

Heavy metals removal from watercourses by low cost natural Tunisian material Environmental protection

L. Aloui, F. Ayari, A. Ben Othman, M. Trabelsi-Ayadi

Abstract— Clays mineral, especially smectite type, are widely used as barriers in landfills to avoid pollution of subsoil and groundwater by leachates containing heavy metals. Hence it is important to study the adsorption of metals by these kinds of clays since it's a low cost material and frequently presented in nature; accordingly many researchers pinpoint their interest to apply this material as adsorbent to reduce heavy metals from wastewater.

In this investigation, we have tried to evaluate adsorption properties of local clay, denoted ArB, collected from south of Tunisia (Stah Gafsa), to remove lead and cadmium from aqueous solution. This clay was tested at the first time to remove heavy metals for environmental protection.

First of all clay was purified and characterized by several physico-chemical methods. Results approve the general smectite group of the sample with fraction of illite and kaolinite.

The adsorptive properties of purified sample, Na-enriched smectite denoted ArP, in cadmium and lead annoying aqueous environment were studied in a batch adsorption system. It was found that the amount of adsorption of metal ion increased with the initial solution pH, metal ion concentration, and contact time, and with the amount of adsorbent.

Adsorption isotherm show an apparent selectivity with the following order: $Pb^{2+} > Cd^{2+}$.

The percentage of ion removal by ArP in certain experimental conditions can reach 98% for cadmium and 57% for lead.

Index Terms— Heavy metals, bentonite clay, adsorption, cadmium, lead.

I. INTRODUCTION

Pollution by heavy metals is serious and complex since they can bio-accumulate to higher levels in biota and are poisonous. Wastewater containing heavy metal contaminants requires a treatment system that can remove these contaminants effectively. These types of waste could come from electroplating processes and mining waste. Heavy metals can be removed in several ways, precipitation and sorption by various media, where choice of method depends upon the type and concentration of both sorptive and sorbent material employed as well as their costs. The metals reactions at the solid-solution interface play important role in determining their treatment by adsorption process, as well as in their fate in the environment. These reactions are often collectively called sorption, which include adsorption, precipitation and polymerization. Adsorption is a much faster process than precipitation.

Clays are used to remove metals from aqueous media. In particular, clay barriers play a key role in the concept of the

long-term disposal of radioactive waste. Compacted bentonite has a very low permeability and a high sorption capability for most heavy metal [1]-[2]. Studies have been conducted to evaluate the potential of clay minerals like montmorillonite, kaolinite and illite in the removal of toxic metals like lead, cadmium, copper, zinc etc... The abundance of bentonite and its low cost make it a strong candidate as an adsorbent for the removal of heavy metal from wastewater. This study was therefore undertaken to evaluate the use of locally available bentonite, collected from Stah Gafsa, in the removal of lead and cadmium from aqueous solution. We tested the adsorptive capacity of this clay fraction to eliminate undesired heavy metal produced and released during agricultural and industrial activities, which may pose a serious threat to the environment.

II. MATERIALS AND METHODS

A. Adsorbent

Crud clay material (ArB) used as adsorbent in this investigation emanated from Stah Gafsa, south of Tunisia, was purified by dispersion quantity of clay in distilled water with a solid/liquid ratio (1:5). The mixture is subjected to vigorous stirring for 12 h until complete homogenization, the fine fraction (particle size $< 2 \mu m$) was taking out then purified using the classical method [3] by several cycle exchanged with NaCl solution (1 mol L^{-1}) under stirring during 24 h for five times to form the sodium-saturated clay sample. At that time, the Na-saturated clay was washed with distilled water until chloride free as confirmed by the $AgNO_3$ test [1]. The obtained sample (ArP) was dried at 80°C and grounding.

