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Competitive Adsorption of Heavy Metals onto Natural and Activated Clay: Equilibrium, Kinetics and Modeling

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***Abstract*—**The aim of this work is to present a low cost adsorbent for removing toxic heavy metals from aqueous solutions. Therefore, we are interested to investigate the efficiency of natural clay minerals collected from south Tunisia and their modified form using sulfuric acid in the removal of toxic metal ions: Zn(II) and Pb(II) from synthetic waste water solutions. The obtained results indicate that metal uptake is pH-dependent and maximum removal was detected to occur at pH 6. Adsorption equilibrium is very rapid and it was achieved after 90 min for both metal ions studied. The kinetics results show that the pseudo-second-order model describes the adsorption and the intraparticle diffusion models are the limiting step. The treatment of natural clay with sulfuric acid creates more active sites and increases the surface area, so it showed an increase of the adsorbed quantities of lead and zinc in single and binary systems. The competitive adsorption study showed that the uptake of lead was inhibited in the presence of 10 mg/L of zinc. An antagonistic binary adsorption mechanism was observed. These results revealed that clay is an effective natural material for removing lead and zinc in single and binary systems from aqueous solution.

***Keywords*—**Lead, zinc heavy metal, activated clay, kinetic study, competitive adsorption, modeling.

I. Introduction

THE natural water is polluted especially by industrial effluents loaded with many toxic chemical products discharged directly into the rivers, and on the earth ground [1].

The discharge of heavy metals from many industries into the environment, such as metallurgical, lead batteries and mining, was increased especially in the developing countries. Heavy metal ions are nowadays the most important pollutants known, as highly toxic in nature, carcinogenic, non-biodegradable and trend to accumulate in living organisms, thus causing a number of diseases and health problems [2].

The lead is one of the most toxic heavy metals in the world due to their high potential impact on the environment and human health [3]. Zinc is an essential element at trace level but at higher level can cause health problems [4].

Due to the environmental regulations for the discharge of heavy metals, it is very important to use an effective treatment method including precipitation, ion-exchange, coagulation, membrane separation and adsorption [5]. Among all these processes, considering the economy and efficiency point of view, adsorption is regarded as the most promising and widely used method for removal heavy metal ions [4].

A lot of researches were carried out for removal of single heavy metal from synthetic solution using various adsorbents [1], [3], [5]. Since single hazardous metal ion rarely exists alone in the discharges of industrial effluents, the adsorption behavior of each metal was the result of competition between various ions present in the system. However, a few published works are interested in competitive adsorption of various metal ions from aqueous solutions due to the difficulty of the experimental studies and the analysis of the interactions mechanism [6]. Due to its high surface areas, selective functional groups and high removal uptake, activated carbon is used as an effective adsorbent for removal metal ions. However, due to its high cost, many researchers have been interested in using low cost materials with high adsorption capacities for removal toxic metal ions [7].

Natural clay minerals are effective adsorbents for the removal of heavy metals, owing to large specific surface area, ion-exchange properties, low cost and large presence in most soils [8], [9].

The main objective of this study is to evaluate the performance of natural and activated clay modified with sulfuric acid to remove lead and zinc ions from aqueous solution in single and binary systems.

II. Methods and Materials

A. Materials

In the present study, natural clay sample, collected from the Djebel EL'Aidoudi of El Hamma area located in south-eastern Tunisia, was used as a low cost material for the adsorption of lead and zinc ions. For adsorbent preparation, the natural clay was purified to remove several impurities such as quartz. The purification method of clay material and their acid activation process were described in [10]. Obtained activated clay material was dried at 105 °C for 24 h and then crushed to collect the particle size lower than 60µm, as mentioned previously [10].

B. Chemicals

All used chemical reagents were of analytical-reagent grade. The stock solution of Pb(II) and Zn(II) were prepared from standard solutions of 1 g/l. The working solutions of Pb(II) and Zn(II) were prepared for dilution of the stock solution with ultrapure water. To adjust the pH of samples, we used a 0.1 M HCl and 0.1 M NaOH. All laboratory material was carefully cleaned before use, first washed with a neutral

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detergent solution and rinsed with distilled water and finally, soaked in nitric diluted solution and rinsed with distilled water.

