

Lead removal from aqueous solutions by a Tunisian smectitic clay

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Abstract

The adsorption of Pb^{2+} ions onto Tunisian smectite-rich clay in aqueous solution was studied in a batch system. Four samples of clay (AYD, AYDh, AYDs, AYDc) were used. The raw AYD clay was sampled in the Coniacian-Early Campanian of Jebel Aïdoudi in El Hamma area (South of Tunisia). AYDh and AYDs corresponds to AYD activated by 2.5 mol/l hydrochloric acid and 2.5 mol/l sulphuric acid, respectively. AYDc corresponds to AYD calcined at different temperatures (100, 200, 300, 400, 500 and 600 °C). The raw AYD clay was characterized by X-ray diffraction, chemical analysis, infrared spectroscopy and coupled DTA–TGA. Specific surface area of all the clay samples was determined from nitrogen adsorption isotherms. Preliminary adsorption tests showed that sulphuric acid and hydrochloric acid activation of raw AYD clay enhanced its adsorption capacity for Pb^{2+} ions. However, the uptake of Pb^{2+} by AYDs was very high compared to that by AYDh. This fact was attributed to the greater solubility of clay minerals in sulphuric acid compared to hydrochloric acid. Thermic activation of AYD clay reduced the Pb^{2+} uptake as soon as calcination temperature reaches 200 °C. All these preliminary results were well correlated to the variation of the specific surface area of the clay samples.

The ability of AYDs sample to remove Pb^{2+} from aqueous solutions has been studied at different operating conditions: contact time, adsorbent amount, metal ion concentration and pH. Kinetic experiments showed that the sorption of lead ions on AYDs was very fast and the equilibrium was practically reached after only 20 min. The results revealed also that the adsorption of lead increases with an increase in the solution pH from 1 to 4.5 and then decreases, slightly between pH 4.5 and 6, and rapidly at pH 6.5 due to the precipitation of some Pb^{2+} ions. The equilibrium data were analysed using Langmuir isotherm model. The maximum adsorption capacity (Q_0) increased from 25 to 25.44 mg/g with increasing temperature from 25 to 40 °C. Comparative study between sulphuric acid activated clay (AYDs) and powder activated carbon (PAC) for the adsorption of lead was also conducted. The results showed that sulphuric acid activated clay is more efficient than PAC.

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1. Introduction

Lead ions have become one of the major environmental pollutants due to its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases [1]. It enters the environment as a result of both natural process and anthropogenic activities [2]. Methods like ion exchange, solvent extraction, reverse osmosis, precipitation and adsorp-

tion are available for its removal from water and wastewater. Among all these methods, adsorption is shown to be economically favourable (compared with ion exchange) and technically easy (compared with precipitation or reverse osmosis) [3].

Due to its inherent physical properties, large surface area, microporous structure, high adsorption capacity and surface reactivity, activated carbon have been received recently a considerable attention for the removal of organic and inorganic pollutants from contaminated water [4]. The high cost of the activated carbon limits however its use as an adsorbent [5] and encourage its substitution by clays. These materials, owing to their high cationic exchange capacity and specific surface area and their good chemical and mechanical stability, often used to

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treat wastewater [6]. It is well known that smectitic clay have very high cation exchange capacities (90–120 meq/100 g) due to substitutions of Mg^{2+} and Fe^{2+} in place of Al^{3+} in the octahedral positions and, to a higher degree, to substitutions of Al^{3+} in place of Si^{4+} in the tetrahedral positions. Moreover, they possess higher elasticity and plasticity. These properties make them particularly suitable as low-cost natural sorbents for the treatment of industrial and processing waters and wastewaters and/or as barriers in landfills to avoid pollutant release. During acid activation, exchangeable cations are replaced by protons and a part of octahedral cations dissolve creating new acid sites in the structure. This makes the smectitic clay more porous and acidic. Moreover, activation of smectitic clay by acid treatment is effective in limiting possible decomposition of the crystalline structure and increasing the specific surface area. For this reason, clays modified in various ways, such as treatment by inorganic and organic compounds, acids and bases have higher adsorption capacity [7]. For example, montmorillonite, coated and intercalated by aluminium hydroxides exhibits much higher adsorption capacity for some heavy metal ions, than that of natural montmorillonite [8]. The bleach of vegetal and mineral oils by smectitic clay increases with inorganic acids treatment [9].

