Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3325-3339

Removal of Lead, Zinc and Nickel Using Sodium Bentonite Activated Clay

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Bentonite collected from Zaghouan (Middle East Tunisia) was reacted with boiling 3M HCl solution at 0.5, 2, 4 and during 6 h. The structural change was studied, cation exchange capacity (CEC) decreased with the increase of the time treatment while specific surface area increase and it's maximum value was attained by the sample treated at 4 h. The chemical and structural characteristics of the purified natural and modified clays were determined. The amount of iron, aluminum and magnesium compounds decreased in the modified clay. Use of purified and modified bentonite clay by HCl (3M) for the removal of some heavy metals (Zn, Pb, Ni) from aqueous solutions has been investigated. They are the most impurities of industrials effluents. The uptake capacity of the modified clay for nickel, zinc and lead did significantly decrease with increase of the time treatment. The sorption process is reflected by Langmuir and Freundlich-type isotherm. The order of the removal capacity is $Pb^{2+} > Zn^{2+} > Ni^{2+}$ for both natural and treated sorbents. Equilibrium modeling of the adsorption showed that the adsorption of these three metals was fitted to a Freundlich isotherm in all cases.

Key Words: Clay, Acid activation, Heavy metals, Adsorption isotherms, Langmuir model, Freundlich model.

INTRODUCTION

The contamination of soils and surface and ground water with non-volatile organic pollutants and heavy metals creates physiological hazards to ecosystems and humans. Owing to their extensive use, these compounds readily enter ecosystems, *e.g.*, by industrial effluents and municipal waste water, by leachates emerging from waste deposits, or by agricultural run-off of pesticides. Many of these substances can be detected in surface and ground water. These compounds may be hazardous to plants, animals and humans for long durations. Pollution caused by heavy metals is serious and complex since they can bioaccumulate to higher levels in biota and being poisonous. These waste need treatment system that can remove contaminants effectively.

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Because clay minerals strongly influence the migration, immobilization and chemical transformation of heavy metals, clay-mineral interaction with metal pollutants has been studied intensely.

Clay minerals are known with a wide variety of cations and organic molecules by adsorption, interaction and cation exchange capacity. These mineral may serve as a cost-effective sorbents for the removal of heavy metals. Their sorptions capacities are usually less than those of synthetic sorbents, these materials could provide an inexpensive substitute for the treatment of heavy metal for wastewaters. To, enhance the sorption capacity, the clays are modified in various ways, such as treatment by inorganic and organic compounds, acids and bases. For example, montmorillonite, coated and intercalated by aluminum hydroxide exhibits much higher adsorption capacity for some heavy metal ions, than that of natural montmorillonite[1]. Treatment of zeolites by NaCl solution convert them into a near homoionic state in Na form, and improves the exchange capacity for lead and zinc ions[2]. Adsorption capacity of clay minerals can also be enhanced by replacing the natural exchangeable cations with organic cations, which makes the clay surface more hydrophobic[3,4]. Recently, the substitution of these materials by low cost natural clays (*e.g.,* montmorillonite) was of increasing interest. This is mainly due to their chemical instability in acidic media which generally cause pronounced dealumination and subsquantent crystallinity loss.

The acidic treatment of clay materials has been well known for many years[5,6]. This process leads to almost full removal of calcium, magnesium, and alkali metal oxides and partially diminishes the iron and aluminum content of clay minerals.

The purpose of this present work is to study the ability of both Na-bentonite and acid activated bentonite to remove Zn^{2+}, Ni^{2+} and Pb^{2+} from aqueous metals solution at room temperature (24°C) under various experimental conditions.

All the experiments were conducted at pH 5, since industrial effluents have acidic media, which generally cause pronounced dealumination and subsquantent crytallinity loss of clay due to their chemical instability in acidic media. In other hand clay mineral exhibits much higher adsorption capacity for some heavy metal ions at pH 5 than that of other value[7], thus the effect of acidic media in the chemical structure of Zaghouan bentonite and its adsorption behaviour for the removal of heavy metal are investigated. The parameters studied were initial cation concentrations and final pH value of mixture solutions (clay-aqueous metal solution).

EXPERIMENTAL

A natural bentonite at the Ca exchange form collected from Zaghouan. This clay was used as the raw material. The fraction < 2 µm was separated by sedimentation. The < 2 µm fraction was purified by classic methods[8], transformed into the sodium form with 1 M NaCl solution. After washing, sedimentation and dialysis, the fine sediment was freeze-dried at 60°C.

X-ray patterns were obtained from the purified and treated samples using a Philips PW 1730/10 With Cu-K_α radiation. IR spectroscopy of samples, purified and treated with 3 M HCl, KBr mixtures (100 mg / 1 mg samples) were measured between 4000 to 400 cm^{-1} (Perkin Elmer 1000 spectrometer). Thermals analyses of purified and treated samples have been realized using setaram 92 TG-DTA thermobalance with 283 K min^{-1} heating rate in argon atmosphere.