C. Batch Experiments

Batch sorption was selected as an effective method in the present study for evaluate the removal of metal ions, by sorption onto the adsorbent under various experimental conditions and for study their effects on sorption mechanism.

A known amount of clay was placed in a polypropylene tube containing a metal ion solution of known concentration and fixed value of initial pH. After shaking time, the samples were filtered through a paper filter and centrifuged. All experiments were run in triplicate. Then, the filtrate of metal ion solutions was analyzed using flame atomic absorption spectrometry (AAS).

Competitive equilibrium adsorption isotherms of lead from synthetic binary systems Pb(II)-Zn(II) were obtained by fixing initial concentration of the target ion Zn(II) and varying the concentration of the interferential metal ion Pb(II).

The quantity of a metal ion adsorbed from the solution was calculated by:

$$q_e = \frac{(C_0 - C_e).V}{m} \quad (1)$$

where V is the volume (l), m is the mass of clay (g), C_0 is the initial concentration of the metal ion (mg/l), C_e and q_e are the metal concentration (mg/l) and the metal quantity adsorbed at the equilibrium (mg/g), respectively.

III. Results and Discussion

A. Characterization of the Adsorbents

The physicochemical properties of the natural and activated clay samples from the previous work [9] are illustrated in Table I. The results indicate that the main constituents of clay are silica (SiO_2), alumina (Al_2O_3) and iron oxides (Fe_2O_3) [10]. Therefore, these data showed the siliceous to alumino-ferrous nature of the clay used in this study. The low contents of K_2O indicate the absence of illitic clay minerals [10]. Also, a low quantity of CaO and MgO were observed.

The acid activated clay showed high specific surface area (167 m^2/g) as compared to natural clay (86 m^2/g) (Table I).

B. Effect of pH

In each study of adsorption of heavy metals, the pH is the most important parameter. The metal uptake is strongly dependent on pH.

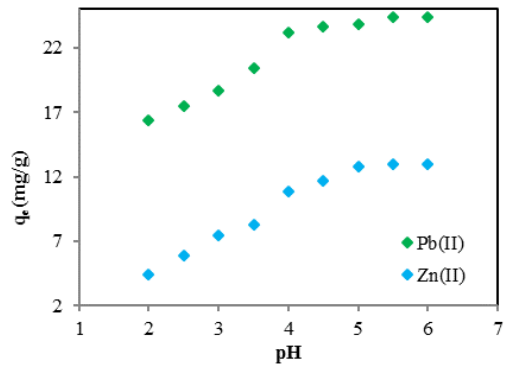
Taking into account the pH value of chemical precipitation of metal hydroxide, all the experiments were conducted at initial pH below these values. The effect of initial pH of the solution on the adsorption of Pb(II) and Zn(II) ions onto natural and activated clay were represented in Fig. 1.

As it can be seen from the curves plotted in Fig. 1, the capacity of adsorption of Pb(II) and Zn(II) increases with the increase of the initial pH of the solution. It reaches a maximum at around pH 6.

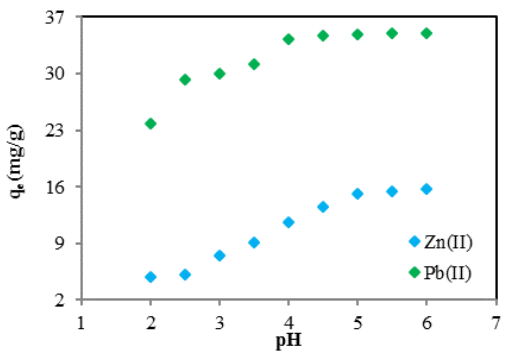
The few capacity of adsorption at low pH can be explained by the competitive adsorption between lead and zinc ions with protons H^+ ions onto the same actives sites of natural and activated clay [13].