The smectitic clay can adsorb heavy metals via two different mechanisms: (1) cation exchange at the planar sites, resulting from the interactions between metal ions and negative permanent charge (outer-sphere complexes) and (2) formation of inner-sphere complexes through $Si-O^-$ and $Al-O^-$ groups at the clay particle edges [10]. Both mechanisms are pH dependent but the latter is particularly influenced by pH because in acidic conditions ($pH < 4$) most silanol and aluminol groups on edges are protonated. For this reason, it is necessary to improve the knowledge of the effect of pH on the sorption capacity of smectitic clay in solid–solution system.

The aim of this work is to study the removal of Pb^{2+} ions from aqueous solution by adsorption on smectite-rich clay (AYD) and on its acid (2.5 mol/l hydrochloric, 2.5 mol/l sulphuric) and thermic activated products. Comparative study between sulphuric

activated clay and activated carbon for the adsorption of Pb^{2+} is also conducted.

2. Materials and methods

2.1. Preparation of the adsorbents

The raw clay (AYD) used in the present study was collected from the meridional Atlas of Tunisia. It was sampled in Jebel Aïdoudi in El Hamma area. It is Coniacian – early Campanian in age (Fig. 1). AYD clay was kept in an oven at 70 °C.

For preparing acid activated clays (AYDh and AYDs), a suspension was made by mixing 10 g of AYD sample with 100 ml of 2.5 mol/l H_2SO_4 or 2.5 mol/l HCl at 60 °C for 0.5, 1, 2, 4 and 6 h. The suspension was then filtered off and the treated material washed several times with distilled water until pH 5. Then, it was dried in an oven at 105 °C for 24 h. The thermic activated clay (AYDc) was obtained by calcination of AYD at different temperatures (100, 200, 300, 400, 500 and 600 °C). The activated carbon used in the adsorption experiments was crushed and sieved to get a product with a particle size lower than 80 μm , then it was washed to remove impurities [11]. Finally, it was heated in an oven at 110 °C for 24 h.

2.2. Adsorbate

Lead solutions of different concentrations were made by dilution of 1000 mg/l stock solution prepared from analytical grade $Pb(NO_3)_2$.

2.3. Instrumental

Mineralogical analysis of the raw sample was carried out by X-ray diffraction (Phillips X' Pert diffractometer). Oriented aggregates were treated with ethylene glycol and dried at 500 °C for 2 h. Chemical composition was determined by ICP-AES. Loss on ignition (LOI) was considered as the weight per-

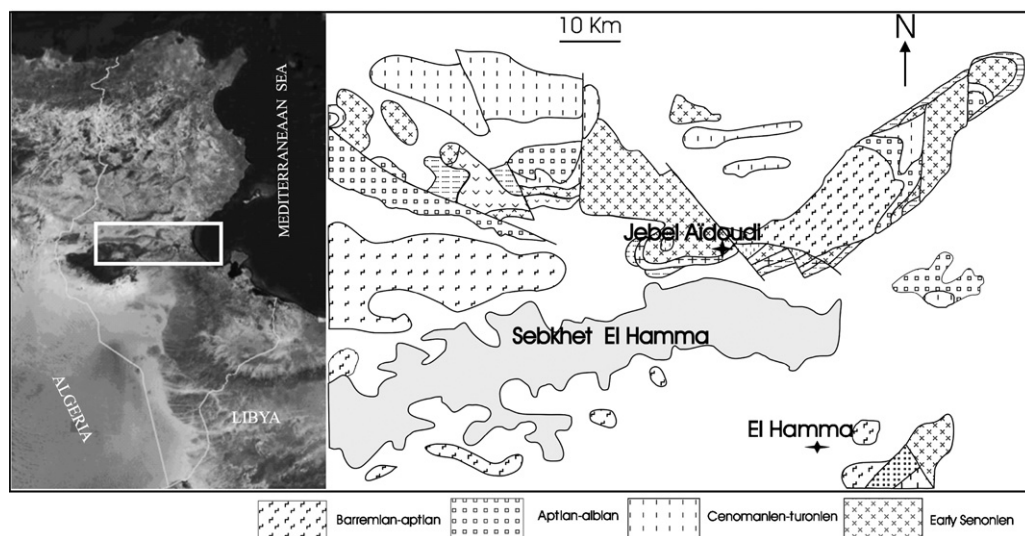


Fig. 1. Localization of the studied clay deposit (Jebel Aïdoudi).

