

Adsorption of Zinc and Lead onto Sediments of the Dam Chorfa

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ABSTRACT: *At the laboratory level, we studied the effects of various factors, the initial concentration of metal ions, the pH of the solution, the amount of mud used and contact time, on the adsorption of zinc and leads ions onto dam material (Mascara, Algeria). The constituents of silt sediment are quartz, calcite and mixture of clays. The equilibrium time was of the order of 60 min. The adsorption diagram is smooth and continuous leading to saturation, suggesting the possible monolayer coverage of zinc and lead ions on the surface of the adsorbent. The extent of adsorption increases with an increase in pH. Furthermore, the adsorption of metals increases with increasing amount of adsorbent. The adsorption modeling was carried out using the Langmuir and Freundlich adsorption models to determine the mechanistic parameters associated with the adsorption process. The Langmuir–Freundlich isotherm model was the best to describe the experimental data. The maximum sorption capacity was found to be 42.73 and 131.57 mg/g for Zn²⁺ and Pb²⁺, respectively.*

KEYWORDS: *Sediment; Mud; Langmuir model; Freundlich model; Kinetics; Adsorption.*

INTRODUCTION

Metallic elements, in small or trace amounts, are indispensable and essential for cellular growth and for maintenance of metabolic functions. In excessive amounts, they often exert an inhibitory influence on all living forms. Heavy metals are toxic, non-biodegradable and persistent and they gradually accumulate in the living tissues and get

distributed throughout the food chain. Among the metals, aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead have received the maximum attention from the environmentalists [1-3].

Lead and Zinc, as a result of their numerous uses can pollute water and soils, and it is well known that heavy

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metal pollution is a serious threat to the environment. Clay minerals are non-pollutant and have very significant capacity adsorbing so they have a privileged place in the purification of water [4, 5], decolorization of oils [6] and the fixing of metals [7].

Heavy metals in water are removed by processes such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption [8]. Development of low cost adsorbents and the ease of application, regeneration and reuse have made adsorption from liquid phase an attractive process for treatment of contaminated water. Various conventional and non-conventional adsorbents have been tried to remove different metal ions from aqueous solutions [9]. For example, silica gel [10], blast furnace slag [11], sawdust [12], canola meal [13], Kraft Lignin-Derived Chars [14], etc. have found use as adsorbents.

In recent years, many porous mineral materials found increasing interest as adsorbents due to their abundance in nature, low cost, good cation adsorptive properties and large surface area [15]. Mineral materials used to remove heavy metals include kaolinite [16], zeolite [17], montmorillonite [18, 19] and bentonite [20]. Among the microporous materials most abundant in nature, one finds the silt, which can be used as adsorbent for metal ions [21]. The material used is the sediment of the dam; it contains generally quartz, calcium, carbonates and a mixture of clays.

The objective of this work is to explore the adsorption potential of Algerian natural silt in the removal of Pb(II) and Zn(II) ions from aqueous solution. The silt was obtained from Chorfa dam (Mascara, western Algeria). We have studied several parameters, such as, concentration of metal, pH and time. The applicability of theoretical models, such as Langmuir, Freundlich, for the equilibrium data fitting was tested.

EXPERIMENTAL SECTION

Materials

All chemicals used in this study were of analytical grade. Stock solutions (1000 g/mL) of Pb (II) and Zn (II) were prepared by dissolving the appropriate amounts of PbCl₂, ZnCl₂·6H₂O in deionized water, respectively. The working standard solutions were prepared daily by stepwise dilution of stock solutions. Adjustment of pH was undertaken using 0.1 mol/L HCl and 0.1 mol/L NaOH.

Instruments

The mud used in this investigation was obtained from Chorfa dam (Mascara, Algeria). The chemical composition of the mud was determined by a Cameca electronic microprobe. The grain size of this material was 72µm. Sample of mud was washed with distilled water, dried at 95°C for 24h and sieved. X-ray analyses were performed using diffractometer employing Co Kα radiation. The specific surface area of solid was measured, at 79K, using the BET N₂ method. Elemental analyses of heavy metals were conducted using an atomic absorption flame spectrometer.

Adsorption experiments

Studies on the adsorption of metal ions were carried out by batch experiments. For this purpose, a portion of 0.02g adsorbents mixed with a 20mL solution of metal ions in special glass-stoppered tubes were shaken under a controlled temperature of (293±1) K. The initial metal concentrations were fixed at 10mg/L unless otherwise stated. Batch adsorption experiments were conducted to investigate metal ions adsorption at certain aqueous pH values (2.0-11.0) and contact time (05-90 min). After reaching the sorption equilibrium, the suspension was filtered through 0.45m filters and the metal concentration in the liquid phase was determined using FAAS. All the experimental work was carried out in triplicate and the average result was presented. The adsorption percentage of metal ions was calculated using Eq. (1) and the adsorption capacity was calculated using Eq. (2).

$$\text{Sorption efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

Where:

C₀; C_e: are the liquid-phase concentrations of metal initially and at equilibrium, respectively (mg/L).