TABLE I
PHYSICOCHEMICAL PROPERTIES OF THE CLAY MINERALS [9]

Chemical composition (%)	Natural clay	Activated clay
SiO_2	47.70	50.12
Al_2O_3	18.71	18.26
Fe_2O_3	11.12	9.12
CaO	2.65	1.93
MgO	2.59	1.89
K_2O	1.05	0.87
Na_2O	0.96	0.17
P_2O_5	0.32	0.02
SO_3	0.91	4.91
LOI	14	12
Structural parameters		
Specific surface area of BET (m^2/g)	86	167
Total pore volume(cm^3/g)	0.1394	0.1986
Mean pore diameter (Å)	40.53	49.03



(a)



(b)

Fig. 1 Initial pH effect on the adsorption of Pb(II) and Zn(II) onto natural (a) and activated clay (b)

The effect of pH can also be explained by considering the adsorbent surface charge evolution with pH. Natural and activated clay have a pH_{pzc} equal to 7.6 and 3.1, respectively. Therefore, when pH of metal solution is lower than these

values, the surface of both natural and activated clay is positively charged and metal ion adsorption is inhibited, due to electrostatic repulsion between the metal cation (Pb(II), Zn(II)) and H^+. At pH>pH_{pzc} of clay, a net negative charge existed on the surface of clay providing electrostatic forces of attraction between Pb^{2+}, Zn^{2+} and the surface of adsorbents [8], [9].

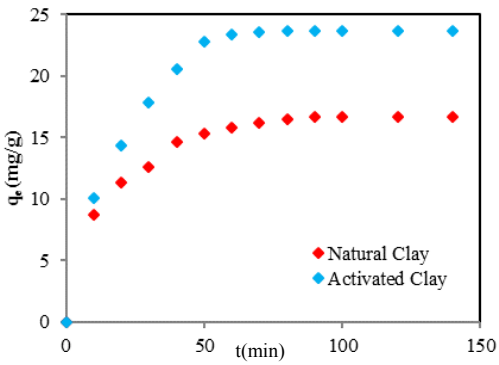


Fig. 2 Effect of contact time on the adsorption of Zn(II) by natural and activated clay (pH: 6; C_0: 50 mg/l)

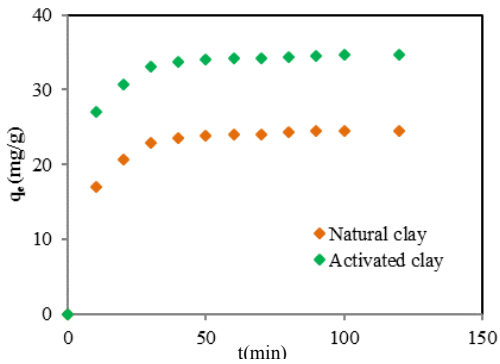


Fig. 3 Effect of contact time on the adsorption of Pb(II) by natural and activated clay (pH: 6; C_0: 50 mg/l)

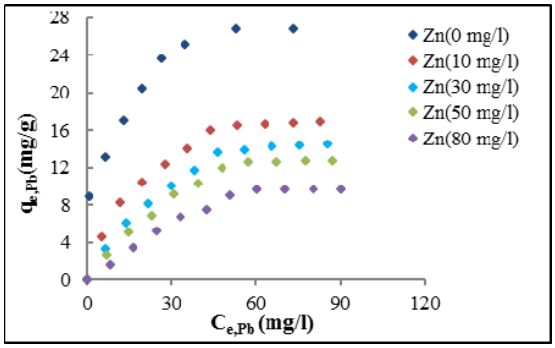
C. Effect of Contact Time

The time necessary to reach the equilibrium of adsorption of lead and zinc onto smectite clay was investigated at initial concentration of 50 mg/l. Experiments were performed using a solid-liquid ratio of 1 g/l and at initial pH 6.0. The variation of adsorption capacity as function of contact time for Pb(II) and Zn(II) ions on natural and activated clay, are shown in Figs. 2 and 3. Results indicate that the rate of adsorption of lead and zinc are fast for the first 30 min and thereafter slowed gradually until the adsorption reaches the equilibrium in about 90 min.