Table 1
Mineralogical composition of AYD clay sample

Sample	Total rock mineralogy (%)					
	Clay minerals			Non clay minerals		
	Smectite (S)	Illite (I)	Kaolinite (K)	Calcite (Ca)	Quartz (Q)	Feldspars (F)
AYD	74	3	9	6	6	2

Table 2
Chemical composition of AYD clay sample

Sample	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	MnO (%)	P ₂ O ₅ (%)	TiO ₂ (%)	LOI (%)
AYD	47.74	18.59	7.39	3.85	1.98	1.94	1.58	0.03	0.27	0.92	15.3

cent difference between sample heated at 100 and 1000 °C. Specific surface area was determined from nitrogen adsorption isotherm according to BET method using a quantachrome Autosorb instrument. FT-IR spectrum of AYD sample was carried out using a PerkinElmer model spectrometer. TGA–DTA of the adsorbent was carried out using NETZSCHSTA 449C model equipment. Hitachi Z-6100 model Atomic Absorption Spectrometer (AAS) operating with an air–acetylene flame was employed to measure residual metal ion concentrations.

2.4. Batch adsorption experiments

Adsorption tests were made by batch technique at room temperature (25 °C). The batch mode adsorption was selected due to its simplicity and reliability. Known amount of adsorbents (AYD, AYDh or AYDs, AYDc) was placed in erlenmeyer flask containing 100 ml of lead solution of known concentration and pH. The resulting mixture was then mixed continuously for a given time period to reach equilibrium. The suspension was then centrifuged and Pb²⁺ remaining in the supernatant was determined by atomic absorption spectrometry.

3. Results and discussion

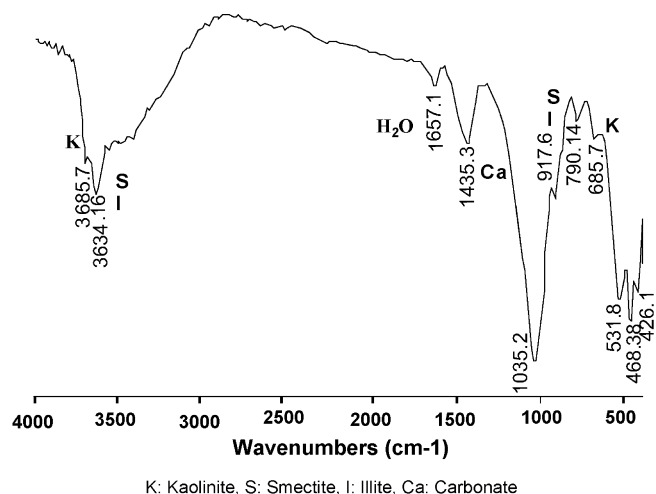
3.1. Characterization of AYD clays

The X-Ray diffraction analysis indicated that the raw AYD clay is mainly composed of smectite (74%) associated to kaolinite (9%), illite (3%), quartz (6%), calcite (6%), and feldspars (2%) (Table 1). The chemical analysis showed that the main constituents of AYD clay are silica (47.74%), alumina (18.59%), and iron oxides (7.39%) (Table 2). The loss of ignition (LOI) is 15.3% (Table 2). It is mainly attributed to the loss of H₂O from clay minerals, especially smectite, and CO₂ originated from the decomposition of calcite. The BET surface areas of AYD, AYDh and AYDs samples were found to be 86.2, 109.2 and 121.2 m²/g, respectively (Table 3). The observed increase in BET surface can be explained by the fact that during acid activation, exchangeable cations are replaced by protons and a part of octahedral cations dissolve creating new acid sites in the structure resulting in more porous and acidic clay [12]. The specific surface of the calcined sample (AYDc) at 100 °C increased from 86.2 to 92.6 m²/g

Table 3
BET surface areas of AYD, AYDh, AYDs and AYDc samples

Samples	Specific surface areas (BET) (m ² /g)
Raw clay (AYD)	86.2
Thermic activated clay (AYDc)	
100 °C	92.6
200 °C	78
300 °C	69.2
400 °C	60.9
500 °C	47.8
600 °C	48.1
Hydrochloric acid activated clay (AYDh)	109.2
Sulphuric acid activated clay (AYDs)	121.2

