for the adsorption of Pb^{+2}. The experimental results indicated that Algerian clay had significant potential for removing Pb^{+2} from wastewater using the adsorption method and a low-cost adsorbent.

Keywords: Pb^{+2}, Algerian bentonite clay; Adsorption isotherm

1. Introduction

Numerous studies illustrate the important role of clay materials as adsorbents for removal of hazardous organic pollutants and of heavy metals ions from water [1–7]. Adsorption of heavy metals onto clay minerals is of interest in the adsorption of metal ions for recovery purposes because of its simplicity and efficiency [3]. The removal of heavy metals, which are hazardous and potentially toxic to the environment, from industrial wastewater remains a challenge and constitutes a difficult problem.

In this study, Algerian bentonite clay was chosen to use as adsorbent for removal of pollutants from wastewater, and equilibrium studies of Pb^{+2} adsorption onto clay have been investigated. The experimental results obtained in this study show that the adsorption efficiency was dependent on a number of factors: solution pH, amount clay, shaking time, and concentration of Pb^{+2}.

The aim of this work was to study the adsorption of heavy metals from aqueous solutions onto clay by means of low-cost materials and basic methods. The use of locally available clay for removing heavy metal ions such as Pb^{+2} from industrial wastewater is the topic of the present study.

2. Materials and experimental methods

2.1. Instrumentation

A Perkin-Elmer analyst, model SAA-110, flame atomic absorption spectrometer, an instrument with a deuterium background corrector, was used. All measurements were carried out in an air/acetylene flame. The operating parameters for working elements were set as recommended by the manufacturer.

A pH meter, Cyber Scan pH 500, was used for measuring pH values in the aqueous phase, and a mechanical shaker (Janke, Hunkel Ika.), model KS 500, was also used.

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2.2. Reagent and solutions

All chemicals used in this work were of analytical reagent grade and were used as delivered (without further purification). These are obtained from: NaOH, M = 40 g/mole (Carlo Erba 98%); KOH, M = 56.11 g/mole (Fluka 99.5%); HCl, M = 36.5 g/mole (Merck, 37% pa, d = 1.18); $Pb(NO_3)_2$, M = 331.2 g/mole (Panreac). The element standard solutions used were prepared with distilled water.

2.3. Characterization of Algerian clay

The natural clay used in this study was an Algerian montmorillonite, a bentonite type from Mostaganem (NW Algeria). It was kindly supplied by the Enof Algerian Bentonite Company. The specific surface was found to be 52 m²/g by using an analyzer (Micromeritics ASAP 2020) using N_2 as an adsorptive. The procedures for treatment and purification of this material clay were prepared according literature methods [8]. The chemical and mineral composition was determined: 55–65% SiO_2; 12–19% Al_2O_3; 0.5–1.8% K_2O; 2–3% MgO; 0–2% Fe_2O_3; 1.5–5.5% CaO; 1–3% Na_2O [9].

The chemical composition of this natural clay mineral indicates:

- presence of an important quantity of silica (SiO_2);
- traces of Ca and K oxides in the form of impurities: CaO and K_2O;
- ignition loss of the clay at 1000 °C was 7.5% (w/w).

The other characteristics were found to be: humidity, 15%; swell, 0.8%; and viscosity, 15 cp min.

2.5. Equilibrium adsorption experiments

One gram of natural clay was added to 100 mL of an aqueous solution containing Pb^{+2} ions into 200 mL conical flasks which were stoppered, sealed and shaken over 2 h. The equilibrium adsorption studies were conducted at room temperature, different initial pH values and Pb^{2+} ion concentrations that varied between 5 and 100 mg/L.

The mixed solutions, different concentrations of metal ions added to 1 g of natural clay, were left shaking for 2 h at room temperature and then centrifuged to separate the liquid and solid phases. The concentrations of metal ions in supernatants were analyzed by SAA using a Perkin Elmer type 110, flame atomic absorption spectrometer.

Differences between the initial concentration, C_i (mg/L) of Pb^{+2} ions and equilibrium C_e of metal ions in solutions (mg/L) were used to calculate the quantity adsorbed Q_e (mg/g of natural clay), using the following mass-balance equation:

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

where V is the volume of aqueous solution and m is the mass of natural clay used.

The standard Langmuir and Freundlich equations are used to describe adsorption equilibrium at solid-liquid interface across the entire range of concentrations examined. The linear representation of the Langmuir isotherm is:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}$$

For the linear representation of the Freundlich isotherm equation is:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where Q_e is equilibrium removal (mg metal ion/g natural clay); Q_0 (mg/g) and b (L/mg) are Langmuir isotherm constants; K_f (adsorption coefficient) and n are Freundlich isotherm constants.