The amounts of extracted elements (iron, magnesium, aluminum) were determined by atomic adsorption spectroscopy. The total specific surface area S_t and extern surface S_{ext} of the samples were determined with methylene blue isotherms, cation exchange capacity (CEC) of these samples was determined by three ways: Kjeldhal[9], Mantin[10] and methylene blue (BM) adsorption isotherm methods.

Acid activation: 10 g of purified clay were treated with 100 mL of 3 M HCl solution. The mixture was boiled in a round-bottom flask with a reflux condenser during 0.5, 2, 4 and 6 h. After these treatments, the resulting samples were washed with hot distilled water until no chloride anions could be detected and then sample was dried up at 60°C. The product is denoted ZG2p before activation and ZG2p 0.5 h, ZG2p 2 h, ZG2p 4 h and ZG2p 6 h where 0.5, 2, 4 and 6 h refer to times hours treatment. The extractable cation, iron, magnesium and aluminum where determined by analysis of the extracted solution using atomic adsorption spectroscopy type AAS varrio6 (Analytic Jena).

Sorption experimental: Nickel, zinc and lead were the metals examined in this study, since they are most common heavy metals in the waste water. The stock solutions of zinc, nickel and lead were prepared by dissolving $Pb(NO)_3$, $ZnSO_4 \cdot 7H_2O$ and $NiCl_2 \cdot 6H_2O$ in distilled water in the desired initial concentration, 5×10^{-3} M which is five time equal the cation exchange capacity of the clay fraction, at pH 5 and at room temperature, working solution imitating waste water. The pH was adjusted either with diluted HCl or NaOH solutions.

The equilibrium adsorption isotherms are essential in determining the adsorption capacity of: purified Na-exchange bentonite and treated bentonite with HCl (3 M) at different time, for zinc, nickel and lead fixed.

The equilibrium adsorption isotherms were obtained by mixing 50 mL of aqueous metal solution with 100 mg of sample, the mixture was shaking on a reciprocating shaker operated at room temperature 24°C for 1 h. Previous time-course studies indicated that this length of time was adequate for the solution to achieve equilibrium stage. Following 1 h reaction period on the mini shaker, the samples were taking out, centrifuged to separate the solid. Then pH of each supernatant was measured. The residual Zn^{2+}, Ni^{2+} and Pb^{2+} concentration remaining in solution was measured by atomic adsorption spectroscopy and the amount it adsorbed was determined. By plotting this amount (Q_{ads}) as a function of the equilibrium concentration of required metal (C_{eq}), the isotherm of each sample was obtained.

RESULTS AND DISCUSSION

The sample contains about 67 % smectite, 26 % illite, quartz and carbonate appropriate as impurity (Fig. 1) eliminated after purification and Na-exchange.

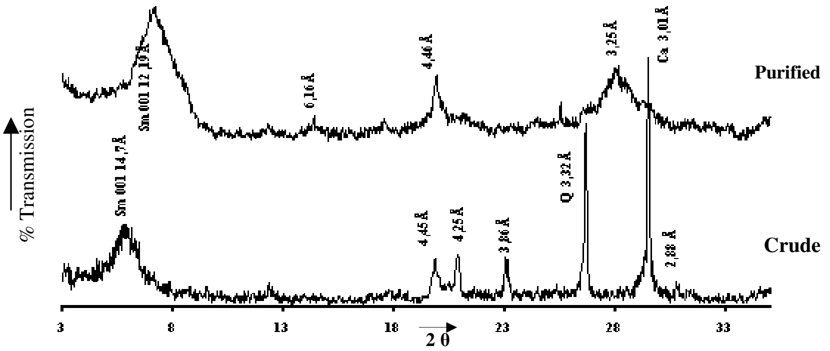

Fig. 1. X-ray diffractograms of raw and purified clay

The structural formula of Zaghouan collected clay, $(Si_{7.56}\,Al_{0.44})\,(Al_{2.933}\,Fe_{0.678}\,Mg_{0.476})\,Ca_{0.043}Na_{0.404}K_{0.16}\,O_{22}$, was determined via chemical analysis of purified sample (w %) using Mauguin's method[11].

The chemical analysis of purified sample was (w %):

SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO	(H_2O)
50.8	17.4	6	3.95	1.39	0.84	0.28	20.31

The cation exchange capacity of the purified sample (interstratified illite-smectite) calcined at 1000°C was 89 meq/100g; the specific surface area is estimated at 504 $m^2\,g^{-1}$.