Composition of the clay sample was identified by X-ray diffractometer (XRD). XRD analysis was carried out using a PANalytical X'Pert HighScore Plus diffractometer, $CuK\alpha$ radiation. Composition of ArP sample was confirmed with an EDX system. The Fourier transform infrared (FTIR) spectra were acquired on a Perkin Elmer 783 dispersive spectrometer in the range of $4000\text{--}400 \text{ cm}^{-1}$. Cation exchange capacities (CEC) was estimated as described in previous studies [4]-[5]. As a complimentary technic for clay characterization, the sample morphology was recognized by Transmission electron microscopy (TEM). BET surface area (S_{BET}) and pore volumes of adsorbent were measured using the physical adsorption of nitrogen by Quantachrome Autosorb-1 instrument. The adsorption of methylene blue dye on bentonite in solutions is used to determine either their cation-exchange capacities (CEC) or their total specific surface area (S_s) via Uv-spectrometer.

III. RESULT AND DISCUSSION

A. Analytical Chemistry

Samples (ArP and ArB) were analyzed by XRay Fluorescence to determine their chemical composition. The result of

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chemical analysis for clay composition is shown in table I.

Table I: Chemical composition (wt %)

%M _x O _y	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
ArB	53.342	15.421	8.213	4.614	4.754	1.326	0.754
ArP	45.511	15.13	9.583	4.383	3.477	0.966	0.994

B. X-ray diffraction

The crystalline structure of the clay sample, before and after purification, identified by XRD measurements (fig. 1 and fig 2) showed that clay is composed mainly of smectite, kaolinite, illite, and quartz. The smectite is deduced by the appearance of peaks at 14.11 Å on the normal diffractogram of the raw sample which was displaced to 12.55 Å after purification and which was enlarged on the glycoled diffractogram to 17.73 Å. The presence of kaolinite is proved by the appearance of peaks at 7.14 and 3.57 Å on the normal and glycoled diffractograms. These peaks disappear in the sample heated at 600°C during 2 h. The appearance of peaks at 4.25 and 3.34 Å marked the presence of quartz and peaks at 10.38 and 2.56 Å marked the presence of illite [6]–[7]. Heating the sample above 600°C collapses the interlayer spacing at 9.90 Å this data support the clay smectite group. data support the clay smectite group.

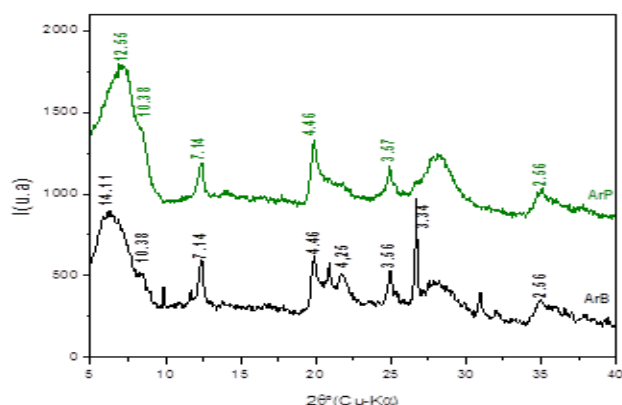


fig.1: X-ray diffractogrammes of ArB and ArP

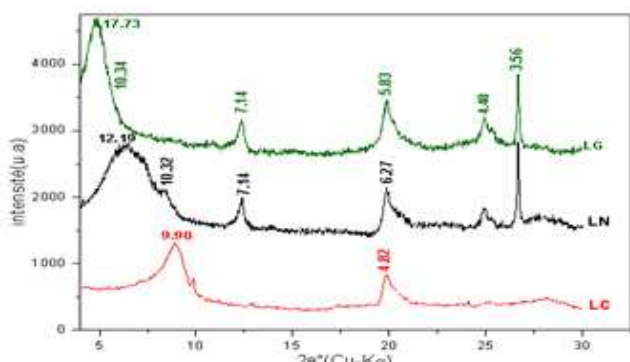


Fig. 2: Oriented diffractograms of Arp material: LN: normal; LC: heated for 2 h at 600°C; LG: glycoled

C. Infrared spectra

As shown in fig. 3, the typical absorption band at 3644 cm⁻¹ is assigned to the stretching vibration of AlOH and

SiOH. Band at 3422 cm⁻¹ was due to the stretching vibration of H₂O, proved the smectitic nature of clay. The attributions of absorption in the range of 469–1129 cm⁻¹ were due to Si–O–Si and Si–O–Al bending and stretching. Bands at 697 cm⁻¹ characteristic of quartz disappear in the spectrum of the purified clay.

