Single and simultaneous adsorption of heavy metal ions from aqueous solution onto ammonium activated clay.

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Abstract: *Sorption of two divalent metal ions (zinc Zn(II) and lead Pb(II)) from aqueous solution onto the ammonium activated clay was studied in single and binary component systems. The effects of initial pH, contact time, adsorbent dose and initial metal concentration on the adsorption process were investigated. Experimental data were analyzed using Langmuir and Freundlich adsorption models. The maximum percent removal of the metal ions was 99% for Pb(II) and 66% for Zn(II) at adsorbent dosage of 4g/l. At optimum pH of 5, the maximum adsorption capacities of the ammonium activated clay in the single adsorption system were 25 and 16.95 mg g^{-1} for Pb(II) and Zn(II), respectively. However, in the binary adsorption system, the maximum adsorption capacities were 17.24 mg g^{-1} for Pb(II) and 9.35 mg g^{-1} for Zn(II). The ammonium activated clay showed high selectivity and interference resistance from coexisting ions for the adsorption of Pb(II). The experimental data obtained for both metals were best described by the Langmuir model while the kinetic studies showed that the adsorption process followed a pseudo second-order rate model.*

Keywords: *Ammonium activated clay, Heavy metals, Adsorption, Kinetics, Thermodynamic.*

I. Introduction

The enormous population growth in the world along with the accelerated urbanization and high development of the industrial and agricultural activities [1] resulted in an increase of the discharges containing various pollutants, such as heavy metals which have particular chemical properties that give these chemical elements a toxicity making of them a permanent risk for human health and a source of pollution for the environment [2,3,4].

Currently, pollution by heavy metals contained in the liquid sewages of industries has become more and more serious and therefore constitutes a threat to human health and wellbeing. Lead and zinc are transferred in soils via the atmospheric dismissals of some industrial processes, mining operations, battery manufacturing, paints and pigments, alloys and steels [5,6], agricultural fertilizers [1] as well as industrial wastewaters [4,5]. Due to their non biodegradability, a fraction of these metals migrates toward the groundwater and surface water sources.

The presence of heavy metals in the drinking water and in the food chain causes a lot of problems to human health. Long term exposure to these pollutants is known to cause cancer, renal dysfunction, bone lesions, hypertension, muscular cramps and lung insufficiency [2,5,7].

To remove heavy metals from wastewater, several technologies including reverse osmosis, membrane filtration, chemical precipitation, ion exchange and electrochemical methods have been developed [2,8,9]. Nevertheless, most of these conventional methods have limitations and are less effective and more expensive in the treatment of high volumes and low metal concentrations [2].

Adsorption is one of the most important processes that have been used to remove heavy metals from wastewater due to its suppleness [3,6]. Natural Clays, which are available in large quantities and at low price, have been widely used to remove heavy metals from wastewater owing to their high specific surface areas, high cation exchange capacity, mechanical and chemical stability and porous structure [3,10].

Single and multi-component adsorption of heavy metals on natural and activated clays(using HCl, HNO$_3$ and H$_2$SO$_4$) has been extensively investigated in the last 10 years[11,12,13,14,15]. However, the use of ammonium chloride activated clay in binary adsorption has not received much attention yet. Because of the need for low cost and abundant adsorbents to remove heavy metals and other containments from wastewater and surface waters; an activated clay with ammonium chloride was prepared under optimum conditions using a central composite orthogonal design (CCOD) of Response Surface Methodology (RSM) [16].

The objective of this work was to evaluate the potential of ammonium activated clay, prepared under the optimum activation conditions, for the single and simultaneous adsorption of lead and zinc ions from aqueous

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solution. The influence of four relevant factors on adsorption such as initial pH, adsorbent content, initial metal concentration, contact time and temperature were investigated.

II. Material And Methods

II.1. Reagents and equipment

All heavy metal solutions used in this study were prepared from Aldrich atomic absorption spectroscopy reference solutions of 1000 mg/l. These reference solutions contain a metal ion (lead or zinc) dissolved in 5% nitric acid solvent. Working solutions were prepared by diluting the stock reference solutions with bi-distilled water. pH was measured by a Sartorious pH meter. A spectrophotometer of flame atomic absorption (VARIAN SpectrAA 880) was used to determine metal concentration in the solution before and after adsorption on activated clay. The spectrophotometer was calibrated beforehand from a set of solutions of known concentrations.

II.2. Clay characterization

Phillips PW 3710 powder diffractometer with an Ni filter and Cu Kα radiation (40kV, 30 mA, λ= 0.15418 nm) was used to carry out the x-ray diffraction (XRD) patterns of the activated clay. Fourier Transform Infra Red (FTIR) spectroscopy was used to assess the interactions between the adsorbent and the adsorbate.