Chemical and structure changes after acid activation: Table-1 shows the amount of iron, magnesium and aluminum, expressed in percentage in oxide form. The percentage of these metal cations decrease with time treatment indicate the destruction of the octahedral sheets. It is observed that quantity of magnesium removed is larger than that of iron or aluminum it reach 90 % after 6 h acid treatment.

TABLE-1
ALUMINUM, IRON AND MAGNESIUM EXTRACTED FROM THE CLAY AFTER ACID ACTIVATION (w %)

Extractable metal (w %)	Time (h)				
	0.0	0.5	2.0	4.0	6.0
Al_2O_3	0	44	59	69	82
Fe_2O_3	0	55	75	83	85
MgO	0	75	83	89	90

X-ray diffractgrams: The X-ray diffractgrams of the purified sample and of the series treated with 3 M HCl are presented in Fig. 2. When the time of the treatment increase, the crystallinity of the sample decreases. The (hk0) reflection intensities clearly decrease without changing the position. The (001) reflection, corresponding to the basal spacing decrease rapidly with changing position (12 to 13.95 Å), indication the transformation of Na saturated clay to Al (or Fe) exchanged clay and became broader as the time of activation increase indication a grown delamination of the original particles.

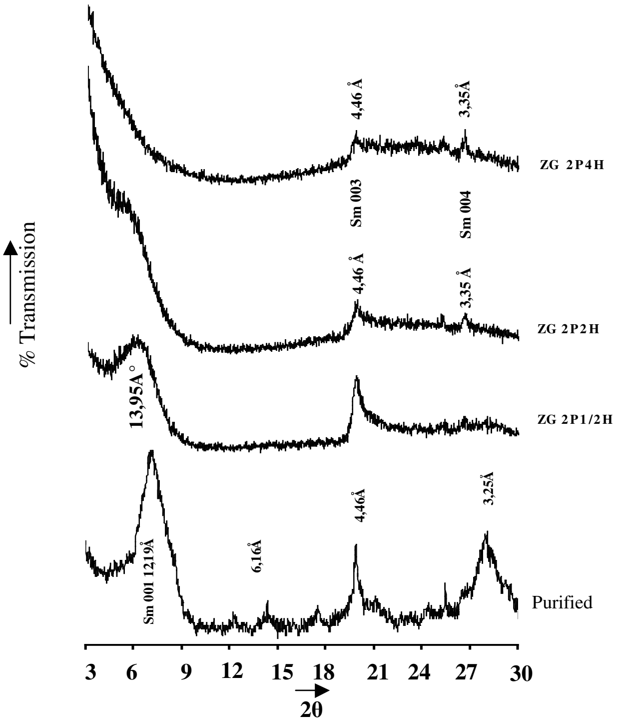

Fig. 2. X-ray diffractograms of purified and activated samples (HCl 3 M)

Infrared spectra: The infrared spectra of the untreated and HCl-treated material are given in Fig. 3. Before acid activation the stretching vibration of OH appears at around 3430 cm^{-1}. The silicate network is characterized by streaching vibration bands at 1030 cm^{-1} for SiO and deformation bands at 420 cm^{-1} for Si-O-Fe, at 520 cm^{-1} for Si-O-Al. After acid treatment the most significant change was the shift in the SiO streaching region. The intensity of the SiO vibration band of amorphous SiO_2, near 1110 cm^{-1}, increase during the course of acid dissolution. The increased intensity of the band at 780 cm^{-1} attribute to the SiO vibration of amorphous silica[12] indicates an increased amount of amorphous silica as acid dissolution progress so deterioration of tetrahedral layer. This treatment leaves material rich in amorphous silica.

The intensity of stretching and bending bands characterized of octahedral sheet for Al-Al-OH at 915 and 3626 cm^{-1}, for Fe-Al-OH at 866 cm^{-1} and Mg-Al-OH at 830 cm^{-1} decrease then disappear with increase of time acid activated, indicate the destruction of the octahedral layer.

