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Application of an Algerian clays in the retention of lead ions

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ABSTRACT

The aim objective of this work is to study the adsorption of lead ion by an algerian clays minerals. These materials were characterized by x fluorescence, FTIR spectroscopy, surface area and cation exchange capacities CEC. The Adsorption tests were carried out by the batch technique at room temperature. The uptake of Pb(II) from aqueous solutions to the clays has been studied as function of contact time, temperature, pH and agitation speed which were regarded as a principal factors in the analysis of the adsorption process, the contact time for the maximum adsorption required is 180m The adsorption kinetics is in better agreement with pseudo-second order kinetics. The results show that the uptake of Pb(II) increases with the pH increasing in the pH range of 2.0–12.0. The increase of the temperature influence negatively the adsorption, what shows the phenomenon of the physisorption of lead ion on the tested materials. The studies on the retention of lead ion showed that it is mainly influenced by the physico-chemical properties of used clays, results show that sorption of lead ion was higher by bentonite clay than for others clays. In consequence, the tests allowed us to choose the bentonite as the material which presents a capacity raised for the adsorption.

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KEYWORDS

Metals;
Clays;
Bentonite;
Adsorption;
Lead.

INTRODUCTION

Heavy metal ions are the most toxic inorganic pollutants which occur in soils and can be of a natural or of anthropogenic origin. The study of adsorption processes is of utmost importance for understanding how a heavy metal is transferred from a liquid phase to the surface of a solid phase^[1]. The adsorption of metals is generally acknowledged to be directly proportional to soil pH^[2]. As soil pH increases, the retention of the heavy metal

cations to soil surfaces increases via adsorption, inner sphere surface complexation, and/or precipitation and multinuclear type reactions^[3-5]. In general, the most important factors that influence the relative selectivity of metal cation in the solution are the valence and the hydrated ionic radius^[2,6]. The selective retention of metals can be also explained by the difference in their electronegativity^[4] Lead pollution has been recognized as a potential threat to air, water and soil. All lead compounds are considered cumulative poisons. Acute lead poison-

ing usually affects the gastrointestinal track, or the nervous system, and sometimes both. The main sources of human exposure to lead include the use 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. Additional sources may be food can, solders, ceramic glazes, lead-containing batteries and cosmetics^[7,8]. In consequence, the safe disposal of wastes containing heavy metals has become a matter of special concern, and adsorption of heavy metals on solid substrates is being extensively studied. Inorganic common substrates used with this aim include oxides and clay minerals; organic substrates are mainly constituted by ion-exchange resins and biomass^[9]. Removal of heavy metals from aqueous solutions can be achieved by different technological methods. These methods include chemical precipitation, ion exchange, membrane filtration, electro-deposition, and flotation. Some of these methods have disadvantages and limitations. Precipitation, for example produces large amounts of sludge in solutions^[10].

EXPERIMENT

Materials and methods

Reagents

A stock solution of Pb(II) was prepared by dissolving required amount of $Pb(NO_3)_2$ in double distilled water.

Clay adsorbents

These clays were chosen according to their different chemical and mineralogical characteristics to represent substantially the different behaviour regarding the heavy metal sorption. Three Algerian clay minerals, bentonite, kaolin and Djebel Debbagh clay. The bentonite used during our work is extracted from the deposit of Hammam-Bougrara to Maghnia (Tlemcen). It was supplied to us by the company (ENOF), Tlemcen. The used kaolin results from the deposit of Tamazert (Mila), and the clay of Djebel Debbagh extracted from the deposit of Ain Barbar (Guelma), these clays were supplied to us by the company of ceramic of Ghazaouet (Tlemcen). The three natural clays were finely crushed. Physico-chemical properties of each material are given

in TABLE 1.

All materials were used as received without other treatment apart from drying at 100 °C for 1 h to remove excess moisture, and then kept in a desiccator until analysed water.

Batch adsorption studies

In each experiment, a 300 mL metal ion (100 mg/l) was continuously stirred at 500 rpm with 1 g of clay at ambient temperature. The contact time was ranged from 5min To 360mn. The concentrations of the lead ions in the solution were determined at given time intervals, after agitation, the suspensions were centrifuged at 2500rpm for 10min and the lead concentration in the supernatants was measured by atomic absorption spectrophotometry. Quantity q_t (mg/g) of the lead ion fixed per gram of the adsorbent was determined as follows:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m}$$

where C_0 and C_t (mg/l) are the initial and time t metal concentrations, respectively, V (l) the volume of lead ion solution and m (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Adsorbents characterization