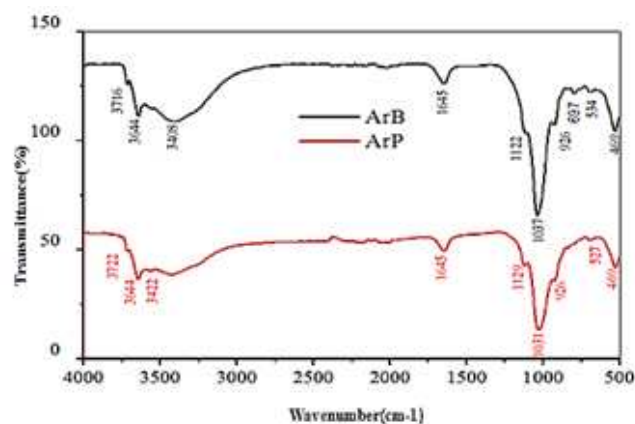


Fig.3: Infrared spectra of crude and purified sample

D. CEC Ss and Specific charge density

Experiments results of SBET, Ss and CEC of clay samples are shown in Table II. After purification these values increases which suggest that the clay sample used belong to smectite group.

Data of the specific charge density ($\sigma = \frac{CEC}{S_s}$) of the raw and purified sample have a lower value ($\sigma < 1 \text{ meq.m}^{-2}$) suggested that this clay is swelling. This result reminded that of Lefebvre et al (1987) [8]

Table.II: Most physical propriety of claysample

Sample	S _{BET} (m ² /g)	S _s (m ² /g)	CEC(meq/100g)	Specific charge density: σ (méq.m ⁻²)
ArB	72.3	507.12	63.4	0.125
ArP	102.9	760.68	93.6	0.123

IV. SORPTION EXPERIMENTS

The heavy metal (Pb and Cd) sorption experiments were conducted by bentonite clay minerals. Two kinds of sorption (ion-exchange and adsorption) equilibrium experiments were carried out with (i) raw bentonite (ArB) containing mainly Ca²⁺, Mg²⁺, Na⁺, and K⁺ as exchangeable cations and (ii) completely Na-saturated bentonite (ArP). The heavy metal stock solutions were prepared by dissolving Pb(NO₃)₂ and CdCl₂·2.5H₂O (obtained from Aldrich-Sigma chemical company and their purity is higher than 99% and used without further purification)

in demineralized water.

The study was performed at room temperature and the closest to the treatment of industrial waste water requirements. The Pb²⁺ and Cd²⁺ solutions

at different concentrations (from 10^{-3} M to 10^{-4} M) were prepared by diluting the stock solutions. The pH value of these initial stock solutions was 5.8 [9].

All metal sorption studies were performed using atomic absorption spectrophotometer. A variable metal concentration was equilibrated with an amount of an air-dried clay mineral sample, placed in 50 mL polyethylene centrifuge tubes. The mixture was shaken on a reciprocating shaker operated at a room temperature of 25°C for 1 h. Previous time-course studies indicated that this length of time was adequate for the solutions to achieve equilibrium stage [9].

After shaking, the supernatant was separated by centrifugation at 5000 tr/min^{-1} for

The amount of adsorbed metals was taken as the difference between the amount added initially and that remaining in 20 min, and analyzed by Atomic Absorption Spectrometer (A.A.S vario'Analytic Jenaprime').solution after equilibration, the pH of the reactions mixtures at the end of the equilibrium time were measured. All measurements were run in duplicate.

