Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.770241

51 (2013) 4447–4458
June

Removal of heavy metals from aqueous solutions by Algerian bentonite

F. Mohammed-Azizi, S. Dib, M. Boufatit*

Faculté de Chimie, Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale, Université des Sciences et de la Technologie Houari Boumediène (U. S. T. H. B.), B.P.: 32, El-Alia, Bab-Ezzouar, Alger 16111, Algeria
Tel./Fax: + 213 21 24 73 11; email: mboufatit@usthb.dz

Received 22 January 2012; Accepted 22 November 2012

ABSTRACT

This study aimed the removal of heavy metals by Algerian bentonite. An Algerian natural clay, a bentonite of Mostaganem (N.W. Algeria), has been first acid-activated (HCl) and characterized by powder X-ray diffraction, FT-IR spectroscopy, electron microscopy (SEM), and specific surface area. The acid-activated clay (AAC) was employed as adsorbent for the removal of Zn^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} ions from aqueous solutions using adsorption method. The sorption process was examined in terms of its equilibrium and kinetics. The study was carried out by varying shaking time, pH, concentration of metal ions and amount of adsorbent. The optimum parameters of our study obtained were pH values range (4–6), mass of AAC (1 g), shaking time (1 h), and initial concentration of metal ions ($10\,\mathrm{mg\,L^{-1}}$). The results have shown that Algerian bentonite clay had significant potential for removing Zn^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} ions from polluted water.

Keywords: Algerian bentonite clay; Removal; Effluent; Kinetic; Zn^{2+}; Pb^{2+}; Cu^{2+}; Ni^{2+}

1. Introduction

The material clays, because of their low-cost and remarkable properties as effective sorbents for heavy metal ions adsorption, were used for the removal of hazardous organic and inorganic pollutants from water [1–9]. The material clays have been investigated for their capacity to remove effluents from industrial wastewater [10–15]. The sorbing properties of acid-activated clays (AACs) for heavy metal ions must be characterized in order to predict the sorbing behavior and the removal of toxic heavy metals such as lead, cadmium, copper, nickel, and zinc from industrial wastewater, which are hazardous and potentially toxic, remains a challenge and constitutes a difficult problem [16–19]. In this work, the Algerian bentonite clay type of Mostaganem (N. Algeria) has been acid-activated and used as adsorbent for the removal of Zn^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} from aqueous systems and the effect of solution pH, amount clay, shaking time, concentrations of heavy metal ions were investigated.

The aim of this work has been to investigate the adsorption characteristics of AAC for the removal of Zn^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} ions from aqueous solutions by mean of low-cost methods. the use of local material clay, for removing heavy metal ions such as Zn^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} from industrial wastewater, is the topic of this study.

---

*Corresponding author.

1944-3994/1944-3986

2. Materials and experimental methods

2.1. 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/mol (Carlo Erba 98%); KOH, M = 56.11 g/mol (Fluka 99.5%); HCl, M = 36.5 g/mol (Merck, 37% pa, d = 1.18); $Pb(NO_3)_2$, M = 331.2 g/mol (Panreac); $CuCl_2$, M = 134.45 g/mol (Fluka, 97%); $ZnSO_4H_2O$, M = 179.45 g/mol (Panreac); $NiSO_46H_2O$, M = 262.86 g/mol (Merck, 99% pa). The elements standard solutions used were prepared with distilled water.

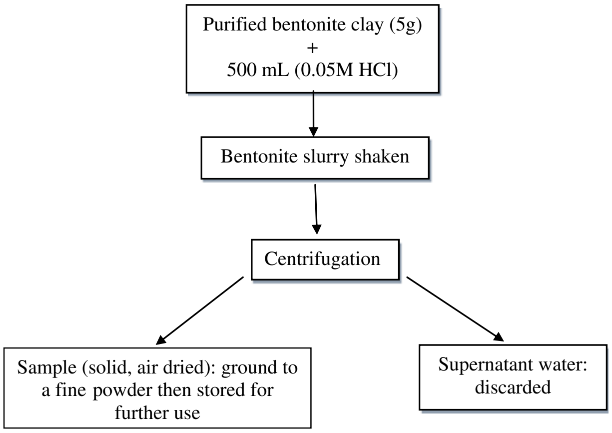
2.2. Preparation and acid treatment of bentonite clay

All early studies in our laboratory for the procedure of purification and acid-treatment of bentonite using a sedimentation method were prepared according to the literature methods, [20].

In this method, 5 g of clay were dispersed in 500 mL distilled water and shaken overnight on mechanical shaker (Janke type, Hunkel Ika. Werk, KS 500). The resulting clay slurry was then left to stand or 2 h to allow sedimentation of silica and other heavy impurities. The suspension was then centrifuged and the supernatant water discarded. The restrained sample was air-dried and reacted with a 0.05 M HCl solution. The acid-activated bentonite was centrifuged, air-dried and ground to fine powder then stored for further use, Scheme 1.

2.3. Equilibrium sorption experiments

1 g of AAC was added to 100 mL of an aqueous solution containing separately Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions into 200 mL conical flasks which were stoppered, sealed, and shaken. The equilibrium adsorption studies were conducted at 25°C, different initial pH values. The mixed solutions were then centrifuged to separate the liquid and solid phases. The concentrations of metal ions in supernatants were analyzed by using a Varian type SAA-110 flame atomic absorption spectrometer instrument with deuterium background corrector was used. All measurements were carried out in air/acetylene flame. The operating parameters for working elements were set at recommended by the manufacturer.



Scheme 1. Schematic diagram for the procedure of purification and acid-treatment of bentonite (adapted from Van Olphen 1963) [20].

3. Results and discussion

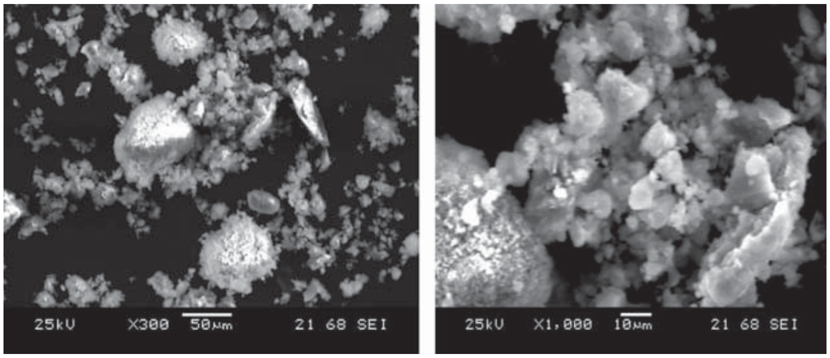
3.1. Characterization of clay

The material clay used in this study was a bentonite type from Mostaganem (N.W. Algeria). It was kindly supplied by ENOF (Ltd Algerian bentonite Company). The specific surface (SS) analysis was obtained by using analyzer Micromeritics ASAP 2020 equipment, using N_2 as an adsorptive. The chemical and mineral composition of the raw clay was determined. It was composed of (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, [21]. The chemical composition of this natural clay mineral indicates presence of important quantity of silica (SiO_2) with traces of Ca and K oxides in the form of impurities (CaO and K_2O).