II.3. Activated clay preparation

In the present work ammonium activated clay, prepared at optimum conditions for maximum specific surface area [16], was used to study the behavior of single and simultaneous adsorption of lead and zinc ions from aqueous solution in terms of thermodynamics and kinetics.

II.4. Batch sorption experiments

In order to understand the influence of the nature of the solution on the adsorption process of lead and zinc, different experiments were conducted. We studied the influence of pH, contact time, initial concentration of the solution and the mass of adsorbent on the removal of lead and zinc.

All adsorption experiments were carried out at ambient temperature 25±2°C by inserting a certain amount of adsorbent into a 250 ml conical flask containing 100 ml of heavy metal solution (lead and/or zinc) in the desired initial concentration. The initial solution pH was adjusted before the addition of the adsorbent by adding the required amounts of 0.5 M H_2SO_4 and 0.5M NaOH solutions. The mixture was shaken for the desired contact time at 300 rpm. When the adsorption was accomplished, the suspension was then centrifuged at 3000 rpm for 10 min and filtered through 0.45 μm filters. The obtained filtrate was analyzed for residual heavy metal concentration using a flame atomic absorption spectrometer.
The percent metal removal (R) was determined as follows:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

Where C_0 and C_e (mg L^{-1}) are respectively the initial and equilibrium heavy metal concentration.
The adsorbed amount of the metallic ions at equilibrium was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)\ V}{m} \tag{2}$$

Where q_e is the adsorption capacity (mg g^{-1}), V (L) is the volume of the heavy metal solution treated, and m (g) is the weight of the adsorbent used.

II.5. pH studies

The pH of the aqueous solution is an important variable that controls the adsorption of metal on the surface of the material. Therefore, the effect of the initial solution pH on the adsorption of heavy metals by the ammonium activated clay was studies in the range of pH 1-10. This study was repeated for three initial metal concentrations of lead and zinc 50, 100 and 150 mg L^{-1} (single metal adsorption). The contact time was kept constant at the time required for reaching the equilibrium for relevant heavy metal. The volume of the solution and the adsorbent dosage were kept constant at 100 mL and 4 g/L respectively for all the tests. Adsorption experiments were conducted in batch system and the optimum pH, at which the maximum lead and zinc was removed, was determined and used for further experiments.

II.6. Adsorbent dosage studies

Adsorbent dosage studies was achieved in batch system, by adding the amount of ammonium activated clay from 1 to 2 g into 100 ml solution containing 50 mg/L of lead or zinc at initial solution pH of 5.

II.7. Contact time studies

The influence of the contact time on single adsorption of Pb(II) and Zn(II) ions onto ammonium activated clay was studied for three initial concentration of heavy metal: 50, 100 and 150 mg L^{-1} at the optimum pH 5. A fixed amount of adsorbent (4g) was added to 100 ml of the heavy metal solution at desired concentration and the suspension was shaken at 150 rpm for 3 hours. Samples were withdrawn at contact times of 10, 20, 30, 40, 60, 80, 100, 120 and 720 min, centrifuged at 3000 rpm for 10 min and filtered through 0.45 μm filters. Final metal ion concentration was determined in each sample by the atomic absorption spectrophotometer. The amount of metal ions adsorbed and the percent metal removal at the selected time were then determined.

Kinetic study for simultaneous adsorption of lead and zinc onto ammonium activated clay was conducted at pH 5 and 4gL^{-1} adsorbent dose.

II.8. Adsorption isotherms studies

Isotherms studies were carried out by varying the initial metal ion concentration, while keeping the adsorbent dose and the solution pH constant at the optimum values. 100 ml of lead and/or zinc ion solution in the range of 10 to 150 mgL^{-1} each were placed into 150 ml conical flask. Before adding the adsorbent, the initial pH of the contents was adjusted to 5 with 0.5 M NaOH or H_2SO_4 solution. Then 4 g of ammonium activated clay was added to the mixture. The suspension was then shaken for the desired contact time at 120 rpm. At the end of these tests, the solutions were centrifuged at 3000 rpm for 15 min then filtered through 0.45 μm filters and the residual heavy metals concentrations were determined by means of the atomic absorption spectrophotometer.