A. Kinetic studies

The adsorption experiments were carried out using a 0.2

meq/L solution of lead or cadmium. 50 mL of each solution were added in a glass flask with 0.1 g of Na saturated bentonite (ArP), and then putted in a shaker at a constant stirring. Temperature and pH were kept constant at 25°C and 5.8, respectively The kinetic experimental data was obtained when each flask was removed from the shaker at different contact times (0-120 min), the solution was centrifuged and the cations in the supernatant was analyzed. The amount of cation removed (Q_{ads}) was calculated. As can be seen in fig. 4 equilibrium was reached after 80 minutes, the majority of cadmium and lead was removed after this length of time. A

more pronounced plateau is related to the isotherm after 80min.

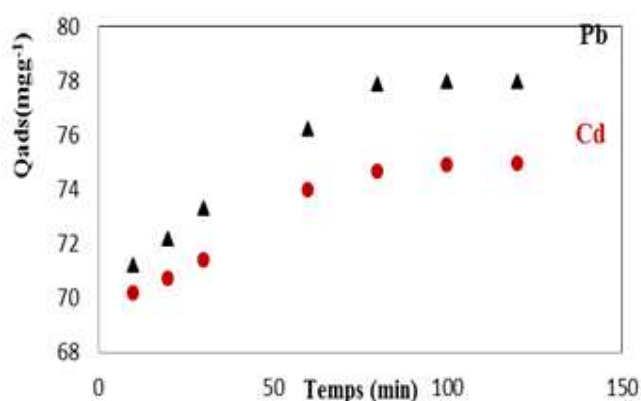


fig.4: Kinetic experimental data

B. Sorption isotherms

Clay minerals cover a diversity of surfaces which exhibit electrical charge properties having a strong influence on the sorption of ionic and polar species. The charge on the surface of the soils must be counterbalanced in the aqueous phase to maintain electroneutrality. As a result, electrical double layer exists at the clay/water interface. On the one hand, the clay mineral was tested in its crud form (ArB), so, in the electrical double diffusive layer, Na^+ , Ca^{2+} , Mg^{2+} , K^+ , etc... elements were expected in both the Stern layer and the diffusive layer. On the other hand the clay mineral was tested in purified form (ArP), after Na saturation, therefore, in the electrical double diffusive layer Na^+ element were expected in both the Stern layer and the diffusive layer

As example if Pb^{2+} is considered as a competing ion, the electrical double diffusive layer can be illustrated as shown in Fig. 5.a and fig 5.b for ArB and ArP respectively.