3. Results and discussion

3.1. Infrared spectroscopy study

The FT-IR spectra of natural and treated clays with HCl acid (different concentrations) were obtained in the region of 4000–500 cm⁻¹ by using a FT-IR Perkin Elmer Spectrum model spectrometer at room temperature dispersed in KBr discs (Fig. 1). The characteristic peaks of the bentonite clays used in this study and the detailed vibrational frequencies with possible assignments being given were obtained from previous studies [10–12].

As can be seen, all products exhibit two moderately intense bands at 3624.64 and 3630.25 cm⁻¹, which might be ascribed to the stretching frequencies of the OH functional groups of co-ordination water and of the hydration OH stretching [10]. The absorption peaks between 1641.95 and 1640.21 cm⁻¹ can be taken such as both OH stretching vibration and $d(H_2O)$ deformation. The rest of the bands between 1040.55 and 523.07 cm⁻¹ in all samples are due to stretching vibrations of Si-O, Si-O-Si, OH attached to Al^{3+}, Fe^{3+} and Mg^{2+} groups and the silica quartz impurities, respectively.

3.2. Effect of shaking time

An adsorption kinetic study was carried out for both natural and treated clays, by adding 1 g of the clay
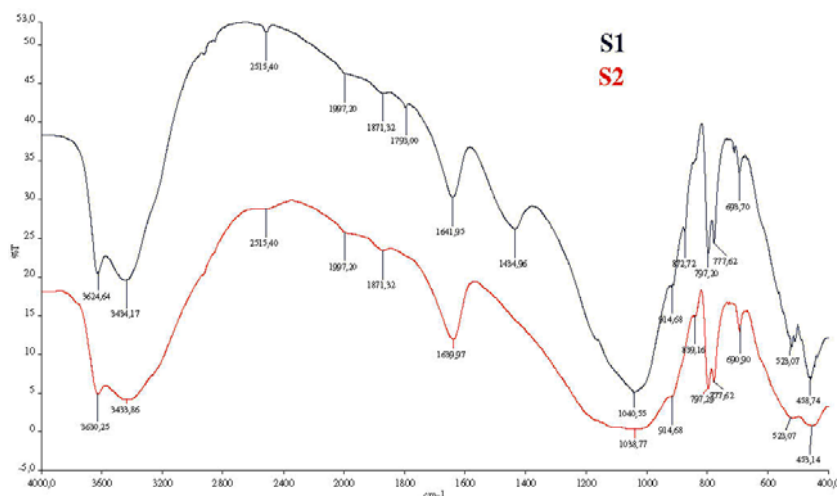
Fig. 1. Infrared spectra of natural (S1) and treated with HCl (S2) bentonite clays.
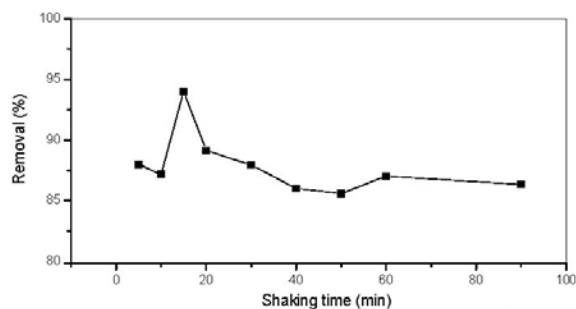

Fig. 2. Effect of shaking time on removal of Pb^{2+} by natural clay from aqueous solutions ([Pb^{2+}]: 10 mg/L, pH: 5, mass (clay): 1 g, T: 25°C).
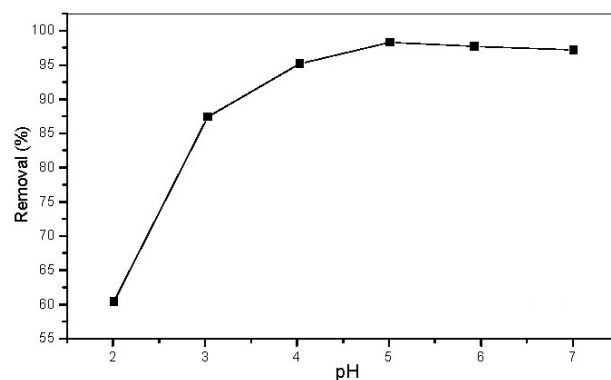

Fig. 3. Effect of pH on removal of Pb^{2+} by natural clay from aqueous solutions ([Pb^{2+}]: 10 mg/L, mass (clay): 1 g, shaking time: 2 h, T: 25°C).

material to 100 mL of solution with fixed concentration of Pb^{2+}. The suspension, in different conical flasks, was then shaken at room temperature and the concentration of the supernatant of metal ions was determined.