Chemical composition

TABLE 1 presents chemical composition of natural clays used as adsorbent in this study. we found that this clays contain a large ratio of SiO_2 . The report SiO_2/Al_2O_3 for the bentonite is in agreement with the one of the montmorillonite understood between 2 and 5.5.^[11,12] large ratio of SiO_2 . The report SiO_2/Al_2O_3 for the bentonite is in agreement with the one of the montmorillonite understood between 2 and 5.5.^[11,12]

We notice that the chemical composition of our kaolinite comes closer a lot that the one of the Indian kaolinite.^[13]

Surface area

The measured surface areas of the three adsorbents are given in TABLE 1. The specific surface area of Djebel Debbagh Clay was increased to 49, 69 m²/g. The bentonite had a specific surface area of 23,76 m²/g and 22,71m²/g for the Kaolin.

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TABLE 1 : Chemical analysis, specific surface and cation exchange capacities CEC of the natural clays

% mass	Bentonite	Kaolin	Djebel Debbagh
SiO ₂	65,97	50,82	46,29
Al ₂ O ₃	16,20	37,50	43,73
Na ₂ O	2,86	0,17	0,23
CaO	4,53	3,01	3,33
K ₂ O	2,15	2,60	1,80
MgO	2,89	0,71	0,60
Fe ₂ O ₃	3,39	3,16	2,02
SiO ₂ /Al ₂ O ₃	4,07	1,35	1,05
Specific area (m ² /g)	23,76	22,71	49,69
CEC (meq/100g)	80	5,2	13,8

Cation exchange capacity (CEC)

Bentonite has a very large CEC (TABLE 1) compared to that of kaolin and Djebel Debbagh Clay, the values obtained being 5,2 meq/100g (kaolin), 13,8 meq/100g and 80 meq/100 g (bentonite). The CEC of the djebel Debbagh is situated inside the interval for a clay of type illite or chlorite the values found in the literature concerning CEC of bentonite and kaolin confirm our obtained results.^[11]

Infrared spectra analysis

The infrared spectrum of the clays are given in figures 1, 2 and 3. While the band assignments of Bentonite, Djebel Debbagh Clay and Kaolin are shown in TABLE 2.

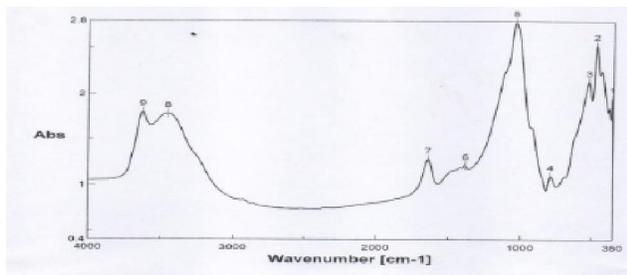


Figure 1 : Infrared spectra of Bentonite

FTIR spectrum was recorded in the region of 400–4000 cm⁻¹. There is a group of absorption peaks between 3440 and 3695 cm⁻¹, which is due to stretching bands of the OH groups. The band at 1639 cm⁻¹ is assigned to the OH deformation of water on natural clays (see Figure 1, 2 and 3). The 1029, 1033 cm⁻¹ component of the Si–O stretching band, assigned to the Si–O vibrations within the layer. The band at 521 and 461 cm⁻¹ was from the Si–O–Al (where Al is an octahedral cation).

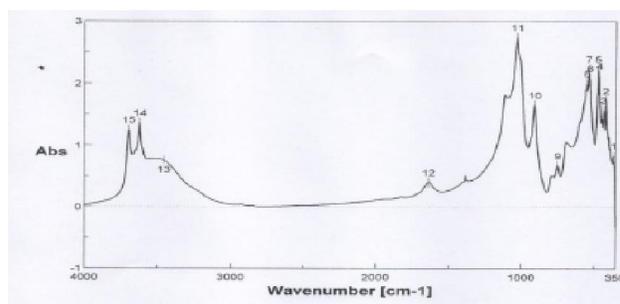


Figure 2 : Infrared spectra of Djebel Debbagh clay

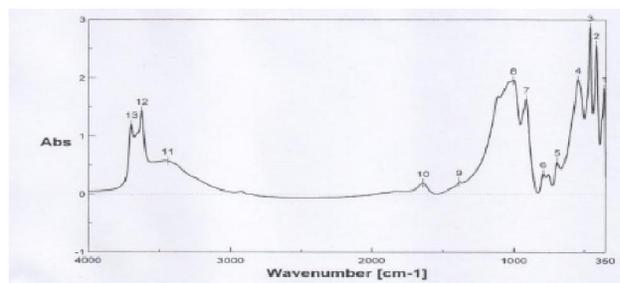


Figure 3 : Infrared spectra of Kaolin

Kinetics study

Figure 4 shows the adsorption kinetic curve of Pb(II) on clays sample, the adsorption amount initially increases rapidly and then it slows down as equilibrium is approached. the equilibrium was attained only after 180min.

