KINETIC STUDY OF ZINC ADSORPTION AND APPLICATION OF REMOVAL OF HEAVY METALS (Zn (II), Pb (II) AND Cu (II)) FROM WASTEWATER BY CRUDE CLAY OF EL MENIA

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The purpose of our study is to remove heavy metals from wastewater through the use of crude clay. The adsorption kinetics of Zn (II) on the clay is of a maximum value with a yield of the order of 58.07% after 30 minutes of contact, and the pseudo-second order model is the most suitable to describe the adsorption kinetics. Wastewater treatment tests perform more than satisfactorily with a three-day contact time. Regarding the removal efficiency of Cu (II) and Pb (II) it is over 31%.

Key words: heavy metals, wastewater, crude clay, adsorption kinetics

1. Introduction

In southern Algeria, the water sector remains marked by the acuity of certain problems, notably the quantitative and qualitative degradation of water resources, to which are added climatic conditions and the proliferation of sources of pollution; water pollution and the scarcity of groundwater have prompted us to look for solutions to reduce the use of groundwater, including the treatment of wastewater by different techniques [1]. Environmental pollution effluents containing heavy metals is a major concern; they are not biodegradable and tend to accumulate in living organisms, causing diseases and disorders [2]. Heavy metals are toxic even at low concentrations and can accumulate throughout the food chain [3]. The adsorption technique is the most favorable method for the

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elimination of heavy metals, very effective and simple in its use. Its principle is based on the fixing of metals of a solid material, called an adsorbent.

In recent years, a wide variety of materials have been investigated as low-cost adsorbents for the removal of heavy metals from water, such as activated carbon, clays, and sludge [4]. Clay in the southeast of Algeria is a very abundant raw material; its use in the purification of wastewater will allow us not only to reduce the cost of purification but also to contribute to the preservation of the environment. The application of these clay materials in the adsorption of micropollutants in an aqueous medium will thus make it possible to know their adsorption capacities and to realize their efficiencies in being able to store these toxic elements. This is justified by the importance of the surface developed by this material; the presence of negative charges on the surface and the possibility of cation exchange [5]. Recently, studies conducted on mixtures of natural clays have shown their effectiveness in the elimination of certain ions in synthetic aqueous solutions [6].

The objective of our study is to make the kinetic test of adsorption of zinc by the crude clay of the region of El Menia and to study the application of elimination of (Zn (II), Pb (II), and Cu (II)) from the wastewater of the city of Ghardaïa by this material.

2. Materials and methods

Description of zinc adsorption tests

For this adsorption experiment, 1g of crushed and sieved crude green clay ($D_{average}$< 0.08 mm) are mixed with 100 mL of zinc sulfate sample ($ZnSO_4.7H_2O$) at different concentrations (dilution of the stock solution 1000 mg/ L with distilled water) varied between 1 up to 18 mg/L on a magnetic stirrer for 30 minutes and pH = 6.8. The solid/liquid separation of the sample taken is carried out by centrifugation at a speed of 250 rpm at a temperature of 25°C then by vacuum filtration using a membrane with a porosity of 0.45 μm.

Experimental protocol and sample preparation

To investigate the lord metal removal performance of the crude clay, we prepared the samples at 100 mg/L (10 g of clay powder in 1 L of wastewater; the sample is mixed by shaking manual then analyzed after settling). We opted for wastewater treatment for 72 hours (three days)

Table 1

Physico-chemical characteristics of El Menia clay

pH	Absolute density (ρ_{ab})kg/m^3	Bulk Density (ρ_{Bu}) kg/m^3	Relative density (D_r)	Porosity (%)	The total specific surface ($m^2.g^{-1}$)	Insoluble (%)	SO_3^{2-} (%)	$CaCO_3$ (%)	Cl^-(%)	NaCl(%)
8.04	1172	1163	2	17	180	80.9	0.795	16	0.115	188

The parameters studied, the methods, and the analytical equipment used are presented in Table 2.

Table 2

The parameters studied, materials used, and analysis methods

Parameter	Method of analysis	Unity	Method reference
Water analysis			
pH	pHmeterWTWpH3110	-	NFT90-008Standard
Zinc (Zn^{2+})	Atomic absorption spectrometer AA-6800 (Shimadzu Europe)	mg / L	[7]
Lead (Pb^{2+})			
Copper (Cu^{2+})			
Clay analysis			
pH	Hach LT2300 multiparametric analyzer	-	[7]
Insoluble	-	%	NFP15-461
The total specific surface (TSS)	-	$m^2.g^{-1}$	$TSS = 20.93 \times VBS$
Absolute density(ρ_{ab})	-	Kg/m^3	EN-1097.7
Apparent density (ρ_{ap})	-	Kg/m^3	NFEN1097-3
Porosity (n)	-	%	$n = V_v/V_t$
Relative density (Dr)	-	/	The pycnometer test
Chloride (Cl^-)	-	%	Mohr's method
Carbonate($CaCO_3$)	-	%	NFP94-048
Sulfate(SO_3^{2-})	-	%	BS 1377 method
Particle size analysis by dry sieving after washing	-	-	NFP 94-056 (March 96)
Particle size analysis by sedimentation	-	-	NFP 94-057 (May 92)
X-ray diffraction	D8 Advance-Bruker AXS type diffractometer	-	X-ray powder diffraction
Infrared spectrometry	SHIMADZU Brand Fourier Transform Spectrophotometer (FTIR)	-	-