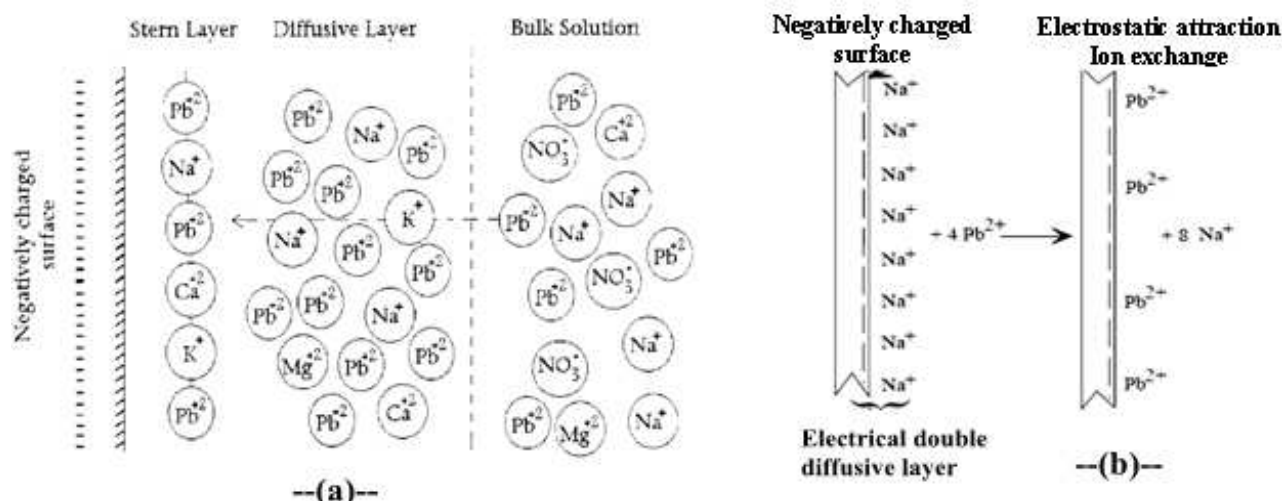


fig. 5 Descriptive illustration of Pb^{2+} sorption ions on: (a) raw bentonite (ArB) and (b) Na saturated bentonite (ArP)

The isotherms were constructed taking into account the equilibrium time obtained by the kinetic data. As seen from the plots given in fig. 6, the sorption of Pb^{2+} and Cd^{2+} exhibit almost the same behavior, except their adsorbed amounts at equilibrium. The affinity sequence is $\text{Pb}^{2+} > \text{Cd}^{2+}$.

In the investigated concentration range it was observed that Q_{ads} could estimate $Q_{\text{ads max}}$ close to 2.5 CEC experimental data for lead ions yet it reach only CEC for cadmium ions. In all cases lead ions are more sorbed than cadmium ions ($\approx 95\%$ of Pb was removed). This result can be confirmed by those of

Kinraide and Yermiyahu (2007)[10]; they demonstrate that metals clay affinity depends notably on the ionic radius of metal cations.

According to Coulomb's law, the exchange affinity increases with the valence of the ion and at equal load, the cation having the largest non-hydrated radius is preferentially adsorbed [10-11]. This information confirms the order of selectivity found in our study (Pb^{2+} ion radius (0.12 nm) > Cd^{2+} ionic radius (0.097 nm)) lead is more adsorbed by ArP then cadmium. In another hand, adsorption reaction, causing the formation of internal sphere complex witch can be described by the following process [11]:



(S=Surface, M= metal)

determines the efficiency of the adsorption of various metals, specific adsorption increases as the pK_a value decreases (pK_a of the constant equilibrium of the hydrolysis reaction (1)). This comment confirms the order of selectivity for lead and cadmium in this investigation, we noted that $pK_{pb} = 7.7 > pK_{Cd} = 10$.

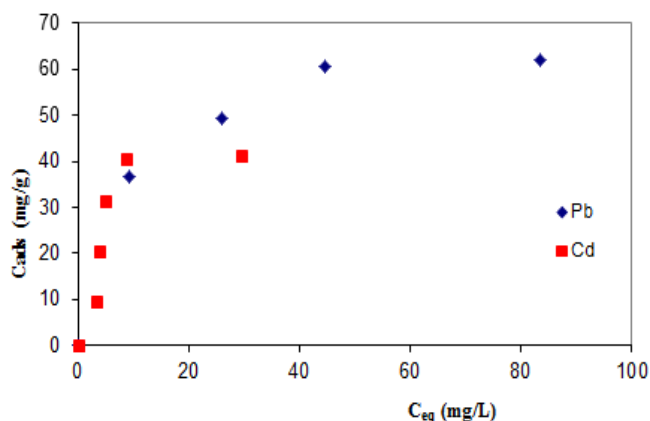


Fig.6: Order of selectivity ([Metal] = initial $10^{-3}M$)

Measuring the final pHs of the suspension after a contact time of 80 min (ArP/metal aqueous solution) can give good information for revealing the above comments. We reported that the final pH values of recuperated suspension ranged between: 6.5–7.2.