V: volume of the solution (L),

M: mass of adsorbent (g)

Q_e: the amount of adsorbed metal at equilibrium (mg/g)

RESULTS AND DISCUSSION

Characterization of The vase

From the elements analysis result, the chemical composition of natural bentonite is follows: 29.37% SiO₂,

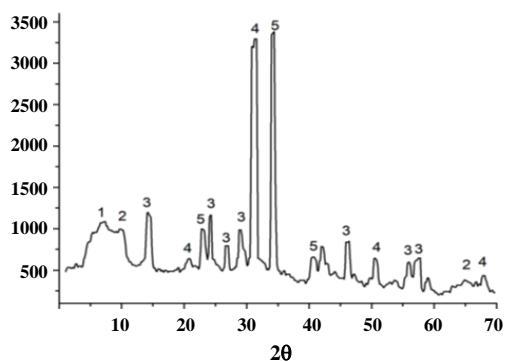


Fig. 1: X-ray diffractograms of the purified vase.

18.22% CaO, 9.12% Al₂O₃, 3.84% Fe₂O₃, 1.33% MgO, 0.20% Na₂O, 0.53% TiO₂, 0.89% K₂O, 0.04% MnO₂ and loss of ignition 1.55%. The Silica, alumina and lime are the major oxides in our sample and the trace elements such as iron, magnesium, sodium, titanium, sulphate and phosphor oxides are considered as impurities.

Sediment dam was recovered from the dam breach of chorfa (western Algeria). The mass ratio SiO₂/ Al₂O₃ is 3/21. This may account with the high SiO₂ content. Some researchers present this report as the index characteristic of montmorillonite when its value varies between 2 and 5.5. Mud was characterized by X-ray diffraction. The spectrum of X-ray diffraction shows that the mud is a mixture of montmorillonite, illite, kaolinite, the presence was noted: quartz as a major impurity in the mud and calcite. This composition is justified by the characteristic peaks (Fig. 1). The specific surface area is calculated by the BET method equal to 70.84 m²/g.

There are three mass losses for most of the vase samples (Fig. 2). The mass loss in the range of 0–200°C (Loss⁻¹), which is 2.37%, is attributed to the removal of physically adsorbed water and/or. This physically adsorbed vase decomposes at a low temperature because of its worse thermal stability compared with the vase. The mass loss in the range of 200–600°C (Loss⁻²) is due to the decomposition of grafted silane and dehydroxylation of vase, and the value is 4.62%.

The mass loss in the range of 600–800 °C (Loss⁻³), which corresponds to the DTG peak at 800-1000°C, is attributed to the decomposition of hydroxyl groups in the octahedron layer of vase, and the value is 12.47%.

Although the physicochemical properties of the raw materials are not significant, they can be easily improved

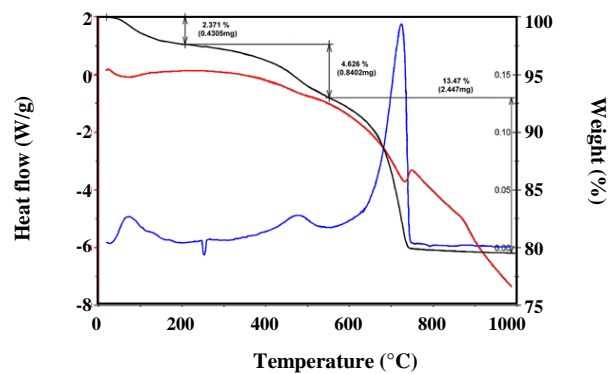


Fig. 2: TG and DTG curves of the purified vase.

by means of heat treatment. During this time we calcined the raw mud in a muffle furnace at temperatures of 600, 800 and 1000°C for a period of one hour, with a heating rate of 10°C/min. These temperatures were chosen following the study carried out by differential thermal analysis (Fig. 2).

Influence of various parameters

A first series of samples is prepared by a mass balance of mud with a volume V of a metal solution of known concentration. After the reaction, the suspension was centrifuged at 4500 rpm for 15 min. the fixed amount of the metals in the sludge is calculated by the method of the radicals:

$$[Q]_{\text{fixed}} = [Q]_{\text{initial}} - [Q]_{\text{solution}}$$

The influence of reaction time, pH and initial metal concentration on the adsorption were examined.