The purification performances were evaluated according to the following formula [1]:

$$\text{Yield } (\%) = (C_R - C_T).100/C_R \quad (1)$$

Where:

C_R: raw water concentration in mg / L. C_T: treated water concentration in mg / L

3. Results and discussion

a. Characteristics of the clay used

Fig.1 shows the diffractograms of the sample. The spectra obtained indicate that this clay is well crystallized, and the peaks are narrow and straight. The X-ray diffraction patterns of the sample are dominated by quartz [SiO_2] and halloysite [$Al_2Si_2O_5\,(OH)_4$]. Quartz and halloysite show a sharp peak at 2ө of 20° and 27.5° respectively, the increase in peak intensity corresponding to quartz due to the decrease of the halloysite peak [1].

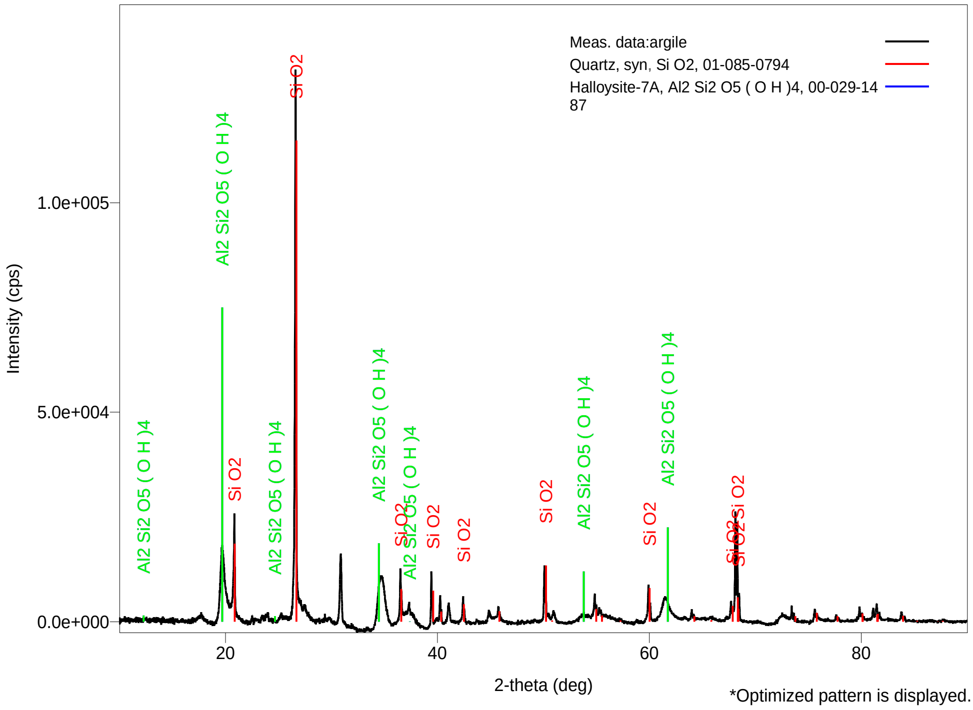


Fig.1. XRD diffractogram of the crude clay of El Menia [1].

Scanning microscopy makes it possible to observe the texture of the clay sample and to characterize mineralogical assemblages. The images obtained by scanning electron microscopy with different magnifications carried out on a fine raw clay powder are represented in Fig. 2.A; 2.B [8]. The observation of our raw clay by scanning electron microscope highlights particles in the form of small grains that characterize the Quartz in agreement with what we obtained in XRD there is no doubt about the presence of Quartz in the sample (indicated in a circle in Fig. 2.B, as well as a significant presence of micropores in Fig.2.A) [8].