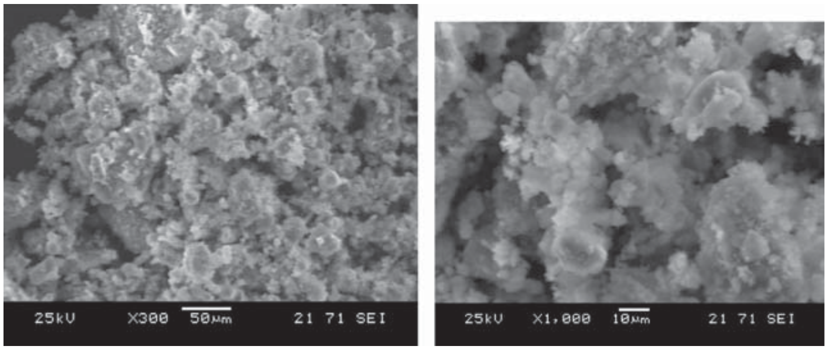
3.1.1. Scanning electron microscopy (SEM)

The electron microscopy (SEM) study of the surface of clay was done using a DCOL JSM 6830 type. The operating parameters were set at recommended by the manufacturer.

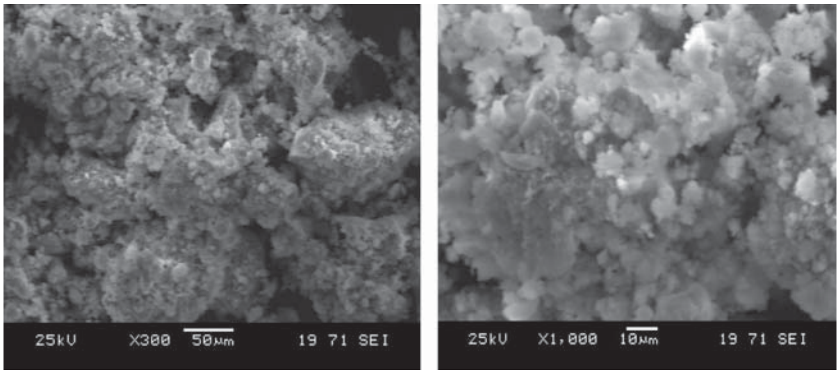
Fig. 1(a_1) shows a micrograph of material clay washed with distilled water revealing a regular structure with shaped flakes with a dimension that adjoins 6 μm for the small and some thick heaps of flakes that adjoin 80 μm. The pores, more and/or less voluminous, present are observed between these thick flakes which when observed at higher magnification (Fig. 1(a_2)), are found to be filled with small flakes. Fig. 1(b_1–e_1) reveal nearly the same morphology of the surface of AAC point of view size and flakes. It is to be noted that the distribution of the pores created by the accumulation of the flakes is uniform for these last powders in relation to the previous. Fig. 1(b_2–e_2), show a particle size of 10 μm. Although in this case, it was not observed the presence of pores or cracks. The homogeneous surfaces reflect the reaction effect between the acid (HCl) in the solution and reactive raw material clay.



a_1: *Raw clay washed (distilled water)* a_2: *Raw clay washed(distilled water)*



b_1: *acid-activated clay (0.05 M HCl)* b_2: *acid-activated clay (0.05 M HCl)*



c_1: *acid-activated clay (0.1M HCl)* c_2: *acid-activated clay (0.1M HCl)*

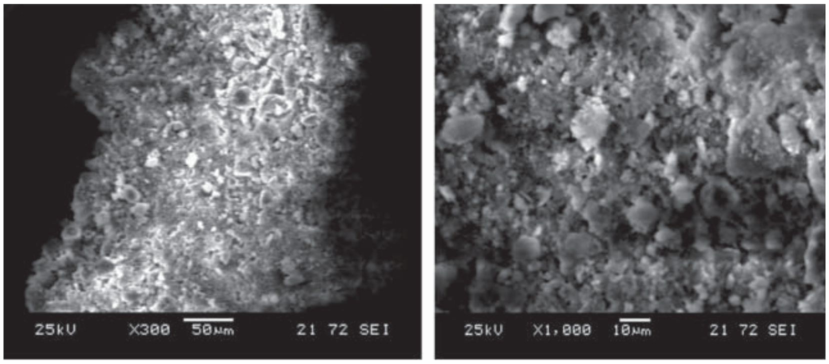
Fig. 1. (a_1–e_1) and (a_2–e_2): Micrographs of the surface of the raw and AAC.

The results of the composition of material clay (a): washed (distilled water) and AAC (b: 0.05 M, c: 0.1 M, d: 0.5 M, e: 1 M HCl), in terms of % by weight are gathered in Table 1.

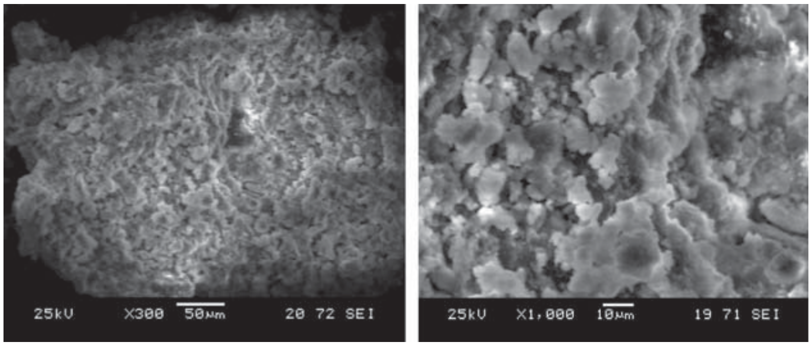
3.1.2. XRD study

X-ray diffraction patterns were obtained using a Philips PW 1730 diffractometer equipped with Cu-Kα radiation (40 kV, 30 mA). The X-ray diffraction patterns of the sample clays in the purified fraction confirm the characteristics of montmorillonite type. It shows quartz impurities, Fig. 2(a–f). Fig. 2(a–f) present the X-ray diffraction patterns of the sample clays of its raw nature, washed with distilled water and treated respectively with a 0.05, 0.1, 0.5 and 1 M solution of HCl. The exam of the XRD spectra leads to identify the different mineral species:

- the calcite whose peak is at $2\theta = 29.5^\circ$, case of the clay washed with distilled water, Fig. 2(b), disappears in the case of the other acid-activated samples;



d_1 : acid-activated clay (0.5M HCl) *d_2 : acid-activated clay (0.5M HCl)*



***e_1* : acid-activated clay (1 M HCl)** *e_2 : acid-activated clay (1 M HCl)*

Fig. 1. (*Continued*)

Table 1
Composition (% by weight) of material clay (a): washed (distilled water) and AAC (b: 0.05 M, c: 0.1 M, d: 0.5 M, e: 1 M HCl)

Element	% by weight (a)	% by weight (b)	% by weight (c)	% by weight (d)	% by weight (e)
C K	17.97	07.91		08.32	13.17
O K	38.20	41.02	41.79	38.48	40.02
NaK	00.88			00.61	
MgK	00.94	01.14		01.11	01.00
AlK	05.63	07.23	07.90	06.86	06.48
SiK	31.49	40.06	46.06	38.71	35.35
ClK				01.14	02.08
K K	02.26	02.64	02.82	02.13	01.90
CaK	02.64			00.44	

- the feldspath considered as impurities in the raw material clay at $2\theta = 24^\circ$, Fig. 2(a), disappears in the acid-activated samples; and
- the peaks, at $2\theta = 9^\circ$, 20°, 27.9°, 35°, 55°, and 62° confirm the presence of the montmorillonite.