The removal percentages increased with increasing shaking time in the range of 5–20 min, but then decreased when time exceeded 20 min to reach equilibrium within 90 min. The optimum metal adsorption percentage was 86.34%. However, 2 h was fixed as the optimum shaking time (Fig. 2).

The adsorption percentage was calculated as

$$\% \ \mathrm{removal} = \frac{C_i - C_e}{C_i}.100 \qquad (4)$$

3.3. Effect of pH

The second parameter we studied was the solution pH and its effect on removal of metal ions. As most of the heavy metal ions tend to form precipitation at high pH values, the process greatly limited. Fig. 3 illustrates the effect of pH on removal of Pb^{2+} at pH values 2–7. The adsorption of these metal ions from aqueous solutions is remarkably influenced by the pH values in the range from 2 to 7 (prepared and adjusted by using either HCl acid or NaOH solutions). The removal percentages were gradually increased in the range of pH 2–5 to reach 97.5% as a maximum at pH 5. The pH values 5–7 were chosen as the optimum studying for avoiding precipitation of Pb^{2+} ions and the true adsorption of Pb^{2+} ions on clay could be masked and difficult to be quantified at a pH value higher than 7. Therefore, pH 5 was selected for all further studies of lead.

3.4. Effect of initial concentration of Pb^{2+} ions

The removal (%) in the solid phase decreased gradually with an increase in the initial concentration of Pb^{2+} ions. However, the removal % is constant after the initial concentration exceeds 60 mg/L (Fig. 4). At low concentrations, the metal ions have a large number of adsorption sites available. However, when there is an increase in metal ion concentration, the competition for adsorption sites becomes important.
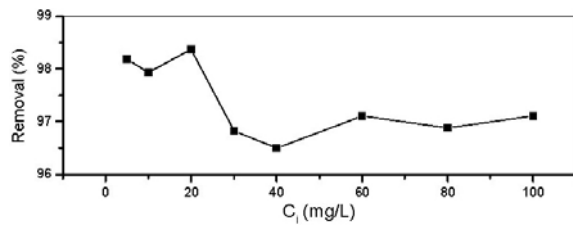
Fig. 4. Effect of initial concentration of Pb^{2+} by natural clay from aqueous solutions (pH: 5, shaking time: 2 h, mass (clay): 1 g, T: 25°C).
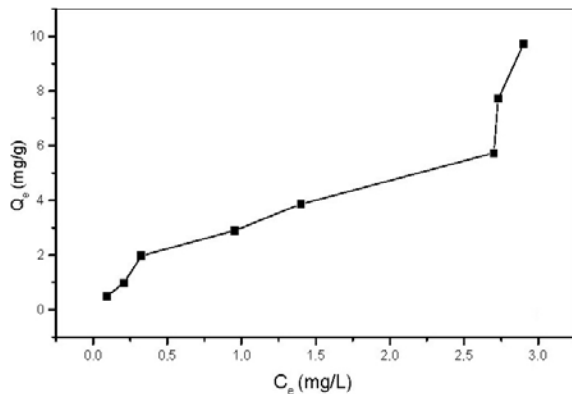

Fig. 5. Linear model isotherm for Pb^{2+} adsorption onto natural clay from aqueous solutions (pH: 5, shaking time: 2 h, mass (clay): 1 g, T: 25°C).

Fig. 6. Langmuir isotherm for Pb^{2+} adsorption onto natural clay from aqueous solutions (pH: 5, shaking time: 2 h, mass (clay): 1 g, T: 25°C).

Fig. 7. Freundlich isotherm for Pb^{2+} adsorption onto natural clay from aqueous solutions (pH: 5, shaking time: 2 h, mass (clay):1 g, T: 25°C).

3.5. Isotherm fitting: amount adsorbed

The adsorption isotherms for Pb(II) sorption on material clay were obtained at various metal concentrations from 5 to 100 mg/L while keeping all other parameters constant (shaking time, solution pH, clay amount at room temperature). The isothermal relationship between the equilibrium concentration of Pb^{2+} ions in the solid and liquid phases is shown in Fig. 5.