Therefore, increase in lead adsorption was also attributable to the hydrolysis reaction and to the increase in Pb hydroxyl species in solution. Because the $Pb(OH)^+$ ion is monovalent, the energetic barrier that must be overcome when it comes closer to the surface of the particle is smaller than in the case of the Pb^{2+} ion. In spite of the fact that at low pH the amount of $Pb(OH)^+$ corresponds to a small proportion of the Pb species in solution the adsorbed amount increases with pH because the hydrolysis reaction is continuously processed and the colloid surface may have an accelerating effect on that reaction. Furthermore, as pH increases, hydrogen ions are released, which favors Pb adsorption at the colloid surface. From the diagrams speciation of cadmium (fig.7) we suggest that, in the pH range studied, Cd^{2+} species is the most pronounced one with negligible amount of complexes. Such differences as well as the nature of the cation may influence in the ion removal. Cadmium is less electronegative than lead and, as a consequence, less attracted to the chemisorption sites witch explain, in all cases, why lead ions are more sorbed than cadmium ions. ArP should have a high affinity for Pb.

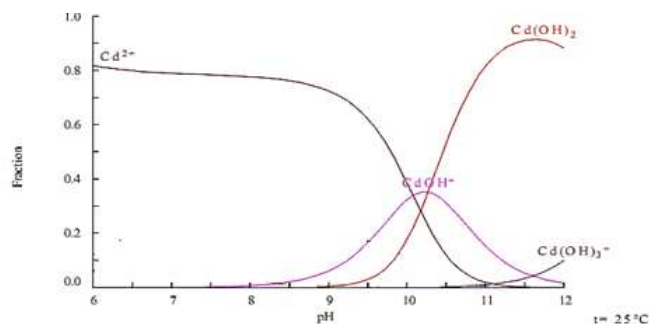
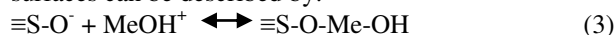


Fig.7: diagrams speciation of cadmium [12]

To finish these results concord with those of Barrow [13], he suggested that although most of the more abundant soil cations, such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , are weakly held by soils as exchangeable ions, many cations can form inner sphere complexes with variable-charge soil surfaces and therefore are strongly held. This specific adsorption of metallic ions occurs most readily for metals that hydrolyze in water. Such metals include most of the transition elements and the rare earths, in addition to other ions, such as Cd^{2+} and Pb^{2+} . The adsorption reaction generally involves the formation of an inner sphere complex between the hydroxo-metal complex and the negatively charged deprotonated surface of oxides, hydroxides, and oxyhydroxides of Al, and Fe [13]. The reactions of divalent hydrolyzed metals at variable-charged surfaces can be described by:



$$\text{at equilibrium } K_a = \frac{[\equiv S-O-Me-OH]}{[\equiv S-O^-] + [MeOH^+]}$$

where K_a is the conditional intrinsic formation constant for the cation. The extent of the reaction, which is dependent on pH, increases to a maximum as the pH is raised. The maximum amount of adsorption generally occurs at a pH somewhat below the pK_a of the hydrolysis reaction of the metal in water. So far, there are only a few values in the literature for the intrinsic equilibrium constant, K_a , between various metals and naturally occurring variable-charge minerals.

However, it has been shown that for any given oxide (hydroxide) surface there is a very close correlation between values for K_a and the formation constant for soluble metal hydroxycomplexes [14].

C. Effect of pH

pH is an important factor controlling the process of adsorption. The data drawn with the 50 ml of aqueous solution having a concentration of $10^{-4}M$ of metals concentration, with different initial pH varying from 4 to 8 are exposed to a adsorbent dosage of 0.1 g are plotted in Fig-8. At low pH values, surface complexation contributes mainly to the adsorption of Pb(II) and Cd(II) on ArP (fig. 8). As the pH increases, the competition between protons H^+ and Pb(II) (or Cd(II)) for surface sites will decrease and Pb^{2+} ion (or Cd^{2+}) is the predominating species and it will attract to the surface of adsorbent by columbic forces. If pH value is greater than 5.0, lead hydroxide such as $Pb(OH)_3^-$ begins to form which results in the decrease of the adsorption of Pb(II) on ArP [9]. We reminder, that at this range of pH Cd^{2+} species predominate.