3.1.3. Infrared spectroscopy (FT-IR) study

The FT-IR spectra of raw and acid-activated bentonite clays were obtained in the region 4,000–400 cm^{-1} by using FT-IR Spectrometer, type Perkin Elmer Spectrum one model, at room temperature dispersed in KBr disks. The characteristic peaks of the bentonite clays, used in this study, and the detailed vibrational frequencies with possible assignments being given are obtained from studies [22–25]. These results are gathered in Table 2. The main change found after the acid treatment is the disappearance of the absorption peak centered at 1,109 cm^{-1} in the material AAC (0.05, 0.5, and 1 M HCl). The treatment acid led to the elimination of band of calcite in AAC spectra [26]. The band at 500 cm^{-1}, due the Si–O–Al (where Al is an octahedral cation), in the raw material clay was waved after acid treatment. It is known that the process of acid treatment leaches out impurities and some ions such as Mg^{2+}, Ca^{2+} and Al^{3+}.

3.1.4. Specific surface (SS) study

The SS areas of the washed with distilled water and acid-activated bentonite clay (a): raw, (b): washed (distilled water), (c): 0.05 M, (d): 0.1 M, (e): 0.5 M,

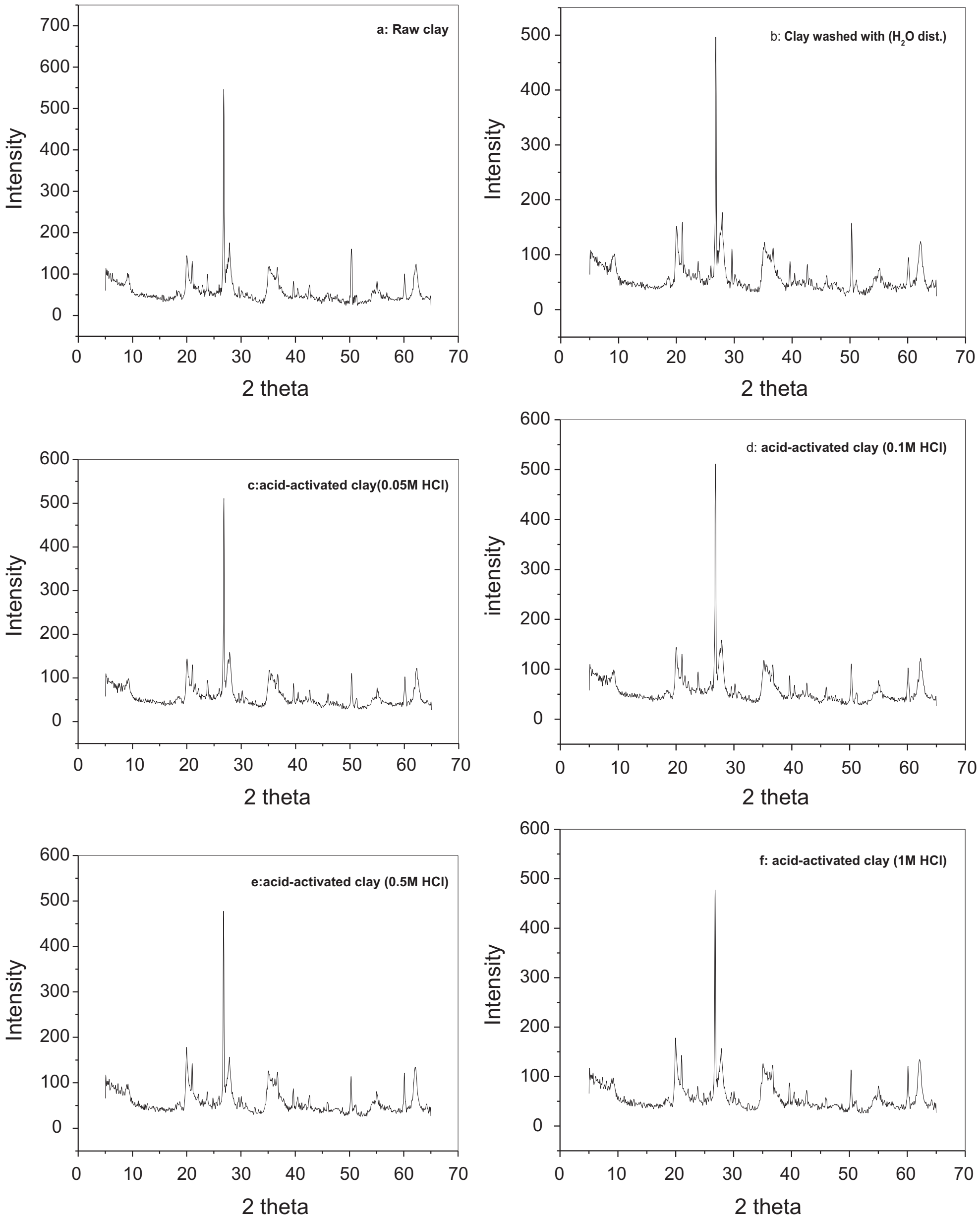


Fig. 2. (a–f): X-ray diffraction patterns of raw, washed with distilled water and AAC (a): raw, (b): washed, (c): 0.05 M, (d): 0.1 M, (e): 0.5 M, (f): 1 M.

Table 2
Compared infrared spectra of clay before and after chemical activation

Raw clay	AAC	Assignment
3460.45–3458.09 cm^{-1}	3434.82–3457.62 cm^{-1}	OH functional group of coordinated water
1638.16–1636.46 cm^{-1}	1634.88–1637.97 cm^{-1}	OH stretching vibration $\delta(H_2O)$ deformation
1045.50–1018.18 cm^{-1}	1047.40–1031.66 cm^{-1}	Stretching vibration of Si–O–Si, OH attached to (Al^{3+}, Fe^{3+}, Mg^{2+})
1,109 cm^{-1}	–	–
579.02–523.07 cm^{-1}	523.07–593 cm^{-1}	Silica quartz impurities

Table 3
SS areas of the bentonite clay: washed (distilled water) and acid-activated with: 0.05, 0.5, and 1 M HCl

Clay	Washed (distilled water)	0.05 M	0.5 M	1 M
SS area (m^2/g)	17.65	27.34	32.14	32.45
External-SS (m^2/g)	15.07	25.59	28.52	29.11
Micropore surface (m^2/g)	2.51	1.75	3.62	3.35

(f):1 M) were obtained by BET (Brunauer, Emett et Teller) method with an analyzer Micromeritics ASAP 2010 equipment type, using N_2 as adsorbate. Table 3 shows the important effect of acidic treatment. The SS areas of the bentonite clay are increasing with the increase in the concentration of Chloridric acid to reach 32.45 m^2/g for 1 M HCl.