III. Result

3.1. Clay characterization

X-ray photoelectron spectrometry (XPS) lines of the raw and the ammonium activated clays are shown in Fig. 1. The main peaks obtained Al2p, Si2p, K2p, Ca2s, O1s and Na1s are situated respectively at ~75, 103, 293-296, 347, 533 and 1072 e. The minor C1s peaks (285 eV) are attributed to an unavoidable hydrocarbon surface contamination. As can be seen in this figure the lack of N1s from the raw clay is very pronounced, however after modification by ammonium chloride it appeared at 402 eV.
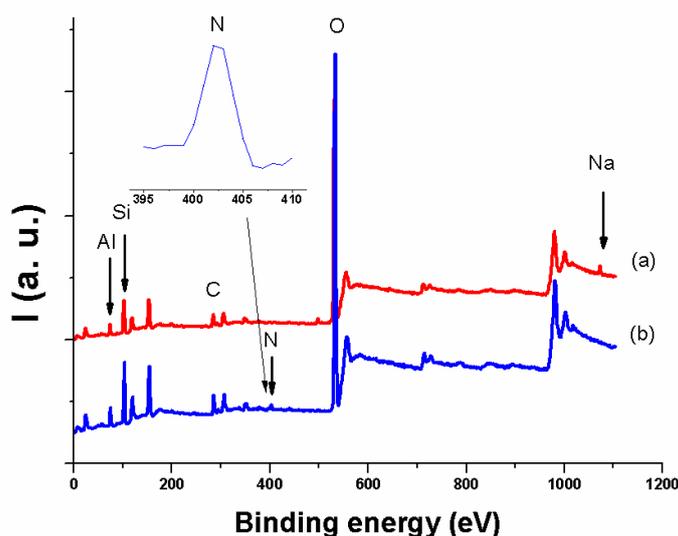

Figure 1: XPS survey regions of raw clay (a) and ammonium activated clay (b).

At the same time, the activation of raw clay causes a drastic decrease in the intensity of the Na1s peak. Table 1 reports the surface elemental composition.

Interestingly, one can clearly note the increase of the K/Na atomic ratio from 0.49 to 2.44 because of the exchange of sodium by the ammonium cations. Since the potassium content does not change considerably, the cation exchanges affect only sodium. The absence of any Cl2p peak at ~198 eV (chloride binding energy peak) indicate that the activation is a true cation exchange as sodium is substituted by the ammonium cation without any adsorption of chlorides from NH_4Cl.

Another important observation concerns the aluminosilicate sheets: the Si/Al atomic ratio increases only by about 10%, i.e. from 2 to 2.3[16].

Table n°1: Apparent surface elemental composition of clay before and after ammonium activation

| Materials	Al	Si	C	K	Ca	N	O	Fe	Na	Mg
Raw clay	10.5	20.9	9.33	0.5	0.36	0	55.1	0.73	1.03	1.64
Ammonium activated clay	9.03	20.6	7.4	0.44	0.31	0.73	59.9	0.97	0.18	1.21

3.2. Adsorbent dose effect

The effect of the adsorbent dose on single adsorption of Pb(II) and Zn(II) ions onto ammonium activated clay was investigated at ambient temperature $(25 \pm 1)°C$ and contact time of 3h for initial concentration of heavy metal of 50 mg L^{-1} at pH 5. As can be seen in Fig. 2, the percent of Pb(II) and of Zn(II) removal steeply increases with the increase of the activated clay dosages. The maximum percent removal of the metal ions, i.e. 99% for Pb(II) and 66% for Zn(II), was attained at adsorbent dosage of 4g/l. Moreover, no significant increase in both Pb(II) and of Zn(II) percent removal was observed above this dosage.
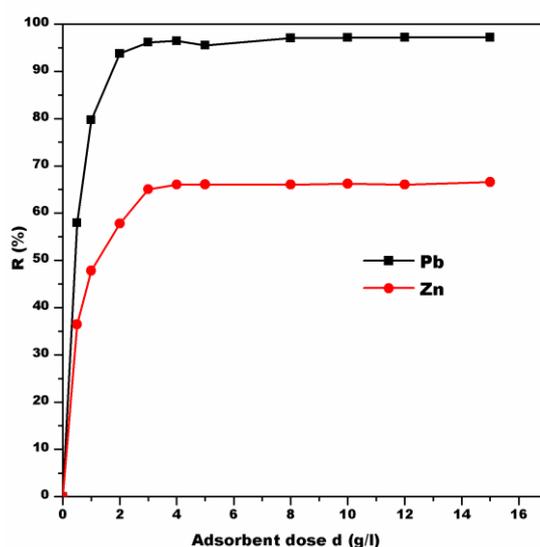
Figure n°2: Effect of the adsorbent dose on the single adsorption of Pb(II) and Zn(II) onto ammonium activated clay (initial concentration : 50 mg/l; pH : 5; temperature : 25°C).
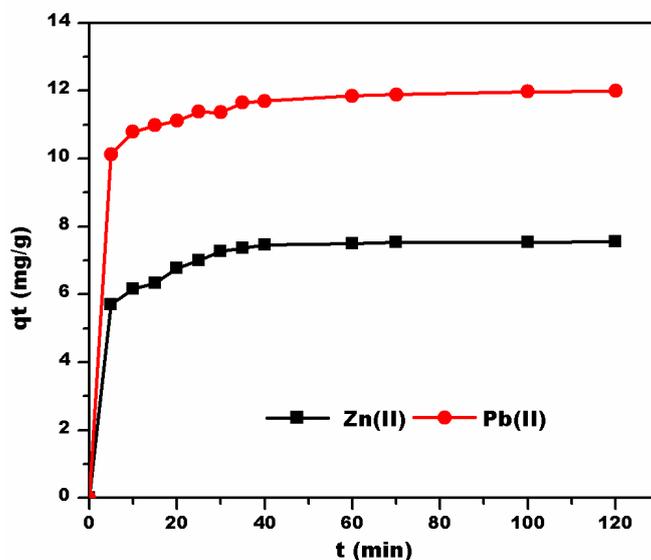
3.3. Contact time effect