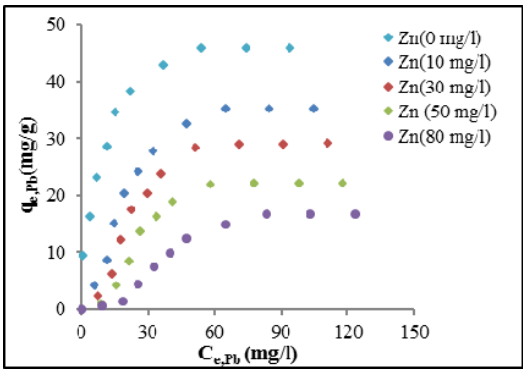
A large number of vacant active sites are occupied by the ions during the initial time of contact. After a period of time, the vacant surface sites are difficult to be available because of the repulsive forces between the metal ions adsorbed on the clay surface and the ions in solution. Therefore, the mesopores of the surface of clay minerals were saturated with metal ions in the initial stage of adsorption. Thereafter, the metal ions have to traverse farther and deeper into the pores encountering much larger resistance. As result was the slowing down of the adsorption during the later period of adsorption [13].

The chosen contact time for further experiments was 3 h in order to be sure that equilibrium was achieved for the rest of this study.

D. Competitive Equilibrium Adsorption



(a)



(b)

Fig. 4 Equilibrium adsorption isotherms of Pb(II) ion on natural (a) and activated (b) clay at varying concentrations of Zn(II) (pH=6 ; t : 3h;T: 20°C, $C_{0,Zn}$: 10-80 mg/l)

The adsorption isotherm curves of Pb(II) in the presence of different concentrations of Zn(II) ranging from 0 to 80 mg/l are presented in Fig. 4. From the analysis of the results of the competitive effect of Zn(II) on the uptake of Pb(II) by natural and activated clay, it shows that the adsorbed amount of lead decreases with the increase of the initial concentration of Zn(II), obviously higher for the higher concentration. It is observed from Fig. 4, that the $q_{e,Pb}$ was decreased from 26.8 to 9.69 mg/g by increasing of the initial concentration of zinc from 0 to 80 mg/l. Despite this reduction, Pb(II) still more adsorbed than Zn(II) in the binary systems. This antagonistic effect of Zn(II) on the adsorption of Pb(II) into natural and activated clay in the competition systems indicates that zinc is unable to occupy more active sites from natural and activated than lead. So, the study of the effect of initial concentration of each metal ion on the binary systems is very important to understand the competitive adsorption mechanism. The same results were shown by [14] in their study of competitive adsorption of Cd(II) and Zn(II) into rice husk ash. They

explained the effect of varying the initial concentration of Zn(II) in the binary aqueous solutions Cd(II)-Zn(II) ranging from 0 to 100 mg/l. It indicates that the amount of Cd(II) decreases from 2.88 to 1.64 mg/g, suggest that the electronegativity plays an important role in competitive adsorption.

E. Kinetic Adsorption Models

The adsorption kinetic study is important for determining the efficiency of adsorption and for determination of the adsorption rate limiting steps being necessary in order to define the rate parameters for design purposes. Kinetic data obtained from the adsorption study of Pb(II) and Zn(II) ions were predicted with different models widely applied to describe the adsorption behavior of heavy metals on natural and activated clay.

In order to determine the mechanism of adsorption and its potential rate controlling step, the tested models were: The pseudo-first order model [15], pseudo-second order model [16] and intraparticle diffusion model [16].