3.2. Adsorption of Zn^{2+}, Pb^{2+}, Cu^{2+}, and Ni^{2+} ions

3.2.1. Simultaneous effect of pH and acid treatment on the removal of Zn^{2+} ions

Fig. 3 shows the simultaneous effect of pH and acid treatment on the removal of Zn^{2+} ions onto AAC (0.05, 0.1, 0.5, and 1 M HCl). The removal percentages are remarkably influenced by the pH values in the range from 2 to 8 (prepared and adjusted by using either HCl acid or NaOH solutions). These removal percentages were increased gradually with increasing of pH to reach a maximum varying between 80 and 95%. As we can see, Fig. 4, one the higher removal percentages was obtained for the lower concentration of HCl acid (0.05 M) used. The surface properties of AACs with 0.05 and 0.5 M HCl seem to play an important role. The AACs with 0.05 and 0.5 M HCl have been found to possess great affinity for Zn^{2+} ions. Therefore, the AAC (0.05 M HCl) was selected for the removal of heavy metal ions, the case of the adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions onto AAC. This is could be considered as an economic aspect of this study.

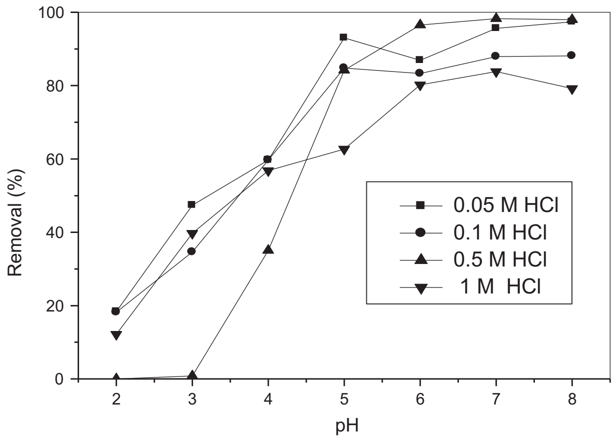


Fig. 3. Removal of Zn^{2+} onto AAC as a function of simultaneous effect of pH and acid treatment ($[Zn^{2+}]_i$: 10 mg L^{-1}; mass of AAC: 1 g; shaking time: 1 h; T: 25℃).

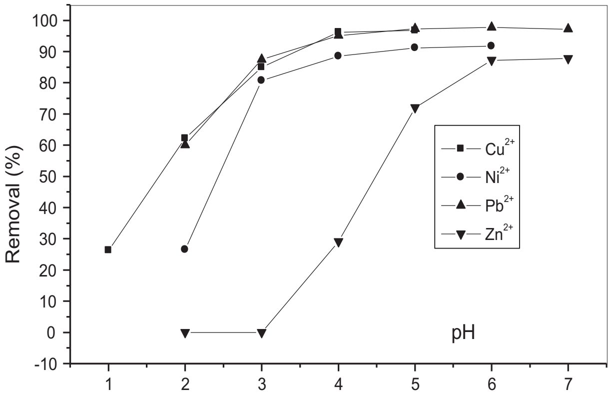


Fig. 4. Removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} onto AAC (0.05 M HCl) as a function of pH (initial metal concentration: 10 mg L^{-1}; mass of AAC: 1 g, time: 1 h; T: 25℃).

As the most of the heavy metal ions tend to form precipitation at high pH values, which limits the process greatly, the effect of pH on the adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} onto AAC (0.05 M HCl) was investigated at pH values 1–7. Fig. 4 illustrates that the removal percentages were increased gradually with increasing of pH to reach a maximum:

- 95% at pH = 4 for Cu^{2+} ions and 90% at pH = 5 for Ni^{2+}. These results confirm those obtained by Dib et al. 2008 [5];
- 98% at pH = 5 for Pb^{2+} ions; and
- 85% at pH = 6 for Zn^{2+} ions.

These pH values were chosen as the optimum studying for avoiding precipitation of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions and the true adsorption of these ions on clay could be masked and difficult to be quantified at higher pH value than 6.

3.2.2. Simultaneous effect of shaking time, acid treatment, and adsorption kinetics

The AACs with 0.05 and 0.5 M HCl have been found to possess great affinity for Zn^{2+} ions. Therefore, the AAC with both 0.05 and 0.5 M HCl were selected for further studies of the removal of heavy metal ions.

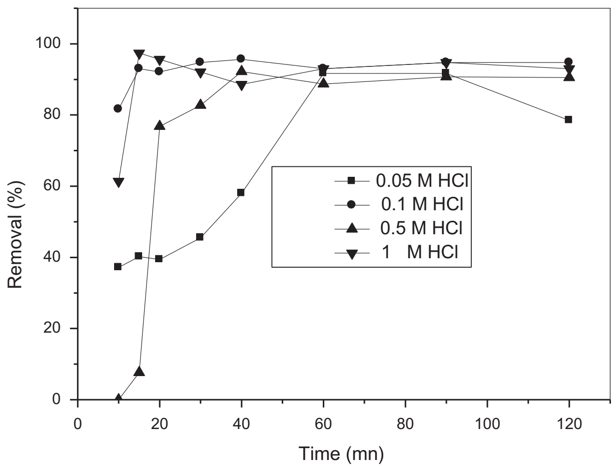


Fig. 5. Removal of Zn^{2+} onto AAC as a function of simultaneous effect of shaking time and acid treatment ($[Zn^{2+}]_i$: 10 mg L^{-1}; pH: 6; mass of AAC: 1 g; T: 25℃).

An adsorption kinetic study was carried out by adding 1 g of the AAC material to 100 mL of solution with 10 mg L^{-1} as initial concentration fixed of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions. The suspension, in different conical flasks, was then shaken at room temperature and the concentration of the supernatant of metal ions was determined.

Fig. 5 shows that the optimum removal of Zn^{2+} ions was varying between 90 and 92% within 20, 40 and 60 mn for AAC with 0.1, 1, 0.5, and 0.05 M HCl, respectively. This optimum Pb^{2+} ions adsorption % was 94% within 20 mn, for AAC with both 0.05 and 0.5 M HCl, (Fig. 6). However, the optimum metal ions adsorption (%) was: 91% for both $Cu^{2+}$and Ni^{2+}ions onto AAC with 0.05 M HCl (Fig. 7).