Fig. 3 (a) and (b) illustrate respectively the amount of Pb(II) and Zn(II) adsorbed as a function of contact time for three initial metal concentrations 50, 100 and 150 mg L^{-1} at pH 5. These curves indicate that the rate of adsorption of the two metals on the activated clay is faster at initial times (in the first 20 min) then reaches equilibrium within approximately 60 min and remains nearly constant. This result can be interpreted by the fact that at shorter times there are enough adsorption sites on the surface of activated clay, which makes heavy metal ions interact easily with the sites. Then, the active sites become saturated which leads to a lower diffusion of the metal ions into the interior of the adsorbent [16], Therefore, the optimum contact time selected for further experiments was 60 min.
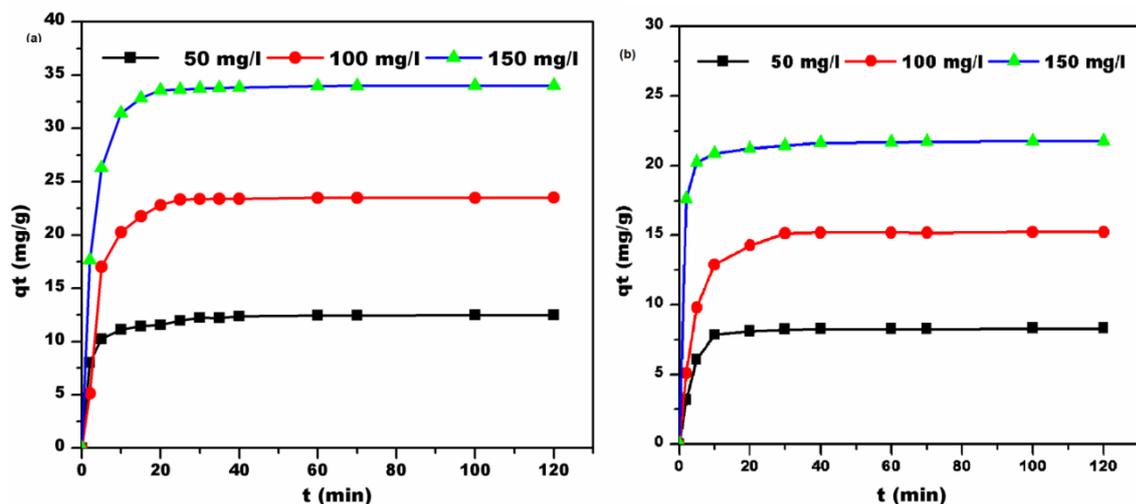
Figure 3: Effect of contact time on the adsorption of Pb(II) (a) and of Zn(II) (b) onto ammonium activated clay at three initial metal concentrations 50, 100 and 150 mg/L; initial pH 5; adsorbent dosage 4 g/L.

Fig. 4 plots the increase of the amount of Pb(II) and Zn(II) adsorbed versus the increase of the contact time at initial solution pH 5 on the Binary adsorption. It is obvious from this figure, that the sorption yield of Pb(II) and Zn(II) increases considerably with the increase in the contact time up to 60 min and then it becomes nearly constant.

Figure n°4: Effect of contact time on the Binary adsorption of Pb(II) and of Zn(II) (b) onto ammonium activated clay. (Initial metal concentration 50 mg/L; initial pH 5; adsorbent dosage 4 g/L)

3.4. pH effect

Fig. 5 shows the rapid increase of the metallic ions removal by adsorption on ammonium activated clay with the increase of pH until pH=4. The adsorption efficiency increases for single adsorption from 19 to 100% for Pb(II) and from 23 to 65% for Zn(II) in the range of pH 1-4. However there is no significant adsorption in the range of pH 4-6 for the two metallic ions. After pH 6 the adsorption of Zn(II) increases considerably. This may be due to the precipitation of the hydroxylated complexes of the metal ions ($Zn(OH)_2$) and not to adsorption.