The isotherms were constructed by plotting the amounts sorbed (Q_e) vs the concentration remaining in the solutions (C_e). Differences between concentration in the initial and equilibrium solutions were used to calculate the quantity adsorbed (Q_e) in mg/g of clay. The plot of $Q_e = f(C_e)$ (Fig. 5) shows that the increase in the quantity adsorbed (Q_e) of Pb^{2+} onto clay reaches a plateau after the initial concentration exceeds 20 mg/L of Pb^{2+} ions.

3.6. Adsorption isotherms

In order to represent the equilibrium adsorptive behaviour and a satisfactory description of the equation state between the two phases composing the adsorption system, the Langmuir and Freundlich equations, from several isotherms equations (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich), were tested to fit the experimental data (Fig. 6). The linear plot of the Langmuir
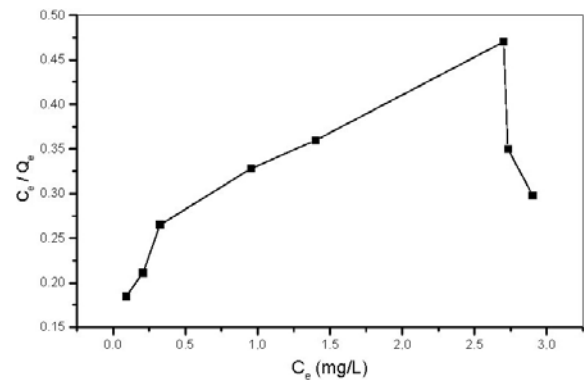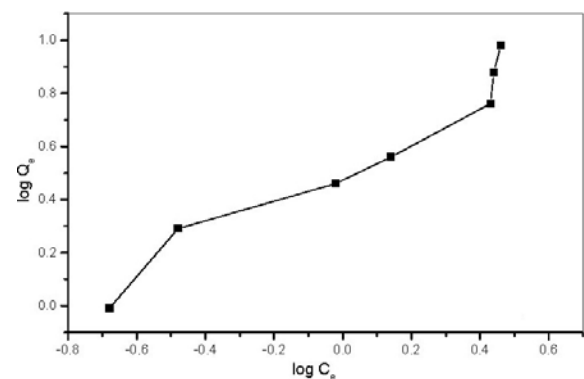
equation is:

$$\frac{C_e}{Q_e} = f(C_e)$$

The sorption equilibrium data were also applied to the Freundlich model in logarithmic form given as follows:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e$$

The linear plot of the Freundlich isotherm equation is: $\log Q_e = f(\log C_e)$ (Fig. 7).

The estimated model parameters with correlation coefficient (R^2) for the two models are given in Table 1. The equilibrium sorption data are satisfactorily fitted in the order: Freundlich, Langmuir for Pb(II) ions (2 h).

The value of n at equilibrium is 1.88, representing favourable adsorption at room temperature, and suggests a physical mechanism with weak adsorption bond of Van der Waals forces. The essential characteristic of the Langmuir isotherm may be expressed in terms of a dimension-

Table 1
Estimated model parameters with correlation coefficients

Constants	Pb(II)
Langmuir:	
Q_0	4.348
b	4.156
R^2	0.738
Freundlich:	
K_F	5.33
n	1.88
R^2	0.969

Table 2
R_L values

[Pb^{2+}] (mg/L)	R_L
5	0.046
10	0.023
20	0.012
30	0.008
40	0.006
60	0.004
80	0.003
100	0.002

less separation parameter, R_L, which is indicative of an isotherm shape that predicts whether an adsorption system is favourable or unfavourable. R_L is defined as

$$R_L = \frac{1}{1 + b.\,C_i}$$

where C_i is the initial concentration of the sorbate (mg/L) and b is the Langmuir constant. The R_L values for the present experimental data were between 0.002 and 0.046 for 2 h as shaking time of adsorbent, which is an indi-cation of favourable adsorption. As the R_L values lie between 0 and 1, the adsorption process is favourable (Table 2).

4. Conclusions

The experimental results suggest that treated Algerian clay is an effective adsorbent for the removal of Pb^{2+} ions from aqueous solutions.

- The effective solution pH for the removal of Pb^{2+} ions was 5.
- The contact time for the maximum adsorption required is 90 min.
- The availability and low cost of this natural clay make it a good candidate in the adsorption process for use in water treatment and purification.
- It is the solution to domestic wastewater treatment.

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