Effect of pH

The initial pH of metal solutions has been regarded by many authors as the major parameter controlling metal adsorption processes [5, 22]. In this study, the adsorption experiments have been conducted in the pH range of 2.0-11.0, and the results obtained are presented in Fig. 2. It is obvious that the adsorption percentage increases significantly as pH increases from 2.0 to 5.0 and then almost keeps constant at pH from 5.0 to 9.0. This phenomenon can be explained by the fact that the ion-exchange interactions exist between the adsorbent and the metal ions. With decreasing pH values, the amount of the ionized carboxylic groups decreases, which leads to the weakening of the ion-exchange interactions.

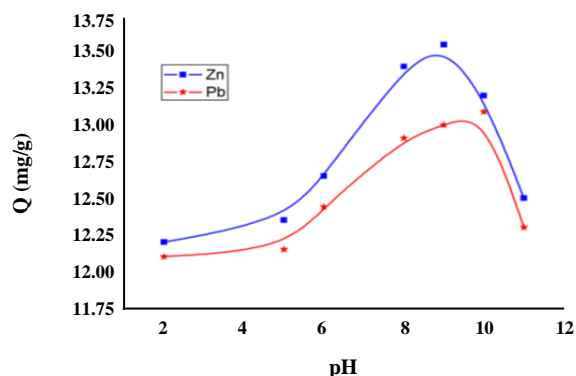


Fig. 3: Effect of pH on Pb and zinc adsorption by Silt.

A low pH (less than 5), there's competition between the H^+ ions in solution and Zn^{2+} ions and/or Pb^{2+} these are the H^+ which are preferentially fixed. There would be competition between Al^{3+} , Mg^{2+} , Fe^{3+} released by the octahedral sites of the clay in acid solution [11].

Under such experimental conditions, poor adsorption performance is achieved. Similar results have also been reported by several earlier researchers for metal ions adsorption with different adsorbents [23]. In order to ensure quantitative adsorption and avoid the hydrolysis of metal ions at higher pH values, a sample pH of 6.0 is chosen as the optimum pH for further studies.

Effect of contact time

It is essential to evaluate the effect of contact time on the adsorption prior to the kinetic study of the adsorption. The experiments are conducted when the contact time varies from 10 to 100 min, and the results obtained are shown in Fig. 3. It can be seen that the adsorption percentage increases considerably until the contact time reaches 60 min. Further increase in contact time does not enhance the adsorption percentage obviously. The phenomenon may be due to the fact that, initially, all active sites on the adsorbents surface are vacant and the solution concentration is high. After that period, few surface active sites are available, so only a very low increase in the metal uptake is observed [24]. Therefore, a contact time of 40 min is selected for all the equilibrium tests.

Adsorption kinetics

Adsorption kinetics, demonstrating the solute uptake rate, is one of the most important aspects of the operation defining the efficiency of the process. In order to evaluate

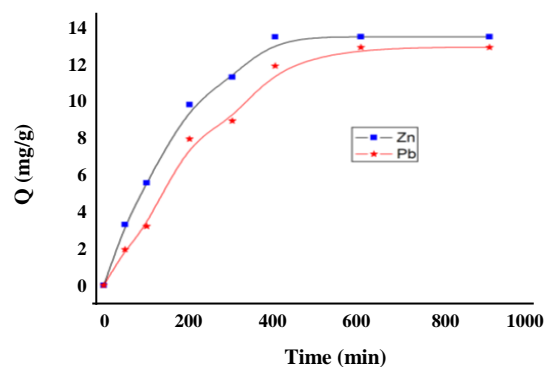


Fig. 4: Kinetic of Zn and Pb adsorption on Silt at pH = 9.0.

the kinetic mechanism that controls the adsorption process, the experimental data are interpreted by the pseudo-first-order and pseudo-second-order models. The linearized form of pseudo-first-order (Fig. 5) rate equation is given as Eq. (3),

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

where q_t and q_e are the amounts of heavy metals adsorbed at time t and at equilibrium (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}).

The experimental data is also applied to the pseudo-second order kinetic model (Fig. 4) given as Eq. (4),

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 is the rate constant of the pseudo-second-order sorption (g/mg min). q_e and q_t are defined as the same as above.

The constants of kinetic models for the adsorption of Pb (II) and Zn (II) ions on vase are listed in Table 1. It is observed that the calculated adsorption capacity (q_{cal}) values estimated by the pseudo-first-order model differ substantially from those measured experimentally, whereas q_{cal} values obtained from the pseudo-second-order kinetic model are very close to experimental data. Moreover, the correlation coefficient values for pseudo-second-order model are much higher than those of pseudo first-order model, suggesting that the adsorbent systems can be well described by the pseudo-second-order kinetic model.

Adsorption isotherms

Analysis of adsorption isotherms is important for developing a model that can be used for adsorption

Table 1: Kinetic parameters for the adsorption of Zn (II) and Pb (II) by Silt.