At low pH the surface is positively charged and is not suitable for retention of heavy metals. The increase of the solution pH from 1 to 4 makes the surface become more negatively charged, which results in higher uptake of metals. In this study, pH 5 was selected as optimum condition for further adsorption experiments for both single and binary systems.
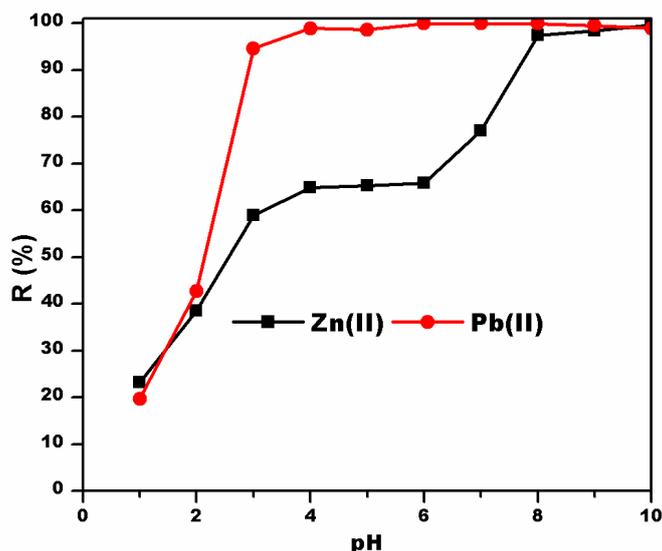
Figure n°5: Effect of pH on Pb(II) and Zn(II) single adsorption

3.5. Adsorption isotherms

The adsorption behavior is described by several models. In this study two models were investigated: Langmuir and Freundlich models. The Langmuir isotherm is usually expressed by the following equation:

$$q_e = \frac{(K_L q_m C_e)}{1 + K_L C_e} \qquad (3)$$

Where:

q_e is the adsorbed amount of the metallic ions at equilibrium (equilibrium adsorption capacity) (mg g^{-1}),

q_m the maximum amount of adsorption (mg g^{-1}),

C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}),

K_L is the adsorption equilibrium constant (Langmuir constant) (L mg^{-1}).

The Langmuir model is rearranged as in Eq. 4

$$\frac{C_e}{q_e} = \frac{1}{K_L \, q_m} + \frac{C_e}{q_m} \qquad (4)$$

The Freundlich model is given as:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

Where

q_e is the adsorbed amount of the metallic ions at equilibrium (equilibrium adsorption capacity) (mg g^{-1}),

C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}),

K_F is the adsorption equilibrium constant (Freundlich constant) (L mg^{-1}),

$1/n$ is an empirical parameter relating to the adsorption intensity, which changes with the heterogeneity of the adsorbent.

The Freundlich model is linearized as in Eq. 6

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \qquad (6)$$

The adsorption behavior was investigated at pH 5 and adsorbent dose 4g/L, each metal element was studied both individually and simultaneously in order to evaluate possible competition effects.

Fittings were carried out and Fig.6 and Fig.7 show the curve-fitting plots of the Langmuir and Freundlich models, respectively. The parameters obtained for these models are presented in Table 2.

Tablen°2: Langmuir and Freundlich parameters for the adsorption of Pb(II) and Zn(II) onto ammonium activated clay

|		Lead Pb(II)				Zinc Zn(II)		
Single solution	*Langmuir parameters*	q_m(mg/l)	KL (L/mg)	R^2	q_{exp}(mg/l)	q_m (mg/l)	KL (L/mg)	R^2
		25	1.379	0.999	24.438	16.95	0.628	0.999
	Freundlich pameters	KF	1/n	R^2		KF	1/n	R^2
		11.917	0.293	0.962		6.334	0.333	0.962
Binary solution	*Langmuir parameters*	q_m (mg/l)	KL (L/mg)	R^2	q_{exp}(mg/l)	q_m (mg/l)	KL (L/mg)	R^2
		17.24	0.558	0.976	16.32	9.35	0.37	0.976
	Freundlich pameters	KF	1/n	R^2		KF	1/n	R^2
		5.181	0.452	0.968		2.323	0.463	0.968

By analyzing table 2, we can observe that:

- In single adsorption all R² values are greater than 0.95, indicating that adsorption of Pb(II) and Zn(II) onto ammonium activated clay gives a good fit to the Langmuir and Freundlich models.
- In both single and binary adsorption, the Langmuir isotherm model presents the highest correlation coefficients (R² close to 1) it therefore provides the best fit to the experimental data.
- The values of 1/n in the range 0.1-1 indicate that adsorption of Pb(II) and Zn(II) onto ammonium activated clay is favorable [1].
- In the single adsorption system, the adsorption capacity (q_m) is 25 mg/l for Pb(II) and 16.95 mg/l for Zn(II).
- In the binary adsorption system, the adsorption capacities of both Pb(II) and Zn(II) reach values as low as 20.41 and 11.49 mg/g, respectively. This decrease indicates that a competitive phenomenon occurs in this case between the two heavy metals. The fact that Pb(II) has a higher adsorption capacity than Zn(II) proves that lead is preferentially adsorbed.

Fig. 8a shows the adsorption isotherm of Pb(II) and Zn(II)) onto ammonium activated clay in the single system. According to classification by Giles et al (1960)[17], the adsorption isotherm is of class L2 (monolayer Langmuir).