(Table 3). For higher temperatures, this surface decreased. The FT-IR spectrum of AYD sample (Fig. 2) shows that absorption bands at 3634 and 917 cm⁻¹ are attributable to Al–Al–OH⁻ stretching and bending modes of vibrations [13]. The band appeared at 1435 cm⁻¹ corresponds to that of carbonate [calcite (CaCO₃) or dolomite (Ca, Mg (CO₃)₂)]. The bands appeared at 531, 426 and 468 cm⁻¹ correspond to Si–O–Al, Si–O–Si and Si–O–Mg, respectively. Thermal behaviour of AYD sample was studied by coupled DTA and TGA (Fig. 3). Results show multiple endothermic peaks: the first stage weight loss (7.9%)



K: Kaolinite, S: Smectite, I: Illite, Ca: Carbonate

Fig. 2. Infra-red spectrum of AYD clay sample.

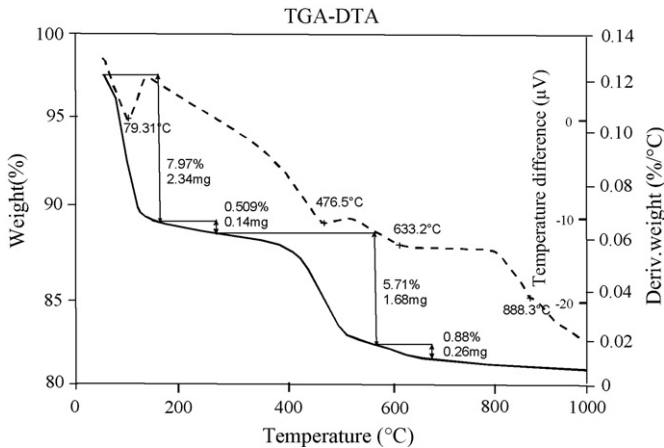


Fig. 3. TGA–DTA curves of AYD clay sample.

with an endothermic peak at 79 °C corresponds to the loosely bound water molecules [14]. The second stage loss (0.5%) with an endothermic peak at 476 °C is due to the deshydroxylation of the octahedral sheet [15]. The third stage loss (5.7%) with an endothermic peak at 633 °C is due to the decomposition of carbonates. Exothermic peak appeared at 888 °C resulting from crystallization of new phases [16]. The total weight loss was about 14.2%.

3.2. Effect of acid and thermic activation on the adsorption process

The study of Pb^{2+} adsorption on AYDh, AYDs and AYDc was carried out by mixing 0.5 g of adsorbent with 100 ml of 100 ppm lead solution. The solution pH was adjusted to 4 with 1 M HNO_3 and 1 M NaOH. The mixtures were agitated during 10 min at room temperature (25 °C). The results obtained with acid activated clays are given in Fig. 4. It is clear from this figure that acid activation increases the number of sites responsible for the adsorption of lead ions: the acid activated clay samples AYDs or AYDh had a higher adsorption capacity compared to the non-activated clay AYD. Under the considered experimental conditions, AYDh and AYDs could remove

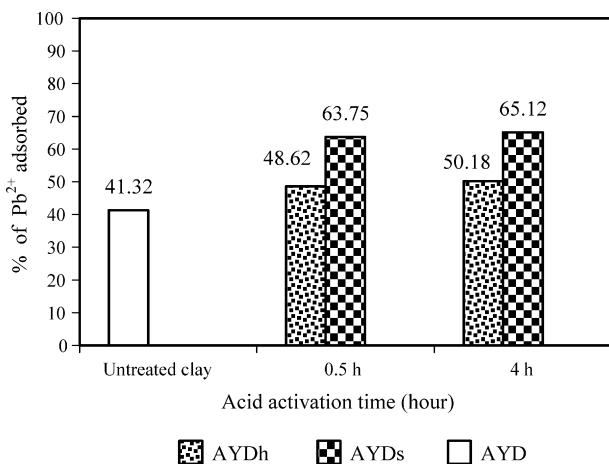


Fig. 4. Effect of acid activation on the Pb^{2+} removal.