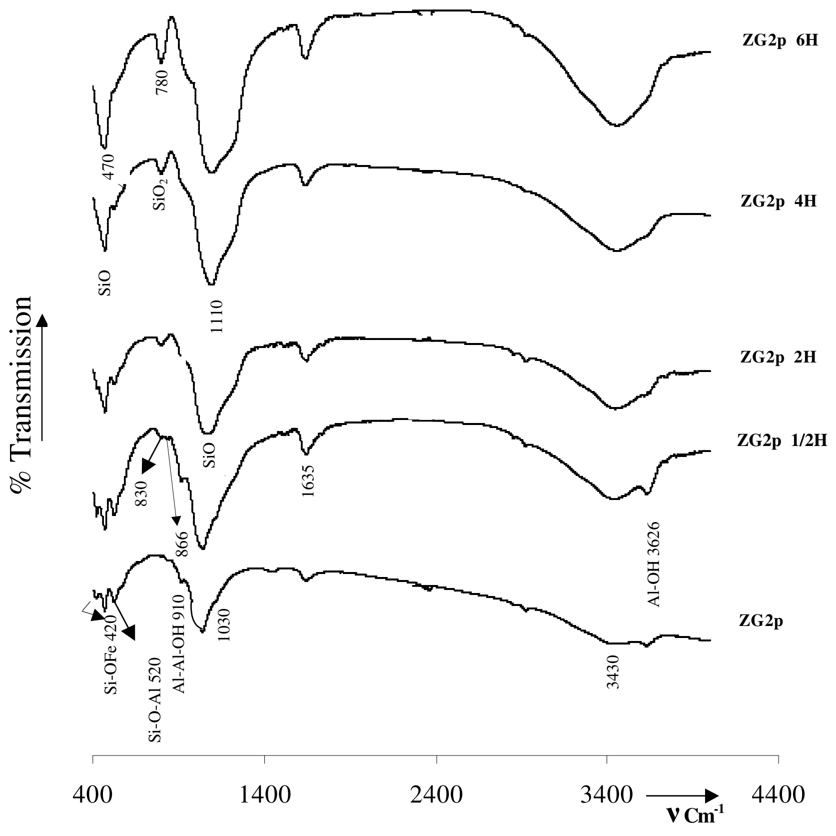

Fig. 3. Infrared spectra of purified and activated samples (HCl 3 M)

Rate of octahedral and interlayer destruction: The rate of octahedral and interlayer destruction studied show (Fig. 4) that the destruction increase with progress of time dissolution, it exceed 50 % with no appearance of stairs indicating that the number of actives sites increase and the sample became rich in amorphous silicate[13,14].

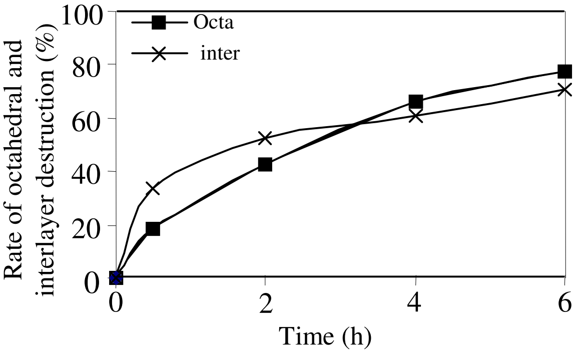

Fig. 4. Rate of octahedral and interlayer destruction with progress of time dissolution (%)

Cation exchange capacity, total and external surface area

Cation exchange capacity (CEC) of untreated and treated samples was measured and the results (Table-2) show that CEC decrease with progress of time dissolution.

TABLE-2
CATION EXCHANGE CAPACITY OF PURE AND ACTIVE SAMPLE WITH HCl (3 M)

Samples	Time (h)	CEC with BM method		CEC with Mantin method	CEC with Kjeldhal method	CEC_m
		Normal sample (not heated)	Sample heated at (873 K)			
ZG_2p	0.0	67	5.30	71	75	71
ZG_2p	0.5	43	10.68	42	50	45
treated	2.0	25	22.23	26	28	27
with HCl	4.0	18	24.03	19	22	20
(3 M)	6.0	11	8.01	12	15	13

$CEC_m = ((CEC)_{kjeldhal} + (CEC)_{Mantin} + (CEC)_{BM})/3$

Total and external surface area: From the methylene blue adsorption isotherms of purified clay and purified acid activated clay (HCl 3 M) heated at 600°C for 24 h, total and external surface area of these samples had been measured (Fig. 5). The results show that total surfaces decrease with increasing of time acid activated whereas external surface area increase and reach the optimal value 195.29 after 4 h of acid treatment then decrease.

Thermal analysis: DTA and TGA curves (Fig. 6), allow other interesting complimentary informations about acid treatment.

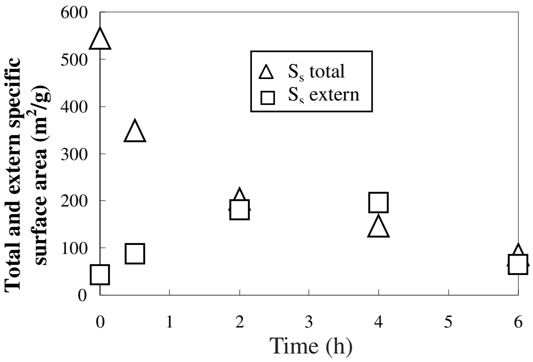

Fig. 5. Estimation of total and external specific surface area of purified and treated samples