The adsorption isotherms in binary system are shown in Fig**.** 8b. As can be seen, the isotherm type changes to L4 (multilayer Langmuir) for both metal ions. The experimental results indicate that the adsorption capacity (q_m) of Pb(II) is higher than that of Zn(II).
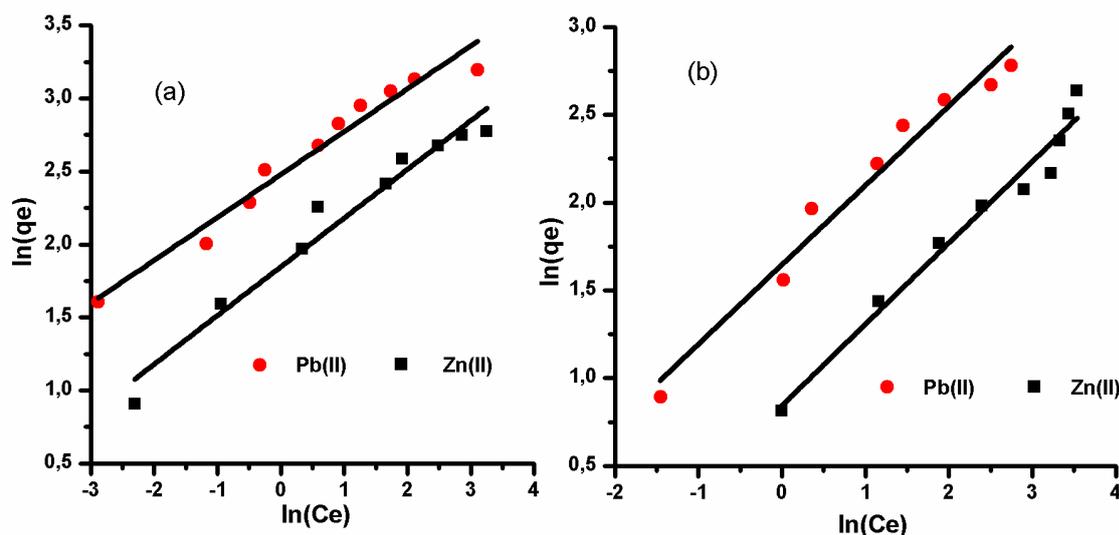
Figure n°7: Fitting plots of the Freundlich model for the single (a) and binary (b) adsorption of Pb(II) and Zn(II) (pH:5;adsorbent dosage:4g/L).
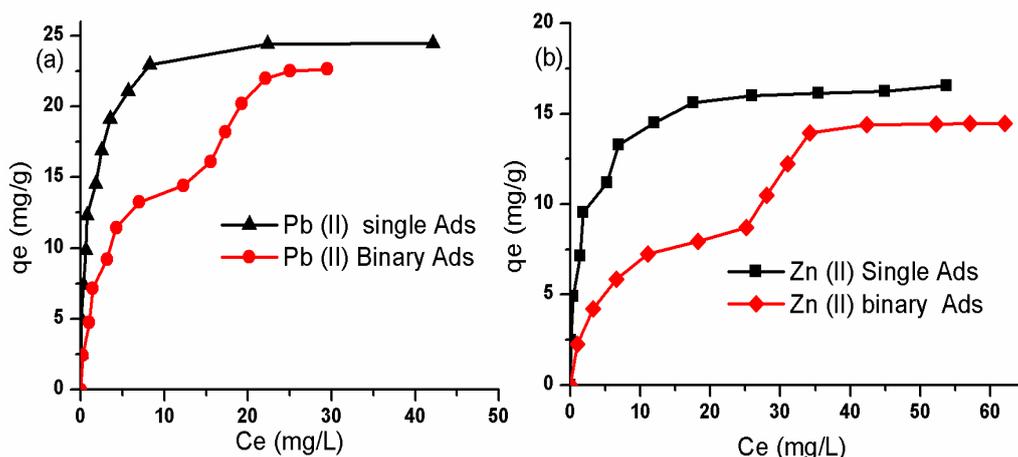
Figure n°8: Fitting plots of the Freundlich model for the single (a) and binary (b) adsorption of Pb(II) and Zn(II) (pH:5;adsorbent dosage:4g/L).

3.6. Adsorption kinetics

In the aim to investigate the mechanism of adsorption and rate controlling steps, a pseudo-first order, and a pseudo-second order models were used to test the experimental data.

3.6.1. Pseudo- first -order model

The pseudo first order adsorption rate is generally expressed as:

$$\frac{dq_t}{dt} = K_1(q_t - q_e) \tag{7}$$

Where q_e and q_t are the amounts of heavy metals adsorbed (mg/g) at equilibrium and at time t respectively and K_1 (min^{-1}) is the rate constant of pseudo first order adsorption. After rearrangement Eq. 8 takes this form:

$$Log(q_e - q_t) = Log(q_e) - K_1.t \tag{8}$$

When sorption is controlled by this model, the plot of $Log(q_e-q_t)$ versus time gives q_e and K_1 values.