Pseudo-first-order:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{2}$$

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{\left(k_2 q_e^{\,2}\right)} + \frac{1}{q_e}.t \tag{3}$$

Intraparticle diffusion model:

$$q_t = k_p \sqrt{t} + C \tag{4}$$

where q_e (mg/g) is the equilibrium adsorption amount, q_t (mg/g) is the adsorption amount at time t (min), k_1 (min^{-1}), k_2 (g/mg .min^{-1}) are constant of the pseudo-first-order, the pseudo-second-order, respectively, and k_p (mg/g.$min^{1/2}$) intraparticle diffusion constant rates, C is proportional to the boundary layer thickness

The pseudo-first order and pseudo-second order kinetic models were applied to predict the mechanism involved in the adsorption process of metal ions.

The linear form of the pseudo and second order model were given by (2) and (3). It is clear from obtained data of Table II that pseudo second order kinetic model is more able to provide a successful description of Pb(II) and Zn(II) adsorption onto natural and activated clay. The kinetic parameters and the correlation coefficients values determined from the slop and the intercept of these plots are illustrated in Table II. The calculated adsorptive capacities values from the pseudo-second order model are in a good agreement with those experimentally determined. Moreover, the correlation coefficient values are quite well > 0.999, and much higher than those find by the pseudo-first order kinetic model. Thus, we can assert that the adsorbent systems are well described by the pseudo-second order kinetic model. Similar results were found by [18] and [19].

Intraparticle diffusion model is given by (4). It can be seen from curves regarding the effect of time, three distinct steps: the external diffusion, the intraparticle diffusion and equilibrium stage. The first slopes covering the time range between 0-15 min, must be the external diffusion. This is related to the binding of metal ions by active sites which are distributed onto the outer surface of the clay.

The second linear portions included the adsorption period of 15-90 min, is assigned to the gradual adsorption limited by diffusion of metal ions in the micropores of the adsorbent particles: the intraparticle diffusion. The third linear portions included the time period of 90-140 min, which denotes establishment of the equilibrium.

The values of the correlation and the diffusion rate constants were determined from the Weber and Morris model and reported in Table II. High correlation coefficient values suggest an important relationship between q_t and $t^{0.5}$ resulting from the adsorption of Pb(II) and Zn(II) onto natural and activated clay.

TABLE II
KINETICS MODELS FOR THE ADSORPTION OF METAL IONS INTO NATURAL AND ACID-ACTIVATED CLAY

Kinetic models	Parameters	Natural Clay		Activated Clay	
		Pb(II)	Zn(II)	Pb(II)	Zn(II)
Pseudo-first order	$q_{e.calc}$ mg/g)	19.9	15.9	15.95	33.82
	k_1(min^{-1})	0.0617	0.0511	0.0764	0.067
	R^2	0.9716	0.9830	0.970	0.933
Pseudo second-order	$q_{e.exp}$ (mg/g)	24.3	16.7	34.5	23.67
	$q_{e.calc}$ (mg/g)	25.51	17.36	35.46	26.66
	k_2 (g/mg . min^{-1})	0.0098	0.012	0.0109	0.003
	R^2	0.9997	0.9991	0.999	0.992
Intraparticle diffusion	k_{p1} (mg/g.$min^{1/2}$)	2.152	1.804	1.603	3.108
	k_{p2} (mg/g.$min^{1/2}$)	0.2152	0.650	0.2194	0.187
	C1	10.582	3.062	3.811	0.900
	C2	22.88	10.73	32.46	21.93
	R^2	0.9608	0.990	0.936	0.999

F. Equilibrium Adsorption Isotherm

The isotherm adsorption studies were investigated to determine the maximum adsorption uptake for lead and zinc ions on natural and activated clay. Isotherms were evaluated using the commonly used equilibrium model: Langmuir and Freundlich models.

Langmuir and Freundlich model can be described respectively as [20], [21]:

Langmuir isotherm model:

$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \tag{5}$$

Freundlich isotherm model:

$$q_e = k_f C_e^{1/n} \tag{6}$$

where q_m (mg/g) is the maximum adsorption capacity and k_l is the Langmuir constant. k_f (mg/l) is a constant representing the

adsorption capacity and n is a constant depicting the adsorption intensity.