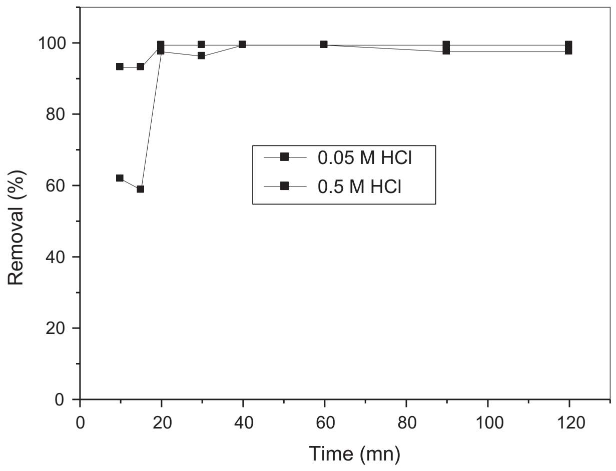


Fig. 6. Removal of Pb^{2+} onto AAC as a function of simultaneous effect of shaking time and acid treatment ($[Pb^{2+}]$i: 10 mg L^{-1}; pH: 5; mass (activated clay): 1 g; T: 25℃).

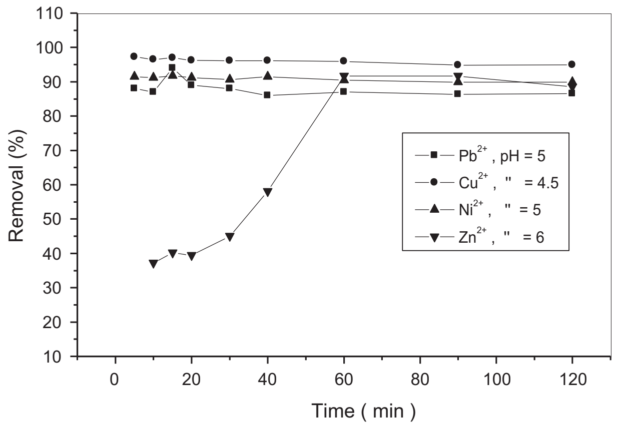


Fig. 7. Removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} onto AAC (0.05 M HCl) as a function of shaking time (initial metal concentration: 10 mg L^{-1}; mass of AAC: 1 g, T: 25℃).

For all these metal ions, their adsorption onto AAC (0.05 M HCl), Fig. 5 shows that the removal percentages were increasing with the increasing of shaking time, in the range of 5–120 min, to reach a highest value at the contact time of 15 mn, then decreasing when time exceeds 20 min to reach equilibrium within 60 min in the case of Pb^{2+} [27], (Fig. 7). Similar results were reported by [16]. However, the removal percentages of Zn^{2+} ions were gradually increasing to reach equilibrium within 60 min. In contrast, the removal percentages of $Cu^{2+}$and Ni^{2+} ions were slightly decreasing to reach equilibrium within 90 min. The metal adsorption (maximum %) was: 94% (Pb^{2+}); 96% (Cu^{2+}); 91% (Ni^{2+}); 91.7% (Zn^{2+}) (Fig. 7).

The removal percentage of metal ions was calculated as:

$$\%\text{Removal} = \frac{C_i - C_e}{C_i} \cdot 100 \tag{1}$$

where C_i and C_e are the initial and equilibrium metal ions concentrations, respectively.

The adsorption sites on the AAC are gradually covered by the metal ions and the removal rate processes become dependent on the rate of at which the metal ions are transported from the liquid phase to the sites of the AAC.

In this part of our study, the pseudo-second order equation has been only used to explain the kinetics of adsorption behavior of heavy metal ions because of its convenient aspect for the determination of the constants, in particular the quantity adsorbed (q_e).

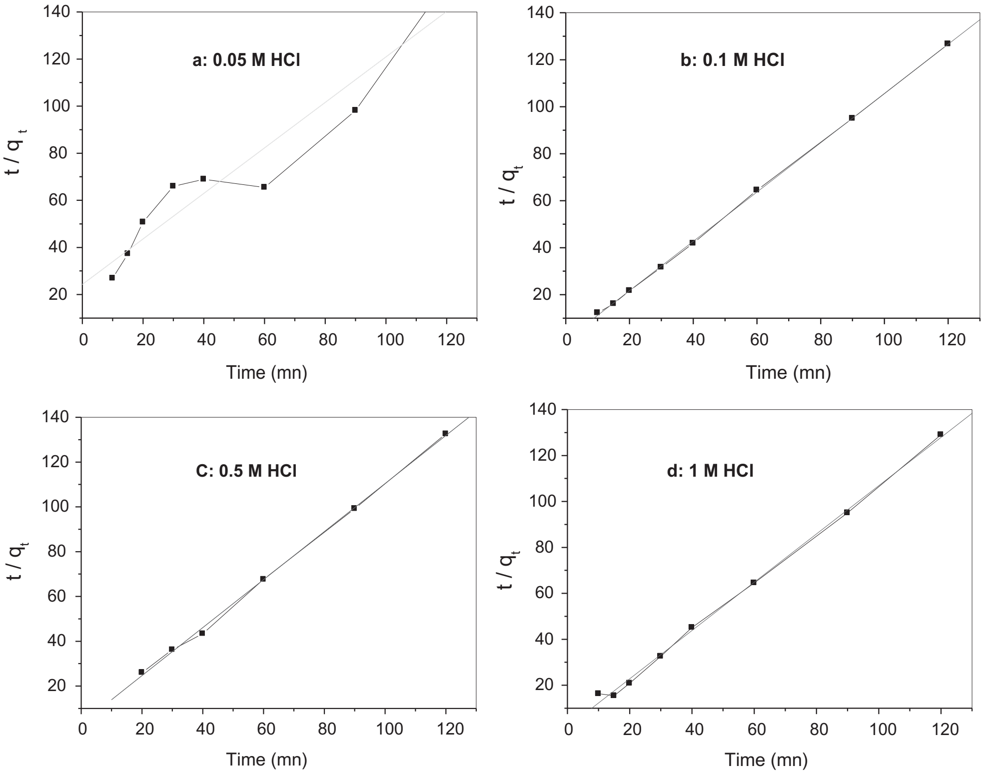


Fig. 8. (a–d): Adsorption kinetics of Zn^{2+} ions onto AAC (a: 0.05 M, b: 0.1 M, c: 0.5 M, d: 1 M HCl). ($[Zn^{2+}]_i$: 10 mg/L; pH: 6; mass of AAC: 1 g; T: 25˚C).

Pseudo-second orderequation : $\frac{t}{Q_t} = \frac{1}{K_2 \cdot Q_e^2} + \frac{t}{Q_e}$

K_2: the second-order rate constant (g/mg/mn).

Q_e: the quantity adsorbed per unit mass at equilibrium time (mg/g).

Q_t: the quantity adsorbed per unit mass at any time t (mg/g).

The pseudo-second order equation was tested by plotting t/Q_t vs. t. The plots were linear ($R^2 > 0.99$, Table 4). The results obtained from plots, gathered in Table 4, show that the model of pseudo-second order gives the agreement over the whole adsorption range for Zn^{2+} (Fig. 8(a–d)) and Pb^{2+} ions (Fig. 9(a, b)).