3.6.2. Pseudo-second-order model

This model is defined mathematically as:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{9}$$

Where K_2 (mg g^{-1} min^{-1}) is the rate constant of pseudo second order adsorption
Integration of Eq. 10 and application of the boundary condition $q_t=0$ at t= 0, yields a linear form of Eq. 9.

$$\frac{t}{q_t} = \frac{1}{K_2}\frac{1}{q_e^2} + \frac{t}{q_e} \tag{10}$$

The plot of t/q_t versus t is used to obtain K_2 and q_e.
The fit of the above models equations to the experimental data was checked and the adjustments carried out are shown in Figs. 9, 10 and 11 while the kinetic parameter values for each model are presented in Table 3.

Table n°3: Pseudo-second-order parameters and coefficient of determination for different initial metal concentration.

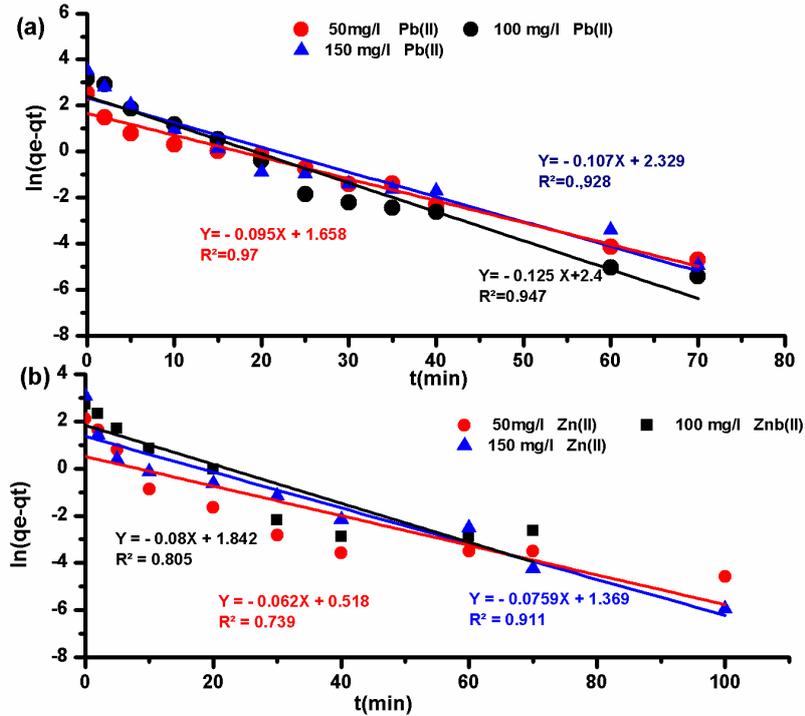|		Heavy metal concentration (mg/l)							
		50				100		150	
Kinetic model		**Pb(II)**	**Zn(II)**	**Pb(II) (with presence of Zn(II))**	**Zn(II) (with presence of Pb(II))**	**Pb(II)**	**Zn(II)**	**Pb(II)**	**Zn(II)**
Pseudo-first order	K_1	0.094	0.062	0.055	0.067	0.125	0.082	0.107	0.077
	q_e	5.249	1.679	3.127	2.366	11.023	6.309	10.278	3.762
	R²	0.972	0.768	0.920	0.949	0.952	0.829	0.928	0.914
	q_{exp}	12.461	8.315	11.983	7.544	23.484	15.243	34.002	21.751
Pseudo-second order	K_2	0.062	0.081	0.054	0.058	0.019	0.028	0.032	0.092
	q_e	12.658	8.475	12.195	7.752	24.390	15.625	34.483	22.222
	R²	0.999	0.999	0.999	0.999	0.997	0.999	0.999	1