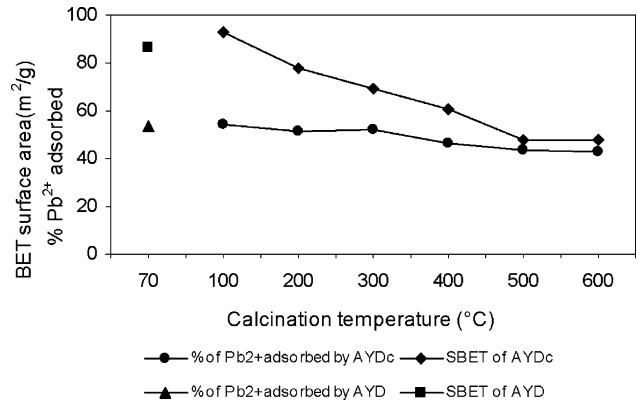


Fig. 5. Effect of calcination temperature on BET surface area (SBET) of AYD clay sample and on Pb^{2+} adsorption.

as much as 50.18 and 65.12% of Pb^{2+} ions respectively, whereas AYD could remove only 41.32%. The higher uptake of Pb^{2+} by sulphuric acid activated clay (AYDs) was very high when compared to hydrochloric acid activated clay (AYDh). This is due to the greater solubility of clay minerals in sulphuric acid compared to hydrochloric acid [12]. According to the literature, it is reported that solubility of clay mineral is more in the acid with an anion having size and geometry approximating to that of the component parts of clay mineral lattice [17].

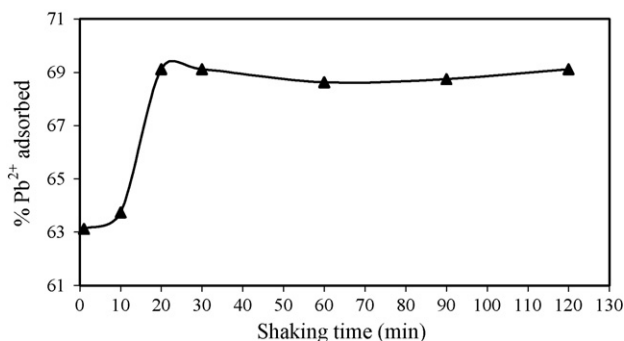
The removal of lead by AYDc sample calcined at 100 °C was 54.22% (Fig. 5). This percentage decreased with increased temperature. The initial increase of adsorption observed when the temperature changed from 70 to 100 °C was presumably due to loss of physisorbed water [18], whereas the decrease of adsorption beyond 200 °C was attributed to the decrease in surface area (Fig. 5).

3.3. Effect of various operating parameters on lead removal

According to the previously results, the sulphuric acid activated clay (AYDs) gave under the same considered experimental conditions (pH 4, shaking time = 10 min) the highest adsorption capacity of lead ions. For this reason, we retained this clay sample for the continuation of the study.

3.3.1. Effect of shaking time

The time-dependent behaviour of lead adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 1–120 min. The initial concentration of Pb^{2+} was kept as 100 ppm, while the dose of AYDs sample was 0.5 g/100 ml and the solution pH was fixed at 4. The data showed that the sorption of lead ions on AYDs was very fast and the equilibrium was reached after only 20 min (Fig. 6). According to the experimental results of several authors [1,19] on the retention of lead on clay minerals, the adsorption process is fast at the beginning of the reaction due to the adsorption of lead on the surface sites of clay, then it becomes slow due to the diffusion of lead from the surface sites to the interlayer of the solid. Therefore, a 20 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent measurements.

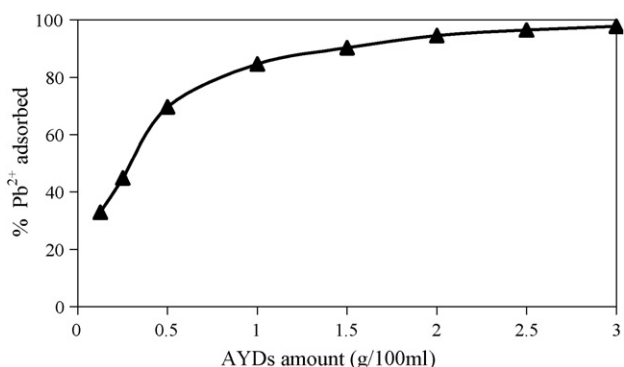
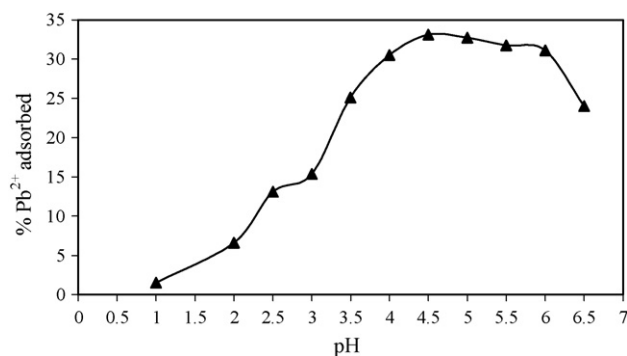
Fig. 6. Effect of shaking time on Pb²⁺ adsorption.