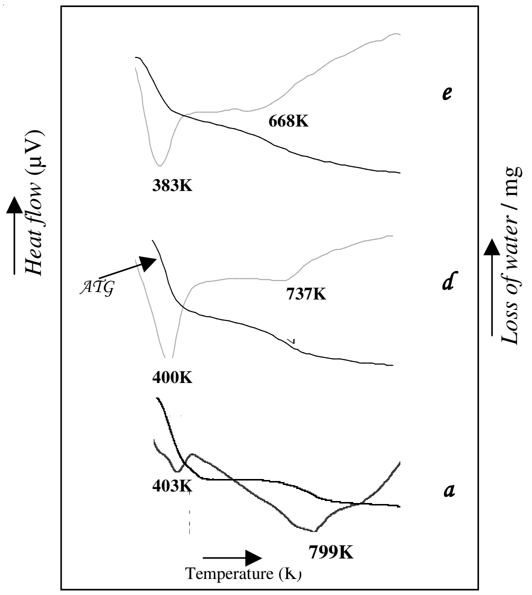

Fig. 6. DTA-TGA curves of pure and treated sample with HCl 3 M
a: Purified sample, d: sample treated 0.5 h, e: sample treated for 4 h

The result shows that relative peak of water constituent loss decrease with increase of progress of time dissolution. Dehydroxylation was executed with more and more favourable temperature; it goes from 799 K to 668 K. We have accordingly estimated the percentage of water constitution after acid treatment (Table-3) consequently the rate of water constitution loss (Fig. 7), result show that this percentage increase with time acid activation.

TABLE-3
PERCENTAGE OF WATER CONSTITUTION
AFTER ACID TREATMENT

Time treatment (h)	0.0	0.5	4.0
ZG_2p treated with HCl (3 M)	4.84	2.60	1.89

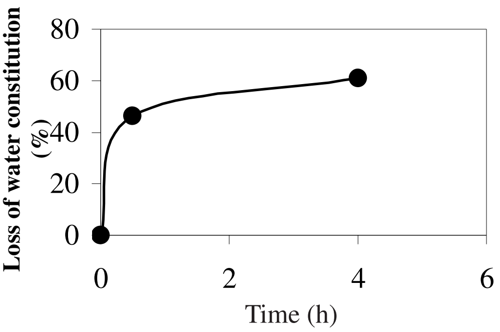

Fig. 7. Percentage of waters constitution loss

Sorption isotherms

The pH in the equilibrium solution, increases by *ca.* 1 to 2 unit which is due to the retention of H^+ by clay fraction. This progress may cause the complexation or precipitation of metal.

The equilibrium adsorption isotherms of purified and modified clay (Figs. 8 and 9), show that the adsorption capacity increases as a function of metal concentration and decreases while time acid activation increase.

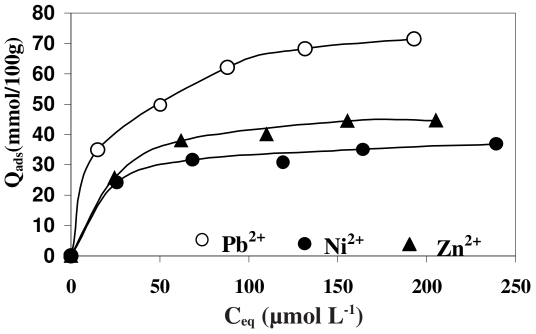

Fig. 8. Adsorption isotherms of Pb^{2+}, Zn^{2+} and Ni^{2+} by purified sample (ZG2p)

This investigation show generally better sorption of lead than nickel and zinc. The retention amount of lead sorption remained higher than the cation exchange capacity of clay fraction and also higher then the amount of retained zinc and nickel. According to pH diagram[15], lead retention onto clay fraction might be supplemented by the sorption of $Pb(OH)^+$. Within the range of pH 6-7 significant amount of species such as $Pb(OH)^+$ may be present in solution, while zinc and nickel had been adsorbed in bivalent form.

Compared with the treated clay, Na-bentonite is a good adsorbent for nickel(II) without the need of any chemical treatment, while the amount of zinc and lead fixed fitted satisfactory with the uptake capacity when the samples used were Na-bentonite and sample treated 0.5 h with acid, for the other times treatment the retention amount of these toxic metals didn't fit with the uptake capacity. So making this clay in contact with industrial effluent to retain the maximum amount of heavy metal shouldn't exceed 0.5 h, because of its chemical instability in acid media witch destroy its adsorption capacity.

Finally metal sorbed onto Zaghouan clay varied in the following order $Pb^{2+} > Zn^{2+} > Ni^{2+}$ for both natural and treated sorbents.