The values of q_t by using the bentonite as adsorbing are increased with regard to the other clays. At the equilibrium, the bentonite fixes more lead ions than the ka-

TABLE 2 : Infrared data of of Bentonite, Djebel Debbagh clay and Kaolin

Bands assignments	IR Frequencies (cm ⁻¹)		
	Bentonite	Kaolin	Argile Djabal Debbagh
v _{OH} stretching vibration (H ₂ O)	3623, 3452	3695, 3622, 3439	3694, 3619, 3455
v _{OH} deformation (H ₂ O)	1639, 1378	1639, 1385	1637
v _{SiO} stretching vibration	1033,	1006	1029
quartz	790	913, 792, 694	911,754
δ _{Si-O-M} ^{VI} (M= Al, Mg, Fe)	521, 468, 360	548, 461, 418, 360	551, 538, 529, 472, 462, 433, 417, 365

olin and djebel Debbagh clay. The results obtained are summarize in TABLE 3.

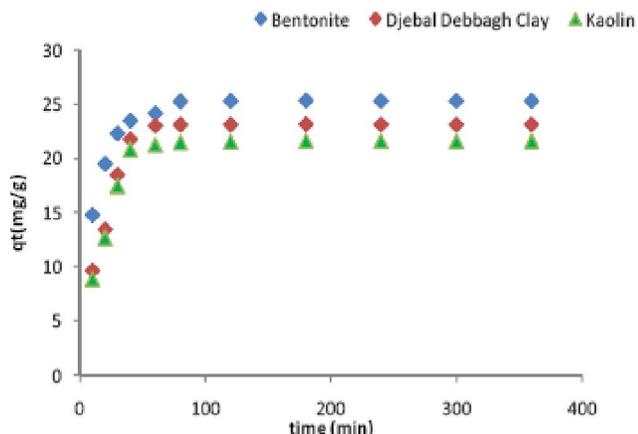


Figure 4 : Kinetic of adsorption of lead ions on clays

TABLE 3 : Results obtained with equilibrium

Clays	Lead ions mass fixe equilibrium (mg/g)
Bentonite	25,34
Djebel Debbagh Clay	23,17
Kaolin	21,62

At the same time as the kinetic study of adsorption of lead ions on these clays, we followed the evolution of the initial pH of the solutions which is represented on Figure 5

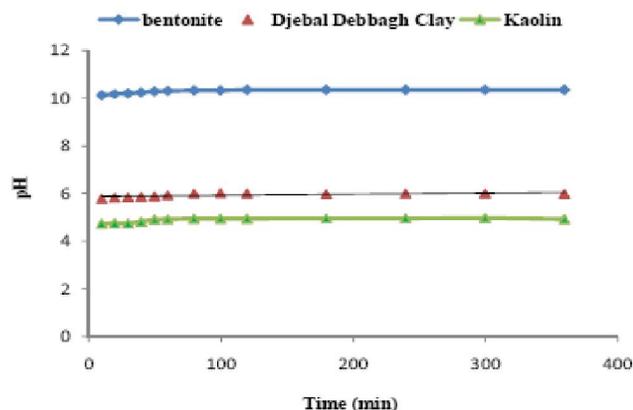


Figure 5 : Evolution of pH of lead ions in the presence of clays

For better understanding of this phenomenon, we studied the evolution of the pH of a distilled exempt water of lead ions in touch with the bentonite, clay of Djebel Debbagh and the kaolin in the same operating conditions as previously. The Figure 6 shows a fast and important increase of the initial pH of the water distilled in the case of the bentonite. For the clay of Djebel Debbagh and the kaolin, this increase is low, what jus-

tifies that the bentonite adsorbs more the acid species than the clay of Djebel Debbagh and the kaolin.