3.3.2. Effect of adsorbent amount

The influence of the amount of AYDs adsorbent (0.125–3 g/100 ml) on Pb²⁺ removal at constant values of initial metal concentration (100 ppm), contact time (20 min) and temperature (25 °C) is shown in Fig. 7. The results showed that the removal of lead increased rapidly (90%) until an adsorbent dose of 1.5 g/100 ml and moderately beyond this value. This was an expected result since as the dose of adsorbent increases, the number of adsorbent sites increases; therefore, these amounts attach more ions to their surfaces [20]. Similar results were reported where many types of materials were used as adsorbents [21].

3.3.3. Effect of pH

The influence of pH on the removal of Pb²⁺ ions by AYDs sample was investigated. In the present work, the adsorption of Pb²⁺ was studied in the pH range 1–6.5 with a constant clay amount of 0.125 g/100 ml of lead solution, a shaking time of 20 min and Pb²⁺ concentration of 100 ppm. The results presented in Fig. 8 reveal that the adsorption of lead increases from 1.5 to 33.1% with an increase in solution pH from 1 to 4.5 and then decreases, slightly between pH 4.5 and 6, and rapidly at pH 6.5 due to the precipitation of some Pb²⁺ ions. The influence of initial pH on Pb²⁺ removal may be explained as follow: in the acidic conditions, both adsorbent and adsorbate are positively charged (M²⁺ and H⁺) and therefore, the net interaction is that of electrostatic repulsion. Besides, the H⁺ ions present in higher concentration in the aqueous medium compete with the positively charged Pb²⁺ ions for the surface adsorbing sites,

Fig. 7. Effect of adsorbent amount on Pb²⁺ adsorption.Fig. 8. Effect of pH on Pb²⁺ adsorption.

resulting in a decrease in the removal of Pb²⁺. According to other works dealing with sorption of lead ions on bentonite [19], kaolinite and montmorillonite [1], palygorskite [21], the removal increases continuously for pH values ranging between around 1 and 6.

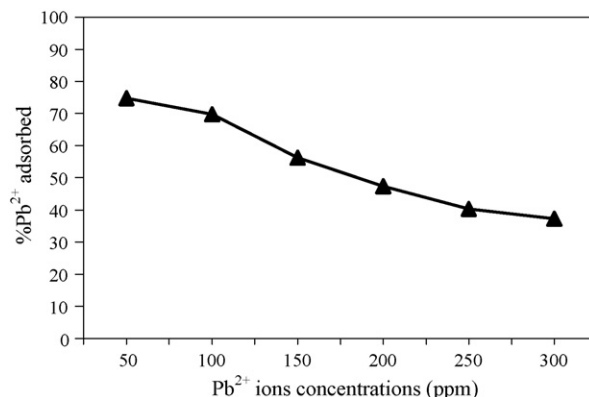
3.3.4. Effect of Pb²⁺ concentration

Fig. 9 shows the effect at pH 4 of varying lead concentration (50–300 ppm) on the adsorption under operating conditions of 20 min shaking time and 0.5 g/100 ml for adsorbent. The results showed a gradual decrease of Pb²⁺ removal when the lead concentration increased in the solution. This decrease is due to the fact that an increase in lead concentration makes the ratio of the number of Pb²⁺ ions present in solution to the number of available adsorption sites more and higher. Since the initial concentration increases more rapidly than the quantity of lead adsorbed, it is obvious that Pb²⁺ removal decreases. When Pb²⁺ ion concentration changes from 50 to 300 ppm, the extent of adsorption on AYDs clay falls from 74.75 to 37.33%.

3.4. Adsorption isotherm

The equilibrium data for Pb²⁺ adsorption over the concentrations range from 50 to 300 ppm at 25 and 40 °C (Fig. 10) have been correlated with the langmuir isotherm [22]:

$$\frac{C_e}{X/m} = \frac{1}{Q_0 \times b} + \frac{C_e}{Q_0}$$

Fig. 9. Effect of initial concentration on Pb²⁺ adsorption.