Langmuir model fit to the experimental data very well with the highest correlation coefficient $0.98< R^2<0.99$ as compared to the Freundlich equation. Table III also indicates that the theoretical maximum values of the monolayer saturation capacities of natural clay and activated clay were equal to experimental ones and were found to decrease in the order Pb(II)>Zn(II).

The 1/n values calculated by Freundlich model were less than 1 showing that the heterogeneous adsorption mechanism. Furthermore, the results indicated that higher removal efficiency was achieved by activated clay sample (Table III). Similar results collected by [9], [12].

TABLE III
SINGLE ADSORPTION ISOTHERM CONSTANTS FOR PB(II) AND ZN(II) ADSORPTION ONTO NATURAL AND ACTIVATED CLAY

Isotherm models	Parameters	Natural Clay		Activated Clay	
		Pb(II)	Zn(II)	Pb(II)	Zn(II)
Langmuir	q_m (mg/g)	29.107	20.85	50.94	26.445
	k_l(l/mg)	0.1413	0.0358	0.1312	0.0626
	R^2	0.9807	0.9967	0.996	0.9908
Freundlich	1/n	0.2778	0.3995	0.2750	0.3287
	k_f (l/mg)	8.7512	2.6272	14.585	5.2268
	R^2	0.9886	0.9813	0.9787	0.9958

G. Competitive Adsorption Models

The equilibrium adsorption data of Pb(II) and Zn(II) from multi-component systems onto natural and activated clay were analyzed by nonlinear curves fitting models, including modified and extended Langmuir models and extended Freundlich competitive model.

Modified Langmuir (ML) isotherm [22]:

$$q_{e,i} = \frac{q_{m,i} k_{l,i} \left(C_{e,i}/\eta_{l,i}\right)}{1 + \sum_{j=1}^{N} k_{l,j} \left(C_{e,j}/\eta_{l,j}\right)} \tag{7}$$

Extended Langmuir (EL) isotherm [23]:

$$q_{e,i} = \frac{q_m k_i C_{e,i}}{1 + \sum_{j=1}^{N} k_j C_{e,j}} \tag{8}$$

Extended Freundlich (EF) isotherm [23]:

$$q_{e,1} = \frac{k_{f,1} C_{e,1}^{(1/n_1)+x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}} \tag{9}$$

$$q_{e,2} = \frac{k_{f,2} C_{e,2}^{(1/n_2)+x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}} \tag{10}$$

The parametric values of all these competitive adsorption models were found using a program in Matlab. The results of the parameters of multi component models are given in Table IV. The correlation coefficients R^2 values were calculated in order to distinct the best fitting isotherm model.

From Table IV, it seems that some of these models can not fit the experimental data in binary systems of isotherms Pb(II) adsorption such as extended Freundlich model. Although, applying model equations (ML, EL) provides good correlation coefficients. Calculated maximum adsorbed amount of lead into natural and activated clay in binary systems Pb-Zn, were determined by ML are consistent with experimental ones and this confirming with fitting of these models to experimental data (Fig. 5).

The effect of ionic interaction on the binary component adsorption process can be presented by the ratio of the adsorbed amount for one metal ion in the presence of the other metal ions, $q_{e,1}^{binary}$ to the adsorbed quantity of the same metal in single adsorption, $q_{e,1}^{single}$ [24].

- If $\frac{q_{e,1}^{Binary}}{q_{e,1}^{Single}}$ >1: The adsorption is promoted by the presence of other metal ions;
- If $\frac{q_{e,1}^{Binary}}{q_{e,1}^{Single}}$ =1: No interaction exists between adsorption species;
- If $\frac{q_{e,1}^{Binary}}{q_{e,1}^{Single}}$ <1: The adsorption is inhibited by the presence of other metal ions.