Table 4
Pseudo-second order kinetic parameters for the sorption of Zn^{2+} and Pb^{2+} ions onto AAC

	Q_e (mg/g)	K_2 ($g\,mg^{-1}\,mn^{-1}$)	R^2
Zn^{2+}			
AAC (0.05 M HCl)	1.04	0.04	0.920
AAC (0.1 M HCl)	0.95	1.45	0.999
AAC (0.5 M HCl)	0.93	0.36	0.998
AAC (1 M HCl)	0.95	0.83	0.997
Pb^{2+}			
AAC (0.05 M HCl)	0.977	−15.62	0.999
AAC (0.5 M HCl)	1.051	0.183	0.993

3.2.3. *Effect of mass-activated clay (0.05 M HCl)*

The AAC (0.05 M HCl) was selected for the removal of heavy metal ions and for further studies because of the economic aspect of this study. Fig. 10 (a–c) show the effect of mass of AAC (0.05 M HCl) on the removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions. As we can see, the removal (%) in the solid phase increases gradually with increase in the mass of AAC. The maximum removal was 91% (Cu^{2+}), 74% (Ni^{2+}), 99% (Pb^{2+}), and 36% (Zn^{2+}). However, the removal % is constant after the mass of clay exceeds 1 g for the tree metals ions Cu^{2+}, Pb^{2+} and Zn^{2+} and 2 g for Ni^{2+} ions. The removal percentages are in agreement with results of Dib et al. 2008 [5]. Therefore, the mass 1 g was selected, for comparison purposes, for further studies.

4. Isotherm fitting

Fig. 11(a–d) show the isotherm plots of the equilibrium concentrations of the metal ions in the solid and

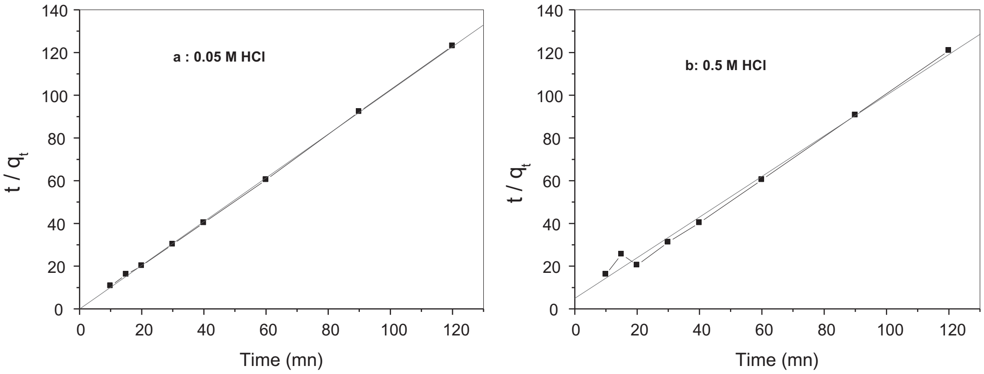


Fig. 9. (a, b): Adsorption kinetics of Pb^{2+} ions onto AAC (a: 0.05 M, b: 0.5 M HCl). ($[Pb^{2+}]_i$: 10 mg/L; pH: 5; mass of AAC: 1 g; *T*: 25°C).

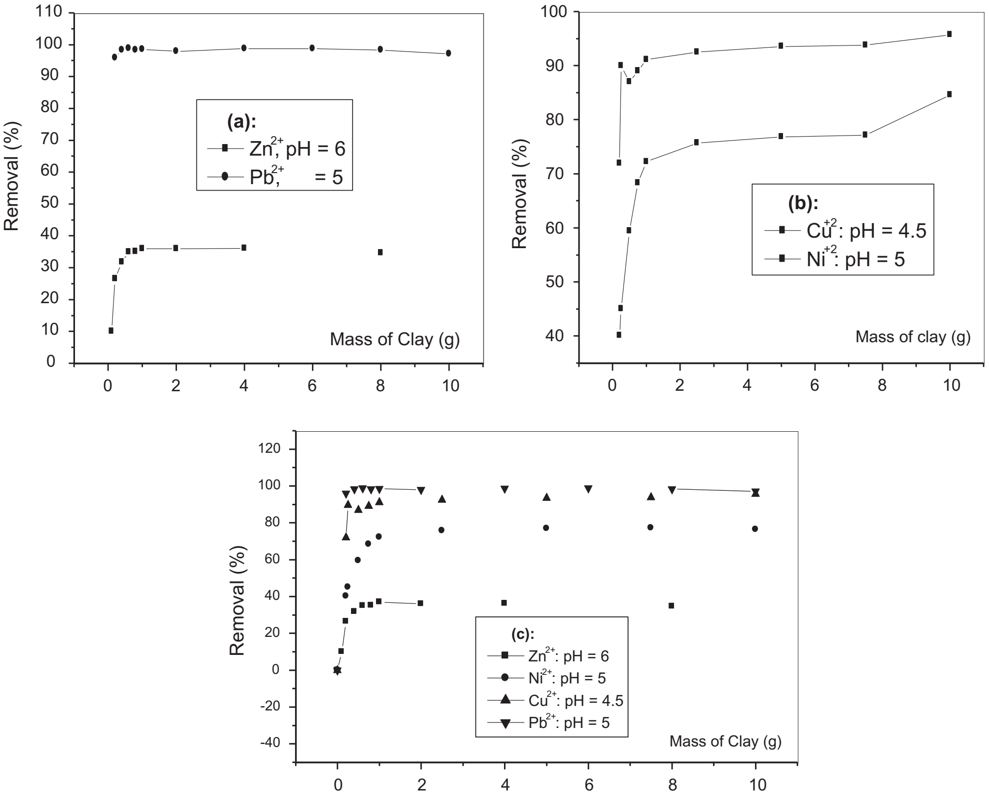


Fig. 10. (a–c): Variation in removal of Zn^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} as a function of AAC mass (0.05 M HCl) (initial metal concentration: 10 mg L^{-1}; *T*: 25°C).

the liquid phases (Q_{ads} vs. C_e). The increase in quantity adsorbed reaches a pseudo-plateau after the initial concentration exceeds 20, 30, and 40 mg/L for Pb^{2+}, Ni^{2+} and Cu^{2+} ions respectively. These isotherms are of «L» type according to the classification of Gilles [28]. However, the isotherm is of «S» type in the case of Zn^{2+} ions. The isotherm plots clearly show that clay has a good adsorption capacity.