D. Effect of adsorbent dosage

The data drawn with the 50 ml of the aqueous solution having a concentration of 10^{-4} M of metals is exposed to different dosages of adsorbent are plotted in fig.9. It is evident from fig.8 that the fraction of the metals removed from the aqueous phase increases with an increase in the adsorbent amount. Such behavior is understandable since the metal uptake capacity of the adsorbent increases as its dosage was increased. This is therefore because the number of active sites accessible for metal uptake would be more as the amount of the adsorbent increases.

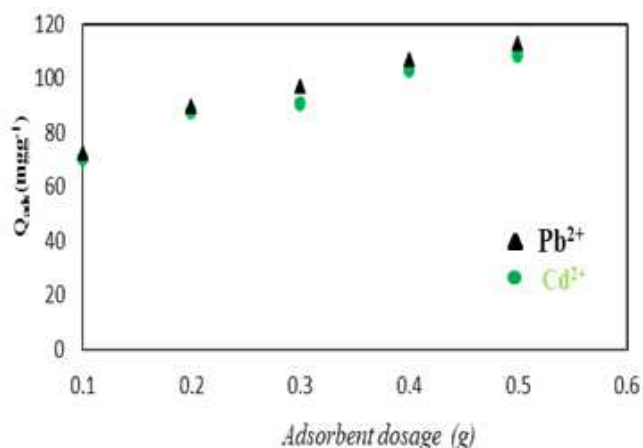


fig.9 : Adsorbent Dosage Vs Q_{ads}

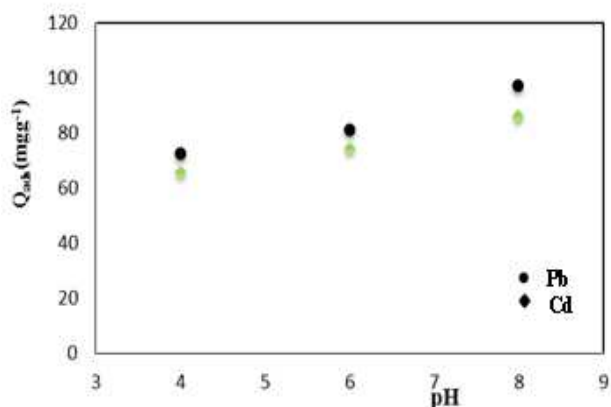


fig.8: Effect of pH on cadmium and lead removal by Na saturated bentonite ($[metal] = 10^{-4}$ M, $T = 20$ °C)

E. Analysis by transmission electron microscopy (TEM)

MET has been used in order to determine the morphology and size of the clay particles after metal adsorption. In this paper we give only the example of Pb adsorption.

Results show that the clay sheets are less aggregated after adsorption (fig.11.b), they appear as a sticks compared with those of Na saturated bentonite (fig.11.a): sheets of ArP seem to be united having a micrometric size. After adsorption the sticks seem to have lost their cohesion and are separated. In another hand a small individual particles can be distinguished in the MET photography (fig.10. b), which by identification via the coupled EDAX, correspond to highly charged particles of lead (fig.10 and tabe.III). These results confirm that this kind of no cost natural material, greatly abounded in countryside, can be a great barrier to remove 90% of lead and cadmium, without any previous treatment.