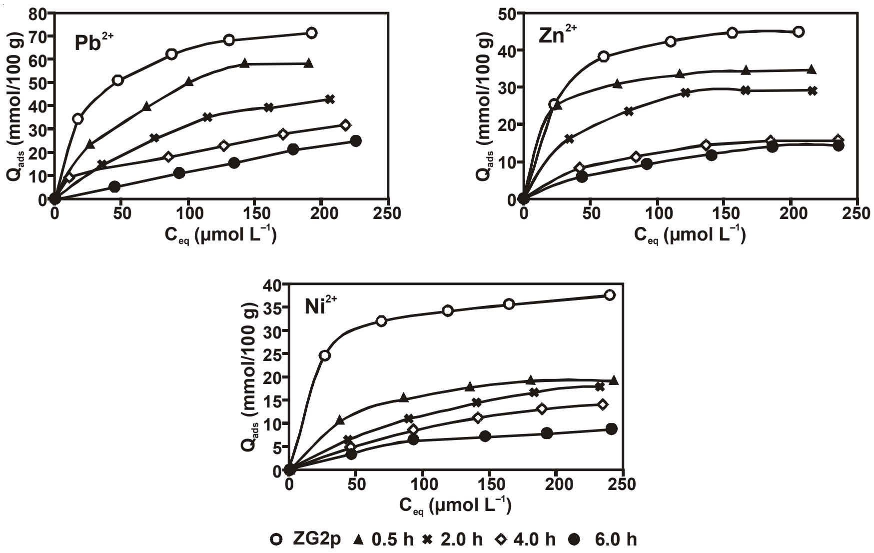

Fig. 9. Adsorption isotherms of Pb^{2+}, Zn^{2+} and Ni^{2+} by acid activated samples

In order to judge the exchange properties of the clay samples to retain metal, the cation exchange capacity values of various pretreated samples, the maximum amount of metal retained and the value of external surface of each sample determined *via* BM isotherms were presented in Fig. 10. From these curves, it is clear that the amount of metal retained by samples decrease with the reduce of cation exchange capacity while the value of external surface increase, which prove that exchange cation phenomena dominate surface adsorption phenomena.

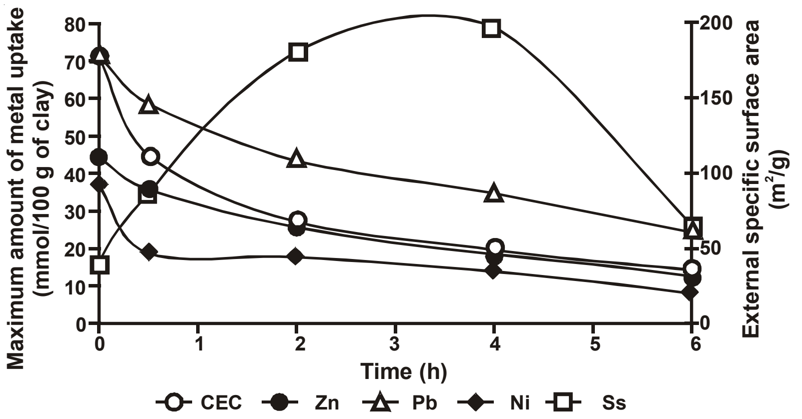

Fig. 10. Domination of exchange phenomena inside retention of metal by clay

Modelling: The adsorption of these toxic heavy metals (lead, zinc and nickel) had been modeled with the aid of Langmuir and Freundlich model, where their linear form were represented respectively by : $C/x/m = 1/a + b/aC$, $x/m = kC^n$ where C is the equilibrium concentration of solute ($g\ L^{-1}$), x/m is the amount of solute adsorbed per unit weight of adsorbent ($g\ g^{-1}$ of clay), a and b were the sorption constant of Langmuir equation, k and n the sorption constant of Freundlich equation[16].

Typical adsorption isotherms for Pb(II), Zn(II) and Ni(II) are presented in Figs. 11 and 12, respectively for Langmuir and Freundlich model. The Langmuir and Freundlich parameters and correlation coefficients relating to the capacity of adsorption were calculated (Table-4) from the linearized Langmuir and Freundlich equations. As seen from the Figs. and Table-4, the experimental data of the adsorption of these three metals fit with both

TABLE-4
LANGMUIR AND FREUNDLICH CONSTANTS OF Pb^{2+}, Ni^{2+} AND Zn^{2+} IONS

Cations	Langmuir parameters														
	Pb^{2+}					Zn^{2+}					Ni^{2+}				
t_{ac} (h)	0.0	0.5	2.0	4.0	6.0	0.0	0.5	2.0	4.0	6.0	0.0	0.5	2.0	4.0	6.0
a ($L\ g^{-1}$)	31.84	11.36	5.00	2.5	*	23.5	17.4	8.32	2.0	*	23.25	5.00	1.78	1.6	1.33
b ($L\ g^{-1}$)	371.00	126	60.00	32	*	757	679	334	120	*	1050	395	107	132	208
R^2	0.99	0.98	0.97	0.97	*	0.99	0.99	0.99	0.95	*	0.99	0.99	0.94	0.98	0.94
	Freundlich parameters														
k	0.25	0.54	0.64	0.76	1.50	0.07	0.05	0.09	0.06	0.30	0.05	0.04	0.14	0.10	0.05
n	0.30	0.53	0.67	0.60	1.00	0.24	0.17	0.36	0.42	0.81	0.18	0.03	0.06	0.57	0.54
R^2	0.98	0.96	0.97	0.99	0.99	0.83	0.99	0.92	0.94	0.94	0.92	0.96	0.95	0.98	0.93

t_{ac}: time acid treatment; *: no interesting result.