4.1. Application: Langmuir and Freundlich models

The sorption data of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} onto AAC have been correlated with Langmuirand Freundlich models:

- For the Langmuir equation:

$$C_e/Q_{ads} = \left(\frac{1}{b} \cdot Q_{ads}\right) + \left(\frac{1}{Q_m}\right) \cdot C_e \qquad (3)$$

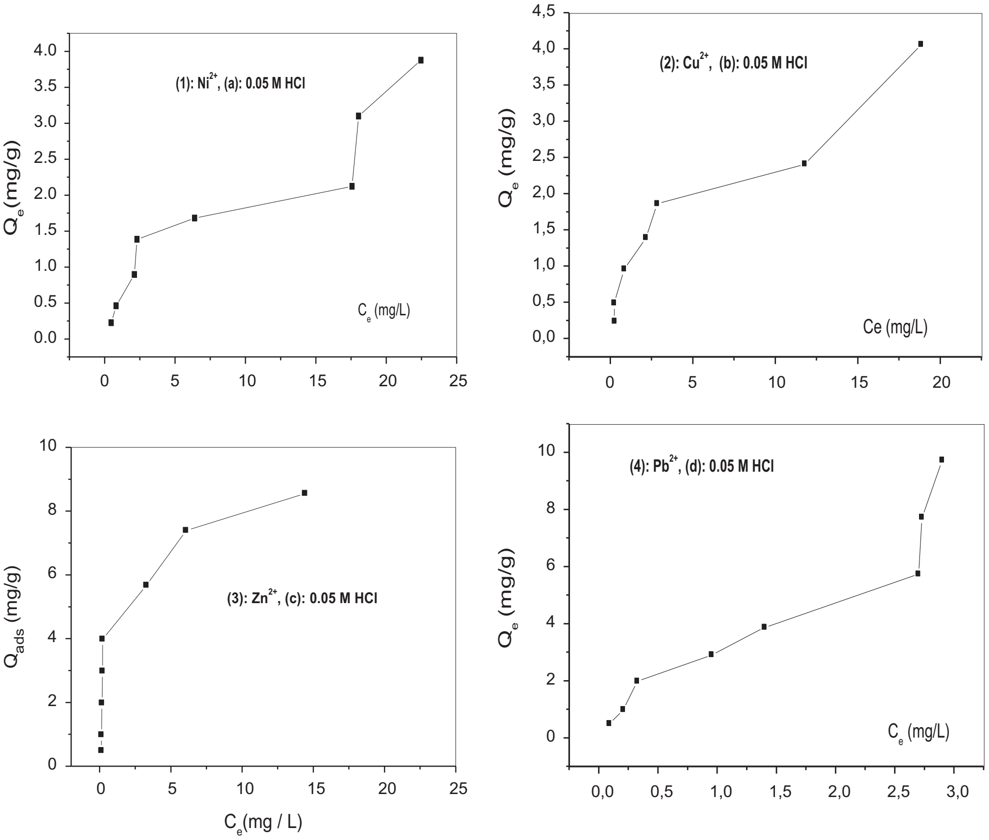


Fig. 11. (a–d): Adsorption isotherms of Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} ions onto AAC (1): Ni^{2+}, (2): Cu^{2+}, (3): Zn^{2+}, (4): Pb^{2+}, (mass of activated clay: 1 g; time: 1 h; T: 25˚C).

Q_{ads}: Quantity of the soluté adsorbed (mg/g);
Q_m: Quantité maximale nécessaire pour compléter la monocouche (mg/g);
C_e: Equilibrium concentration of the solute (mg/L); and
b: Langmuir constant (L/g).

- For the Freundlich equation:

$$\log Q_{ads} = \frac{1}{n} \log C_e + \log_F \tag{4}$$

Q_{ads}: Quantity of the soluté adsorbed (mg/g);
C_e: Equilibrium concentration of the solute (mg/L); and
K_F and n are Freundlich constants.

Regression values (R^2) presented in Table 5 indicate that the adsorption data for Zn^{2+} $Cu^{2+}$and Ni^{2+} ions removal fitted well the Langmuir isotherm for all the adsorption. The comparison of Zn^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} sorption capacities, according to the b (L/mg) parameter, sorption onto AAC 0.05 M and 0.5 M HCl is produced following the sequence: $Cu^{2+} > Zn^{2+} > Pb^{2+} > Ni^{2+}$ and $Cu^{2+} > Zn^{2+} > Pb^{2+}$, respectively. However, the Freundlich isotherm gives the best agreement for Cu^{2+} and Pb^{2+} ions removal sorption onto AAC 0.05 and 0.5 M HCl, respectively. The AACs with 0.05 and 0.5 M HCl seem to possess great affinity for Zn^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} ions.

5. The case of inorganic effluents of LRC-ONEDD, In Ben Aknoun (Alger)

For a better assessment and reliability of our experimental conditions, we applied the optimum parameters of our study for the removal of heavy metal ions by adsorption onto two different types of AACs from Mostaganem and Maghnia. The results of this application in the case of inorganic effluents (liquid) of LRC-ONEDD, In Ben Aknoun (Alger), are very eloquent and very encouraging, Table 6. The comparison of adsorption capacity of the acid-activated of Mostaganem and Maghnia clays used in this part of our work shows a better removal of Ni^{2+}, Co^{2+}, and Zn^{2+} ions sorption onto AAC from Maghnia. However, AAC from Mostaganem has good affinity towards Pb^{2+} ions. These results indicate, in comparison with those

Table 5
Langmuir and Freundlich adsorption isotherm constant values (Acid-activated clay: AAC)

	Langmuir			Freundlich		
	Q_m (mg/g)	b (L/mg)	R^2	K_F	n	R^2
Zn^{2+}						
AAC (0.05 M HCl)	8.87	1.19	0.987	4.75	0.21	0.93
AAC (0.1 M HCl)	5.0	1.90	0.99	2.48	0.41	0.84
AAC (0.5 M HCl)	3.09	3.88	0.988	2.33	0.44	0.96
AAC (1 M HCl)	7.14	0.83	0.999	3.48	0.22	0.84
Pb^{2+}						
AAC (0.05 M HCl)	9.6	0.48	0.81	2.09	0.53	0.49
AAC (0.5 M HCl)	3.13	2.32	0.87	2.28	0.37	0.96
Cu^{2+}						
AAC (0.05 M HCl)	7.01	6.41	0.90	1.16	0.48	0.97
AAC (0.5 M HCl)	10.44	9.18	0.96	3.98	0.25	0.73
Ni^{2+}						
AAC (0.05 M HCl)	0.99	0.44	0.98	0.51	0.63	0.96

Table 6
Removal of heavy metal ions by adsorption onto two different types of AAC. The case of inorganic effluents of LRC-ONEDD, In Ben Aknoun

Element	AAC: HCl (Mostaganem)		AAC: HCl (Maghnia)	
	0.05 M	0.5 M	0.05 M	0.5 M
Zn^{2+}	25	26	35	46
Pb^{2+}	68	52	–	–
Cu^{2+}	–	–	25	26
Ni^{2+}	–	–	85	90
Co^{2+}	15	13	95	98

reported in the literature [26,29–31], that the acid-activated of both Mostaganem and Maghnia clays can be used as adsorbent for heavy metals removal from wastewaters.

6. Conclusion

In this study, the removal of divalent metal ions, that is, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} from aqueous solutions onto AAC was investigated over pH range (1–7) via batch adsorption technique. The chemical activation of clay with 0.05 and 0.5 M HCl enhanced the removal efficiency of clay after acid treatment. The adsorption equilibrium was well described by Freundlich and Langmuir isotherm models. The numerical values of the removal of Ni^{2+}, Co^{2+}, Zn^{2+} ions, and Pb^{2+} ions sorption onto AAC from Maghnia and clay from Mostaganem, respectively, indicated the feasibility of the sorption process in the wastewater treatment (the Case of Inorganic Effluents of LRC-ONEDD, In Ben Aknoun).