Figure n°9: Pseudo-first order kinetic plots at different metal concentrations; (a) for Pb(II) single adsorption and (b) Zn(II) single adsorption; (temperature =25°C; pH=5; adsorbent dosage= 4g/l).
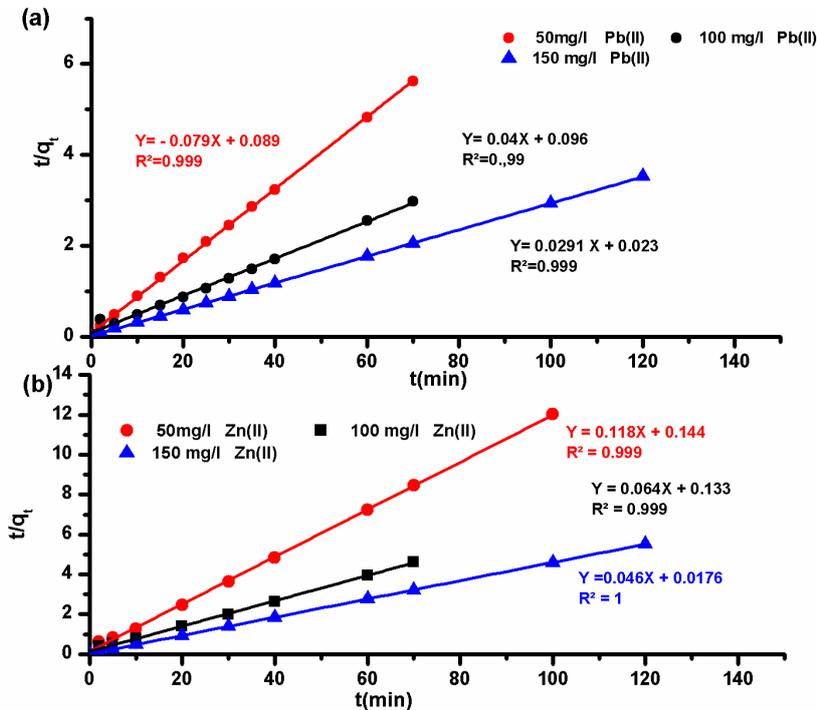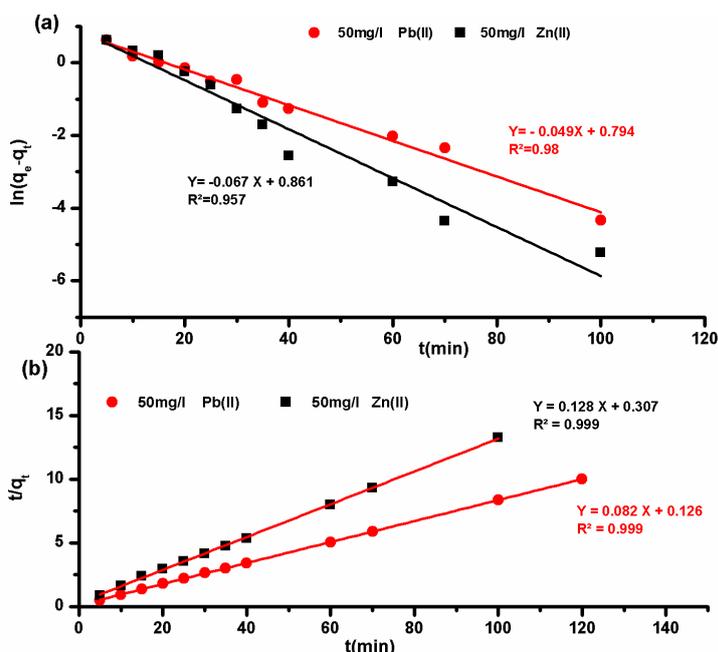

Figure 10: Pseudo-second order kinetic plots at different metal concentrations; (a) for Pb(II) single adsorption and (b) Zn(II) single adsorption; (temperature =25°C; pH=5; adsorbent dosage= 4g/l).

Figure 11: Pseudo-first order (a) and Pseudo-second order (b) kinetic plots for binary adsorption of Pb(II) and Zn(II); (temperature =25°C; pH= 5; adsorbent dosage= 4g/l; metal concentration=50mg/l).

From the kinetic results obtained in this study (Table 3), it can be seen that the pseudo-second order kinetic model is the best model that obeyed the sorption process of Pb(II) and Zn(II) for single and binary adsorption, since the calculated correlation coefficients are closer to 1 and the calculated adsorption capacities (q_e) agree very well with those obtained experimentally (Table 3).

IV. Conclusion
This study investigated the single and simultaneous adsorption of lead and zinc ions from aqueous solution onto ammonium activated clay.
The following main conclusions can be drawn:
- The maximum adsorption uptake was achieved at pH 5 within 60 min, and the results show that the capacity of adsorption increases with the increase in the initial concentration of lead or zinc in the solution.
- In both single and binary adsorption, Langmuir isotherm model described the adsorption of Pb(II) and Zn(II) ions onto ammonium activated clay adequately.
- In both single and simultaneous adsorption of lead and zinc ions from aqueous solution the adsorption system followed the pseudo-second-order kinetics model with high correlation coefficients.
- In the single adsorption system, the maximum adsorption capacities of the ammonium activated clay for Pb(II) and Zn(II) were 25 and 16.95 mg g^{-1}, respectively. These were higher than those found in the simultaneous adsorption system (20.41 mg/g for Pb(II) and 11.49 mg/g for Zn(II)).
- Ammonium activated clay is an attractive adsorbent for Pb(II) and Zn(II) removal from aqueous solutions.
- The two divalent metal ions Pb(II) and Zn(II) have different affinities for the binding sites present in the activated clay.

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