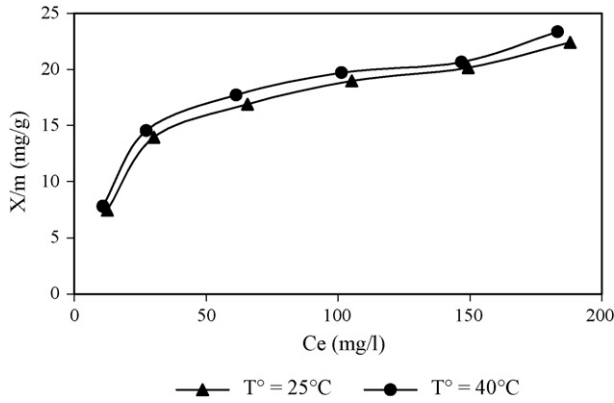


Fig. 10. Adsorption isotherms of Pb²⁺ onto AYDs at 25 and 40 °C.

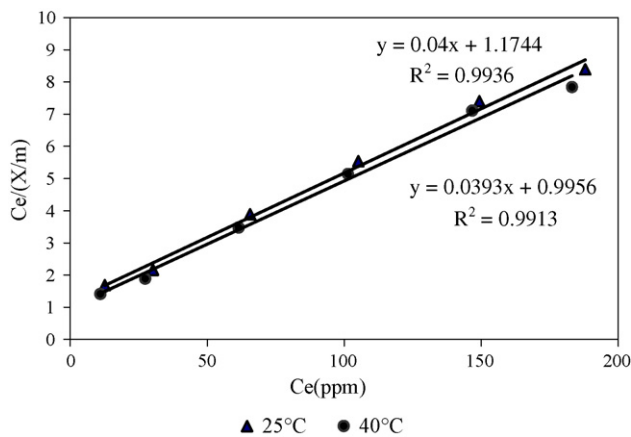


Fig. 11. Plot of $C_e/X/m$ against C_e for lead adsorption onto AYDs.

where C_e is the equilibrium concentration of adsorbate (mg/l), X/m is the amount adsorbed at equilibrium per mass unit of the adsorbent (mg/g), b and Q_0 are Langmuir constants related to energy of adsorption and maximum sorption capacity of the adsorbent respectively. The values of Q_0 and b were determined from the intercept and the slope of the line obtained by plotting $C_e/(X/m)$ versus C_e (Fig. 11). Results in Table 4 show that the maximum adsorption capacity values, Q_0 , are 25 and 25.44 mg/g at 25 and 40 °C, respectively. The observed maximum sorption capacity of AYDs for Pb²⁺ removal remained slightly lower compared to maximum sorption capacities of montmorillonite, palygorskite clay and sulphuric acid activated montmorillonite reported in previous studies [1,21,23], whereas the obtained results are higher to other materials such as kaolinite and sulphuric acid activated kaolinite [1,23]. The results show also that Q_0 and b values increases slightly as the temperature increases. Hence, the interaction between adsorbent and adsorbate is endothermic. The correlation coefficients (R^2) given in

Table 4
Langmuir adsorption parameters

T (°C)	Q_0 (mg/g)	b (l/mg)	R_L	R^2
25	25	0.99	0.0033	0.99
40	25.44	1.17	0.0028	0.99

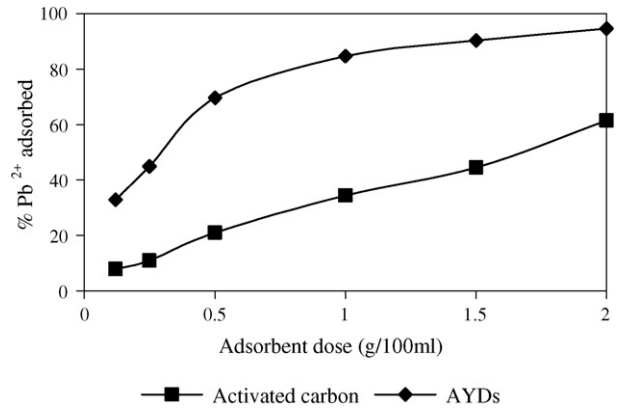


Fig. 12. Effect of AYDs and activated carbon amounts on Pb²⁺ adsorption.