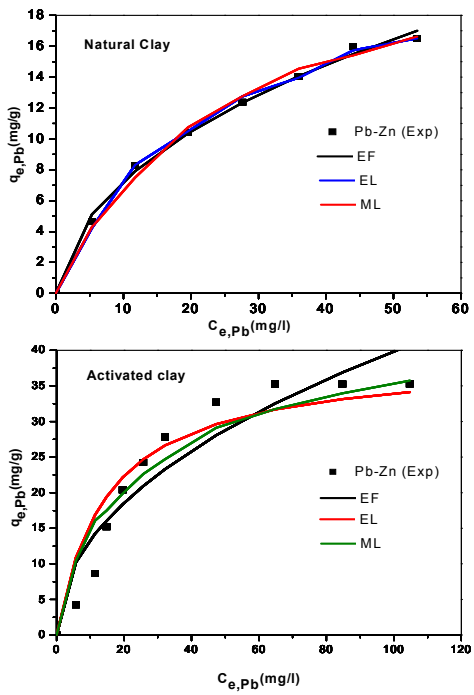


Fig. 5 Comparison of experimental and predicted adsorption isotherms of Pb(II) in presence of 10 mg/l of Zn(II) according to Extended Freundlich, Extended Langmuir, Modified Langmuir models (pH:6;T=20°C)

The ratios for the adsorption of Pb(II) metal ion in the presence of Zn(II) metal onto natural and activated clay are shown in Table IV.

For the adsorption of lead and zinc in binary systems onto both natural and activated clay, the values of the ratio are less than the unit indicating antagonist, indicating that the adsorbed amount of Pb(II) in competitive aqueous solution with the presence of Zn(II) ions is lower than that of individual ion in single solution system. Similar results were observed in [21] and [22].

From Table IV, it can also be noticed that for the binary and single system, the adsorption uptake of Pb(II) into activated clay prepared with sulfuric acid is higher than that of natural clay. This can be resulted from the greater affinity of studied ions to activated clay.

TABLE IV
COMPETITIVE ADSORPTION ISOTHERM CONSTANTS FOR PB(II) AND ZN(II) ADSORPTION ONTO NATURAL AND ACTIVATED CLAY

Isotherm models	Parameters	Natural Clay		Activated Clay	
		Pb(II)	Zn(II)	Pb(II)	Zn(II)
Extended Freundlich	x_i	0.4404	1.078	0.368	0.890
	y_i	1.9970	1.838	0.589	0.131
	z_i	0.0012	0.029	0.111	0.753
	R^2	0.9982		0.9511	
Extended Langmuir	q_m (mg/g)	18.784	-	39.02	-
	k_l (l/mg)	0.0457	0.1225	0.067	0.001
	R^2	0.9992		0.9693	
Modified Langmuir	R^2	0.9969		0.9695	
	$ń_i$	4.6303	0.490	3.086	0.218

TABLE V
COMPARISON EQUILIBRIUM ADSORPTION CAPACITY BETWEEN SINGLE AND BINARY PB-ZN ADSORPTION

Clay minerals	$q_{e,1}^{single}$	$q_{e,1}^{binary}$	$q_{e,1}^{binary} / q_{e,1}^{single}$
Natural clay	21.107	18.784	0.889
Activated clay	50.94	39.027	0.766

IV. CONCLUSION

In this work, the removal of lead and zinc from aqueous solution into natural and activated clay has been investigated. The adsorption results showed that the activated clay is an effective adsorbent for removal Pb(II) ion with high adsorption uptake (50.94 mg/g) under the optimum operating condition: 90 min contact time, pH 6 and adsorbent dose 1g/l.

The isotherm adsorption results were best predicted by Langmuir model as compared to Freundlich, and the maximum adsorption quantity to natural and activated clay increase in the order: Zn(II)<Pb(II).

The examination of the data collected from competitive adsorption system Pb(II)-Zn(II), showed that the adsorption amount of Pb(II) decreases in the presence of Zn(II) and dependent on the initial concentration of zinc varying for 10-80 mg/l. It can be concluded that both natural and activated clay collected from south Tunisia are a greater low cost adsorbent with a high capacity of uptake of lead and zinc in single and binary systems.

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