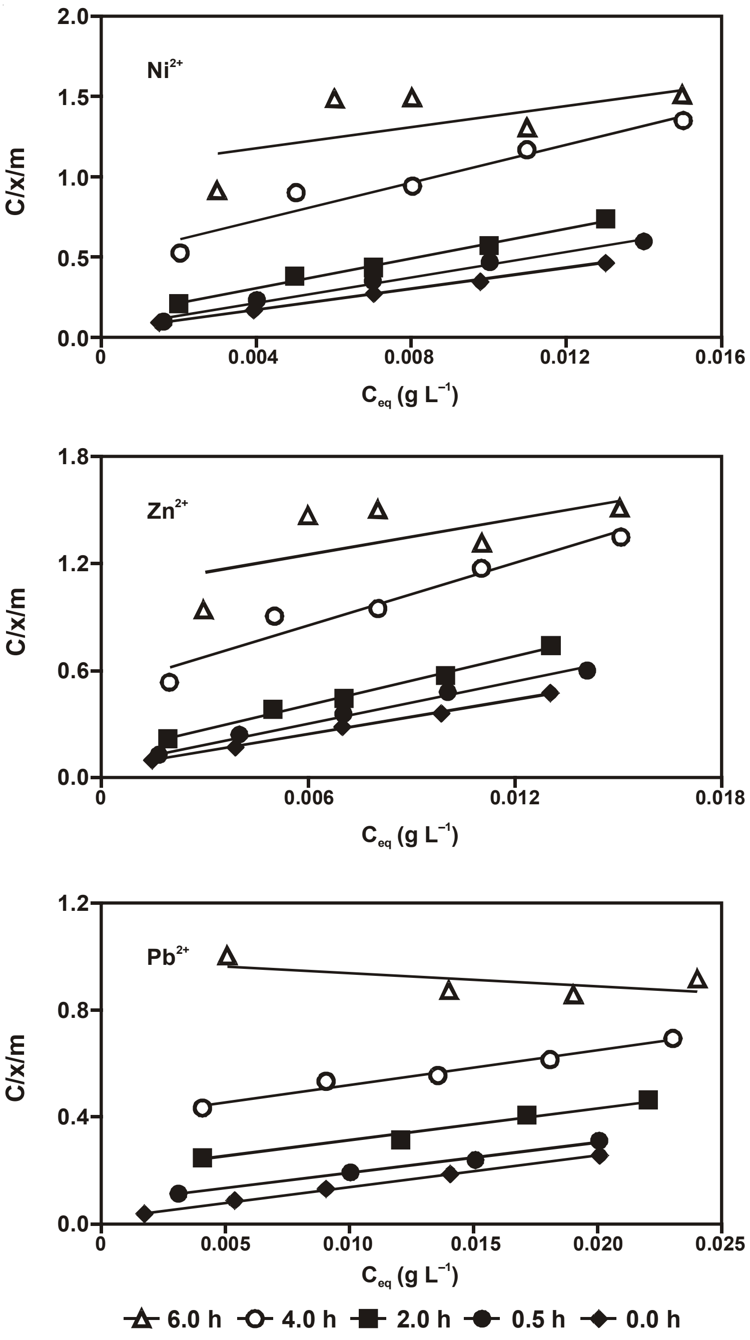

Fig. 11. Adsorption isotherms of Pb, Zn and Ni by purified and acid activated samples (HCl 3 M); Langmuir model