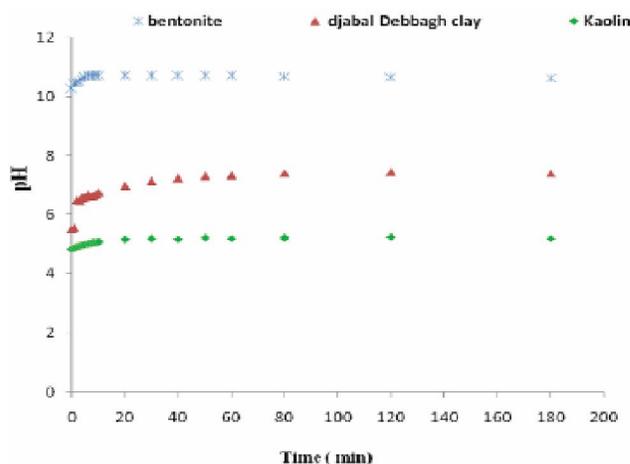


Figure 6 : Evolution of the pH of a distilled water exempts from lead ions in presence clays

In order to optimize the design of an adsorption system to remove the lead ions, it is important to establish the most appropriate correlation for the kinetic data for each system. Several kinetic models can be used to express the adsorption rate constant of solutions on solids. The adsorption kinetics was tested with the following well known models:

Pseudo-first order kinetics by using the Lagergren equation^[14,15]

$$\log \frac{(q_e - q_t)}{q_e} = -\frac{K_v t}{2,3}$$

For the pseudo-second order kinetics^[16,17]. If the pseudo-first order kinetics does not properly account for the kinetics of the adsorption process, pseudo-second order kinetics may be applied by the linear equation,

$$\frac{t}{q_t} = \frac{1}{2K'q_e^2} + \frac{t}{q_e}$$

where k' is the pseudo-second order adsorption rate constant. The kinetic models are shown in Figures 7, 8.

Although, the pseudo-second order kinetic plot of t/qt versus t was of better linearity, considering all the above results, the kinetics of lead ions adsorption on the clays is fitter for pseudo-second order equation.

Effects of operating factors

Effects of pH

The pH of the solution may affect the adsorption process^[11-13,18,19] Studies on the influence of lead solu-

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tion pH on the adsorption efficiency of each clay were carried out in the pH range of 2–12.

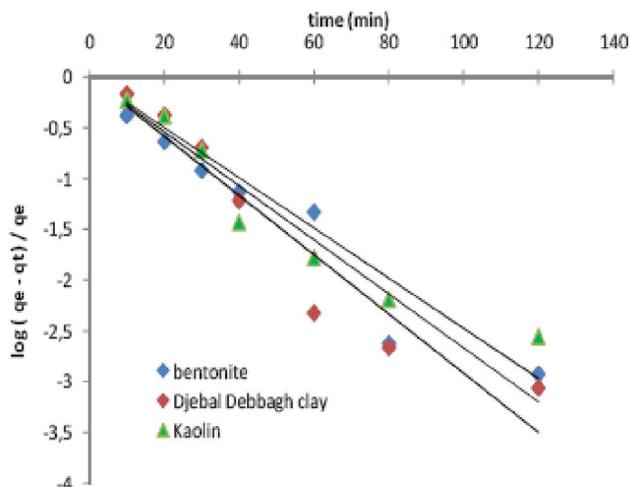


Figure 7 : Linearization of lead ions adsorption kinetics by clays for the first-order rate

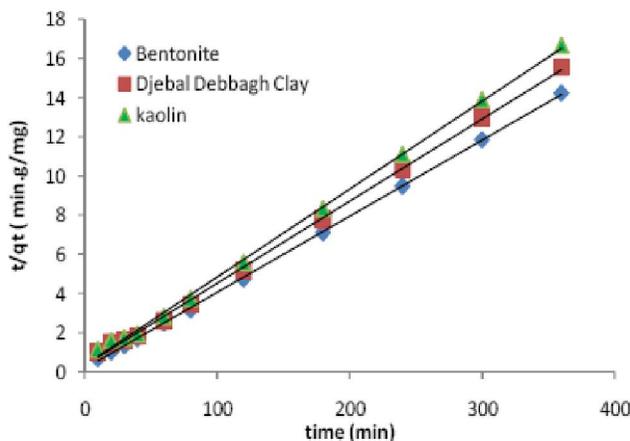


Figure 8 : Linearization of lead ions adsorption kinetics by clays for the pseudo second order rate

TABLE 4 : First-order rate constants

Parameters of first-order	$kv(\text{min}^{-1})$	R^2
Bentonite	0,059	0,924
Djebal Debbagh Clay	0,066	0,912
Kaolin	0,055	0,896

TABLE 5 : Pseudo second-order rate constants

Parameters of pseudo second-order	q^e (mg/g)	K' ($\text{min}^{-1} \cdot \text{g}/\text{mg}$)	R^2
Bentonite	26,31	0,0007	0,999
Djebal Debbagh Clay	24,39	0,0008	0,998
Kaolin	22,22	0,001	0,998

Figure 9 shows that bentonite takes up more of the metal ions than djebal debbagh clay and kaolin. The removal efficiency of Pb(II) tended to increase

with increasing pH value. The uptake of Pb(II) is in surrounding of pH 6.0 due to the low solubility of Pb(II) hydroxide. Metal hydroxide might have also been precipitated at high pH which has also been observed by other workers.^[20,21]