Table 4 show that the Langmuir equation gives a fairly good fit to the sorption isotherm. The main characteristics of the Langmuir isotherm can be also expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which was defined as:

$$R_L = \frac{1}{1 + (b \times C_0)}$$

where C_0 is the initial Pb²⁺ concentration. The R_L value indicates the shape of the isotherm as follows: favourable adsorption is indicated by $0 < R_L < 1$ while $R_L > 1$, $R_L = 1$ and $R_L = 0$, describe respectively unfavourable, linear and irreversible adsorption [24]. The R_L values calculated for Pb²⁺ initial concentration of 300 ppm were 0.0033 and 0.0028 at 25 and 40 °C, respectively. Hence, the adsorption of Pb²⁺ ions on AYDs was favourable.

3.5. Comparative study of lead adsorption with sulphuric acid activated clay and activated carbon

Activated carbon, among a large variety of adsorbents, was still the most important one in current use in the environmental pollution control due to its large surface area, high adsorption capacity and porous structure. The comparative study between sulphuric activated clay (AYDs) and activated carbon for lead removal from aqueous solution ($C_0 = 100$ ppm) showed that 0.125 g of activated clay gave the same result that 1 g of activated

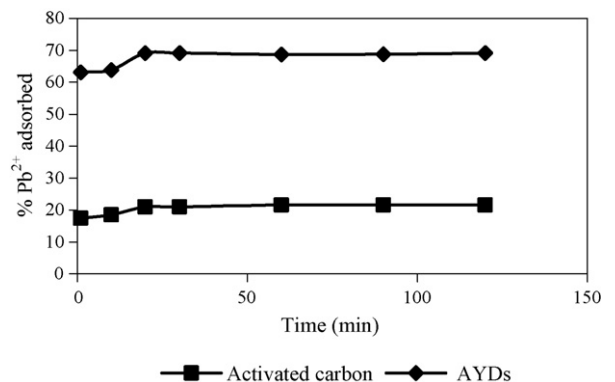


Fig. 13. Effect of shaking time on Pb²⁺ adsorption by AYDs and activated carbon.

carbon (Fig. 12). Moreover, the kinetic study of Pb^{2+} adsorption with activated carbon and sulphuric activated clay showed that the adsorption capacity of the latter was better than that of activated carbon whatever the contact time considered (Fig. 13).

4. Conclusions

Four smectitic clay samples: untreated clay (AYD), hydrochloric activated clay (AYDh), sulphuric activated clay (AYDs) and thermic activated clay (AYDc) were used for the removal of Pb^{2+} ions from aqueous solutions, the following conclusions have been drawn from this investigation:

- Raw smectitic clay, sampled in Jebel Aïdoudi in El Hamma area (meridional Atlas of Tunisia) has high surface charges resulting from the spread of isomorphous substitution in tetrahedral and octahedral sheets. This clay sample is capable of removing 41.32% of Pb^{2+} ions from aqueous solution under the following conditions: initial Pb^{2+} concentration 100 ppm, pH 4, shaking time 10 min, adsorbent amount 0.5 g/100 ml and temperature 25 °C.
- Sulphuric acid and hydrochloric acid activation of AYD sample enhanced the adsorption capacity under the same conditions compared to the untreated clay minerals due to the increase of surface area. The uptake of Pb^{2+} by AYDs (65.12%) was very high when compared to that by AYDh (50.18%). This is due to the greater solubility of clay minerals in sulphuric acid compared to hydrochloric acid.
- Thermic activated clay (AYDc) obtained by calcination of AYD at different temperatures (100, 200, 300, 400, 500 and 600 °C) is capable of removing 54.22% of Pb^{2+} ions from aqueous solution when calcination temperature is 100 °C. This percentage decreased to 42.75% with increased temperature.
- Good adsorption results were obtained with AYDs clay (Pb^{2+} removal 69%) under operating conditions of 20 min shaking time, pH 4, 100 ppm initial Pb^{2+} concentration and 0.5 g/100 ml clay dose. The removal reached 90% when the clay dose increased from 0.5 to 1.5 g/100 ml.
- Results related to adsorption isotherms showed that the equilibrium data obtained with AYDs clay fitted very well to the Langmuir model. It was observed that the isotherm constants increased slightly with increasing temperature. The values of maximum adsorption capacity Q_0 increased from 25 to 25.44 mg/g, when the solution temperature increased from 25 to 40 °C.
- Comparative study between activated carbon and sulphuric acid activated clay showed that 0.125 g of activated clay gave the same result that 1 g of activated carbon. Moreover, the results showed that adsorption capacity of sulphuric acid activated clay was better than activated carbon whatever the shaking time considered.

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