References

[1] F. Mohammed-Azizi, S. Dib, M. Boufatit, Algerian montmorillonite clay as adsorbent for the removal of aniline from the aqueous system, Desalin. Water Treat. 30 (2011) 74–79.

[2] M. Boufatit, H. Ait-Amar, W.R. McWhinnie, Development of Algerian material montmorillonite clay. Adsorption of phenol, 2-dichlorophenol and 2, 4, 6-trichlorophenol from aqueous solutions onto montmorillonite exchanged with transition metal complexes, Desalination 206 (2007) 394–406.

[3] M. Boufatit, H. Ait-Amar, Removal of N, N-dimethylaniline from dilute aqueous solution by Na^+/K^+ saturated montmorillonite, Desalination 206 (2007) 300–310.

[4] T. Okada, T. Morita, M. Ogawa, Tris(2,2´-bipyridine)ruthenium(II)-clays as adsorbents for phenol and chlorinated phenols from aqueous solution, Appl. Clay Sci. 29 (2005) 45–53.

[5] S. Dib, A. Khouider, M. Boufatit, Removal of Cu^{2+} and Ni^{2+} from aqueous solution by Algerian clay materials, in: I. Dincer, A. Hepbasli, A. Midilli, T. Hikmet Karakoc (Eds.), Global Warming: Green Energy and Technology, Springer, New York, NY, 2010 (Chapter 43), pp. 621–628.

[6] G. Bereket, A.Z. Aroguz, M.Z. Ozel. Removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions by adsorption on bentonite, J. Colloid Interf. Sci. 187 (1997) 338–343.

[7] E.S. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (11) (1999) 2469–2479.

[8] S.S. Gupta, K.G. Bhattacharyya, Interaction of metal ions with clays: I, a case study with Pb(II), Appl. Clay Sci. 30 (2005) 199–208.

[9] O. Khazali, R. Abu-El-Halawa, K. Al-Sou'od, Removal of copper (II) from aqueous solution by Jordanian pottery materials, J. Hazard. Mater. 139(1) (2007) 67–71.

[10] K.G. Bhattacharyya, S.S. Gupta, Adsorption of Fe(III), Co(II) and Ni(II) on ZrO-kaolinite and ZrO-montmorillonite surfaces in aqueous medium, Colloids Surf., A: Physicochem. Eng. Aspects 317 (2008) 71–79.

[11] M. Boufatit, H. Ait-Amar, W.R. McWhinnie, Development of Algerian material montmorillonite clay—intercalation with selective long chain alkylammonium cations (Octadecytrimethylammonium, Cetylpyridium and Tetrabutylammonium) and with tellerium complexes, Desalination 223 (2008) 366–374.

[12] O.Y. Kwon, K.W. Park, S.Y. Jeong, Preparation of porous silica-pillared montmorillonite: Simultaneous intercalation of amine-tetraethylorthosilicate into H-montmorillonite and intra-gallery amine-catalyzed hydrolysis of tetraethylorthosilicate, Bull. Korean Chem. Soc. 22(7) (2001) 678–684.

[13] D. Pérez-Quintanilla, A. Sanchez, I. Del Hierro, M. Fajardo, I. Sierra, Preparation, characterization, and Zn^{2+} adsorption behavior of chemically modified MCM-41 with 5-mercapto-1-methyltetrazole, J. Colloid Interface Sci. 313(2) (2007) 551–562.

[14] A. Uribe, P.L. Bishop, N.G. Pinto, The influence of pH and temperature changes on the adsorption behaviour of organophilic clays used in the stabilisation/solidification of hazardous wastes, J. Environ. Eng. Sci. 1 (2002) 123–133.

[15] S. Yapar, Physicochemical study of microwave-synthesized organoclays, Colloids Surf., A: Physicochem. Eng. Aspects 345 (2009) 75–81.

[16] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, Adsorption of Pb(II) from aqueous solution to MX-80 bent: Effect of pH, ionic strength, foreign ions and temperature, Appl. Clay Sci. 41 (2008) 37–46.

[17] M.H. Al-Qunaibit, W.K. Mekhemer, A.A. Zaghloul, The adsorption of Cu(II) 152 ions onto bentonite-a kinetic study, J. Colloid Interface Sci. 283 (2005) 316–321.

[18] R. Donat, A. Akdogan, E. Erden, H. Cetisli, Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions, J. Colloid Interface Sci. 286 (2005) 43–52.

[19] Ö. Yaruza, Y. Altunkaynaklo, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37 (2003) 948–952.

[20] H. Van Olphen, An Introduction to Clay Colloid Chemistry, App. I: Preparation of Clay Suspensions, Interscience Publishers, John Wiley and Sons, New York, NY, London, 1963, pp. 239–243.

[21] Anonymous, Internal study—ENOF, Subsidiary, Algerian Bentonite Co. (Bental), (2007).

[22] R.L. Ledoux, J.L. White, Infrared study of selective deutertion of kaolinite and halloysite at room temperature, Science 145 (1964) 47–49.

[23] H. Slosiarikova, J. Bujdak, V. Hlauaty, IR spectra of octadecylammonium-montmorillonite in the range of Si–O vibrations, J. Inclusion Phenom. Mol. Recognit. Chem. 13(3) (1992) 267–272.

[24] Van der H.W. Marcel, H. Beutel Spacher, Atlas of infrared spectroscopy of clay minerals and their admixtures, Elsevier, Amsterdam, 1979, pp. 275–276.

[25] B.N. Campbell, Jr., M. McCarthy, Organic Chemistry Experiments, Brooks/Cole Publishing Co., Pacific Grove, 1994, pp. 192–196.

[26] A. Sdiri, T. Higashi, R. Chaabouni, F. Jamoussi, Competitive removal of heavy metals from aqueous solutions by montmorillonitic and calcareous clays, Water Air Soil Pollut. 223 (2012) 1191–1204.

[27] S. Dib, M. Boufatit, Equilibrium study of adsorption of Pb^{2+} from aqueous solution onto Algerian bentonite clay, Desalin. Water Treat. 5 (2009) 106–110.

[28] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, Studies in adsorption: 11. A systematic classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and measurements of specific surface areas of solids, J. Chem. Soc. 111 (1960) 3973–3993.

[29] A. Sdiri, T. Higashi, F. Jamoussi, S. Bouaziz, Effects of impurities on the removal of heavy metals by natural limestones in aqueous systems, J. Environ. Manage. 93 (2012) 245–253.

[30] A. Sdiri, T. Higashi, T. Hattab, F. Jamoussic, N. Tasea, Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems, Chem. Eng. J. 172 (2011) 37–46.

[31] A. Mellah, S. Chegrouche, The removal of zinc from aqueous solutions by natural bentonite, Water Res. 31(3) (1997) 621–629.