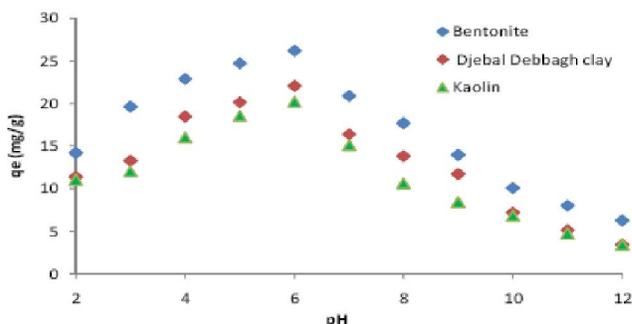


Figure 9 : Influence of the pH on kinetics adsorption of lead ions on clays

The adsorption mechanism of Pb(II) on clays used may be explained in two aspects: the chemical binding between Pb(II) ions and surface hydroxyl groups; and the electrostatic binding between Pb(II) ions and the permanent negatively charged sites of clays.

Effect of temperature

The effect of temperature on the adsorption of metals by using different clays was studied in the range of 15–55 °C. The results showed that temperature had a significant effect on the adsorption, but the adsorption slowly came down as the temperature was further increased to 40°C.

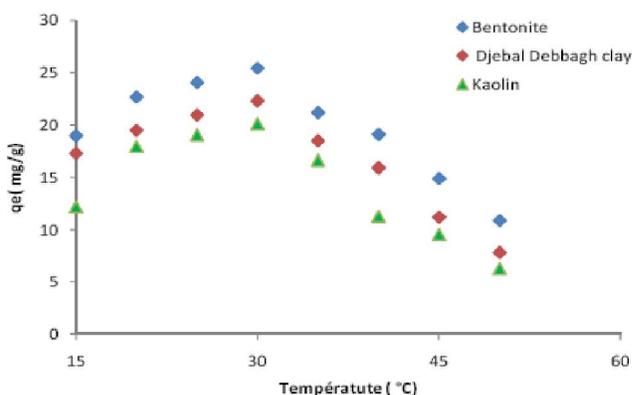


Figure 10 : Influence of the temperature on kinetics adsorption of lead ions on clays

Effect of agitation speed

To study the influence of the agitation speed on the kinetics of adsorption of adsorbats on clays, we chose the range of agitation speeds of 0-1000 rpm. The ca-

capacity of adsorption of lead ions is obtained with agitation speed of 500 rpm (Figure 11), which assures a good distribution of adsorbats towards clays

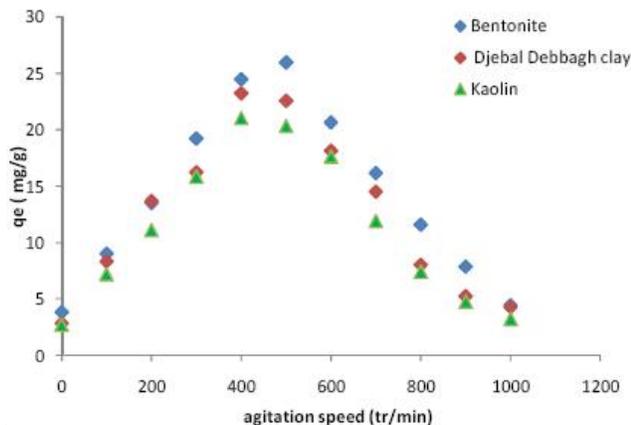


Figure 11 : Influence of the agitation speed on kinetics of adsorption of lead ions on clays

In the case of the high agitation speeds, we notice a decrease of the capacity of adsorption of adsorbats. While, for the absence of agitation speed, we notice a very significant decrease of the capacity of adsorption of adsorbats.

CONCLUSIONS

Three Algerian clay samples: bentonite, kaolin and djebel Debbagh Clay were used for the removal of lead ions from aqueous solutions, clays tested were capable of removing Pb(II) from aqueous solution. Adsorption of Pb(II) increased with pH increasing. The adsorption kinetics is in better agreement with pseudo-Second order kinetics,

The adsorption mechanism of Pb(II) on clays used may be explained in two aspects: the chemical binding between Pb(II) ions and surface hydroxyl groups; and the electrostatic binding between Pb(II) ions and the permanent negatively charged sites of clays.

Good adsorption results were obtained with bentonite. The kinetics of adsorption of lead ions on clays allowed us to choose the bentonite as the best adsorbing.

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