Table.III : atomic percentage of major elements in ArP before and after Pb(II) removal

éléments	%atomic Before Pb adsorption	%atomic after Pb adsorption
Si	54.6	55.2
Al	26.2	25.3
Mg	1.9	1.8
Fe	5.5	4.7
Na	1.8	0,5
Pb	0	1.3

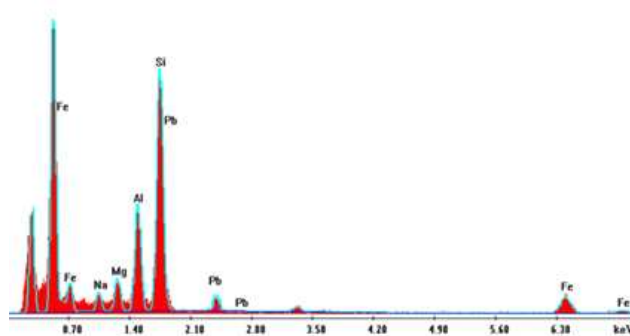


fig .10 : EDAX Spectrum of ArP after Pb(II) adsorption

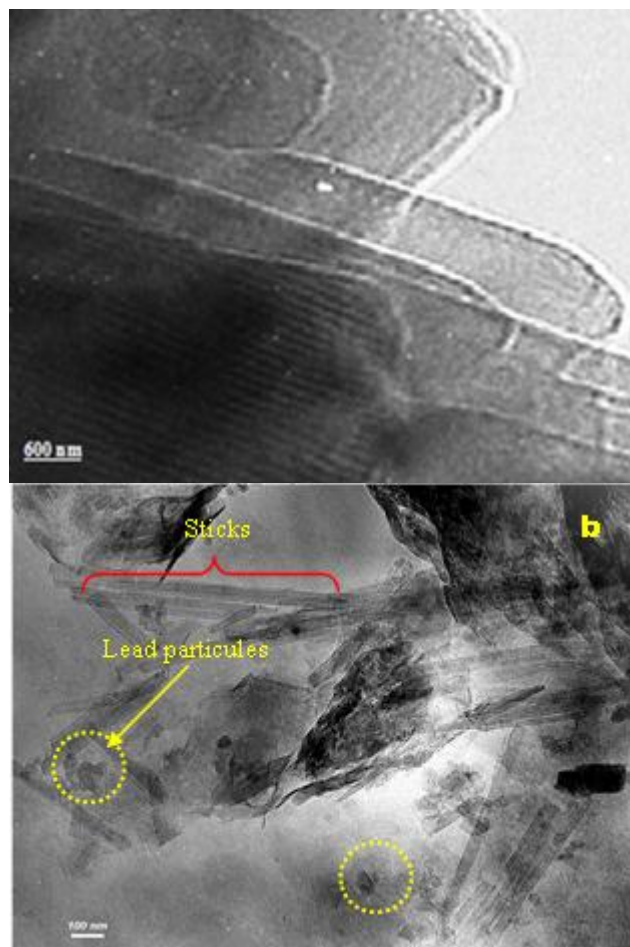


Fig.11. Morphology of ArP before (a) and after lead removal (b) given by TEM

V. CONCLUSION

Composition of bentonite collected from Stah Gafsa, south of Tunisia, was determined according to physicochemical analysis. The result shows that it was an interstratified illit-smectite with 93,6 meq/ 100 g CEC of calcined clay and 760,68 m² g⁻¹ specific surface area.

This clay was tested in sorption of two heavy metals (Pb, Cd). The results suggest that metal sorbed onto bentonite clay varied in the following order $Pb^{2+} > Cd^{2+}$, and fit satisfactorily with the uptake capacity. The amount of Pb sorption remained higher than the CEC of the clay fraction due to sorption of its Pb hydroxy complex, in addition of sorption of its bivalent form which remained the high amount of Pb removal from aqueous solution. Indeed the nature of the adsorption process for nonspecifically adsorbed ions dependent only on the relative charges of the metal species in solution and to the charged surface.

Bentonite of Stah Gafsa, analyzed at the first time, present a good behavior for a heavy metal removal without needing any specific treatment

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