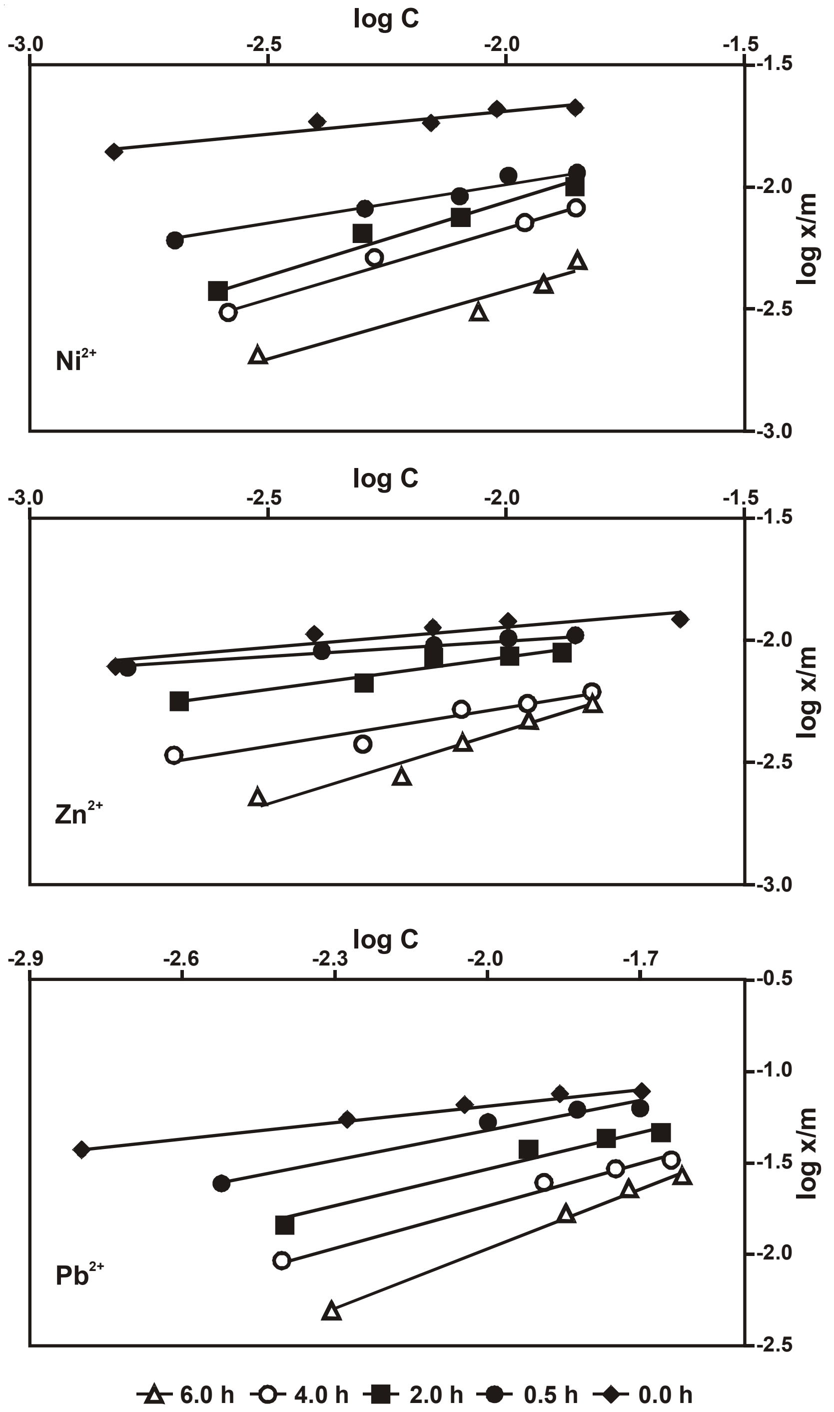

Fig. 12. Adsorption isotherms of Pb, Zn and Ni by purified and acid activated samples (HCl 3 M); Freundlich model

models in all cases. Only for Pb and Zn adsorption with ZG_2p 6 h, correlations coefficients from their linearzed Langmuir equation were low indicated that data experimental adsorption for this two metals didn't fit to a linear form of the Langmuir equation.

Conclusion

The clay fraction used in this work was an interstratified illit-smectite with 89 meq/100 g cation exchange capacity of calcined clay and 504 m^2 g^{-1} specific surface area, which is used in the purified and modified form, to test its proprieties of sorption for the removal of some toxic metals (Zn, Pb, Ni) from aqueous solutions.

The uptake capacity of the modified clay for nickel, zinc and lead significantly decrease with increase of the time treatment. Pure sample and sample treated during 0.5 h with acid seems to be a good sorbent for these metals, without the need for any other chemical treatment, since the amount of metal adsorbed corresponding to the value of cation exchange capacity. So making this clay in contact with industrial effluent to exchange most of metal ions shouldn't exceed 0.5 h, because of its chemical instability in acid media which destroy its adsorption capacity.

The order of the removal capacity is $Pb^{2+} > Zn^{2+} > Ni^{2+}$ for both natural and treated sorbents.

The sorption process is reflected by Langmuir and Freundlich-type isotherm. Correlation coefficients related with Langmuir and Freundlich equations, are higher for both adsorption equations, which reflect that these models fit. Only for same cases Langmuir model didn't fit, especially for lead and zinc adsorption with sample 60 h acid treatment.

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(*Received*: 1 January 2005; *Accepted*: 12 February 2007) AJC-5409