Metal	$q_{e\text{-exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1	$q_{e\text{-cal}}$	R^2	k_2	$q_{e\text{-cal}}$	R^2
Zn(II)	2.67	0.211	0.10	0.810	0,109	1,66	0.998
Pb(II)	7.90	0.274	0.217	0.776	0,017	2,08	0.999

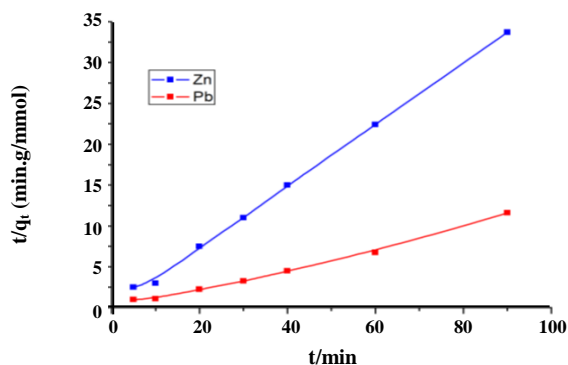


Fig. 5: Pseudo-second-order kinetics plots for the adsorption of Pb (II), Zn (II), onto Silt.

process design, and the isotherms obtained under different temperatures can provide basic data for thermodynamics study to deduce adsorption mechanism. In the present work, the results obtained from the equilibrium adsorption experiments, were analyzed according to the most frequently employed models Freundlich and Langmuir isotherms:

$$Q_e = K_f C_e^{1/n} \quad (5)$$

$$\frac{Q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (5)$$

And the linear forms of these models are as follows, respectively

$$\ln Q_e = \ln K_F + 1/n \ln C_e$$

where C_e is the adsorbate equilibrium concentrations in the liquid (mg/L); Q_e is the adsorbate equilibrium amount in solid phases (mg/g); Q_0 is the maximum adsorption capacity according to Langmuir monolayer adsorption (mg/g); K_L is constant according to the Langmuir model (L/mg); K_F (mg.g⁻¹.L.mg) and n is Freundlich constant related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The values of K_F and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental

data of $\ln Q_e$ versus $\ln C_e$. And the values of Q_0 and K_L can be calculated from the slope and intercept of the linear plot of $1/Q_e$ versus $1/C_e$.

In Table 2, the parameters of Langmuir and Freundlich, along with correlation coefficients are summarized. Higher correlation coefficients indicate that Freundlich model fits the adsorption data better than Langmuir model. The reason may be that Langmuir model assumes that the surface of the sorbent can accommodate only a monolayer of the sorbate ions and no interaction between the sorbed species. Freundlich isotherm model, on the other hand, does not have any restriction on the sorption capacity of the sorbent, and is more appropriate in situations where the sorption sites possess a hetero-geneous nature. As can be noticed, the values of n are all between 1 and 10, indicating that the adsorption is favorable [25]. Isotherms and follow the Freundlich model, indicating that the adsorption sites are heterogeneous and the adsorption of these metals in the mud is a physical type of adsorption [26]. The results obtained its confirmed with other work [21].

CONCLUSIONS

The aim of our study was to test the power and the adsorbent mud of chorfa (Algerian clay) vis-à-vis the removal of zinc and lead. Although it is difficult to link the actual structure of the clay shape and the position of these reflections on the XRD diagrams, we could precede in a first step a qualitative interpretation. The X-Ray diffraction patterns have enabled us to identify the different minerals that make up the material. In comparison with data available in the literature, we identified montmorillonite, illite and kaolinite as clay minerals. Other minerals as major impurities are quartz and calcite.

The present study deals with the adsorption of metal ions, Zn(II) and Pb(II) on Silt from aqueous solutions. The effects of pH value and contact time, kinetics, adsorption isotherms are examined in batch experiments.

Table 2: Parameters of the Langmuir and Freundlich isotherms for Zn (II) and Pb (II) adsorption.

Metal	Langmuir model		
	q_{max} (mg/g)	b (L/mg)	R^2
Zn(II)	42.73	0.231	0.9838
Pb(II)	131.57	0.01546	0.769
	Freundlich model		
	n	k	R^2
Zn(II)	0.8818	11.33	0.9882
Pb(II)	0.3308	0.8301	0.9061

It is found that pH 9.0 is the best pH to obtain the maximum adsorption amount; also the equilibrium of the adsorption can be attained within 60 min for all the investigated metal ions. The kinetics study reveals that adsorption rate is fast and can be satisfactorily modeled by a pseudo-second-order equation. The Langmuir, Freundlich isotherm models for the metal ions onto Silt have been studied, illustrating that Freundlich model fits the adsorption data best. The regeneration studies show that Silt can be used repeatedly without changing significantly their adsorption capacities for the adsorption of Zn (II) and Pb (II) from aqueous solutions.

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