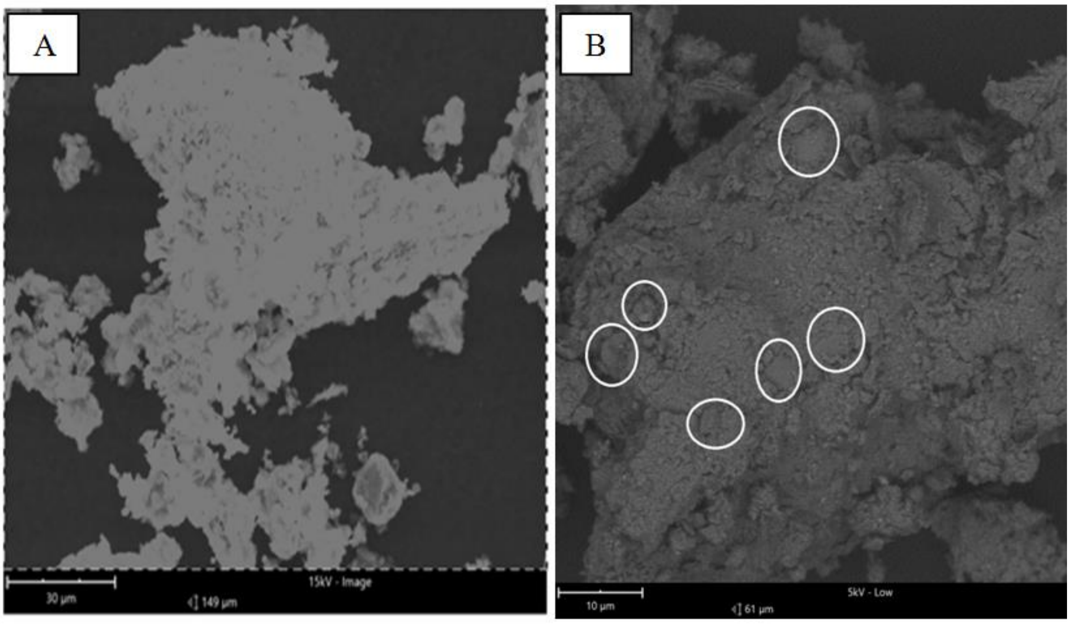


Fig.2. SEM images of El Menia raw clay

The examination of the IR spectra allows us to distinguish the main absorption bands as well as the vibration modes. The main bonds that can exist are O-H and Si-O bonds. The spectra obtained are illustrated in Fig. 3.

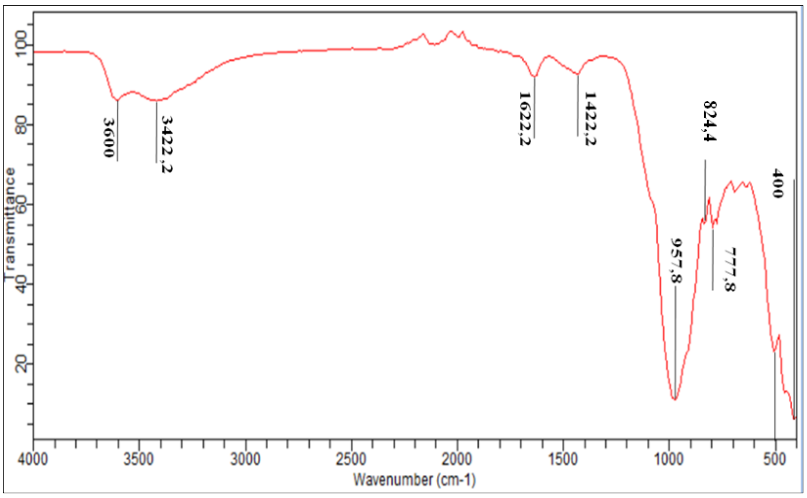


Fig.3.Infrared spectrum of the raw clay of El Menia

The bung which spreads between 1577 and 1700 cm^{-1} can be attributed to the valence vibrations of the OH group of the water of constitution as well as the bending vibrations of the adsorbed water located at 1622.2 cm^{-1}.The bung spread between 3300 and 3700 cm^{-1} corresponds to the stretching vibrations of the OH groups (Al-OH-Al) and the intense absorption peak at 3600 cm^{-1}. The bands located between 500 and 1500 cm^{-1} correspond to the deformation vibrations, the gap observed between 924.6 and 1177.8 cm^{-1} corresponds to the deformation vibrations of the Si-O-Si bond. The absorption bung at 777.8 cm^{-1} may correspond to Quartz [9]. The bands located between 400 and 500 cm^{-1} are attributed to the deformation vibrations of the Si-O or Si-OH bonds, even the peak at 666.7 cm^{-1} could be interpreted by the deformation vibrations of the OH [10].

b. Zinc adsorption kinetics

We followed the evolution of Zn (II) elimination as a function of contact time (0 to 4 hours) for distilled water solutions initially containing 5 mg/L of zinc. The dose of the clay introduced is 1 g / 100 mL. According to the results obtained, the removal efficiency varies with the stirring time. Maximum efficiency (58.07%) is obtained after 30 min.

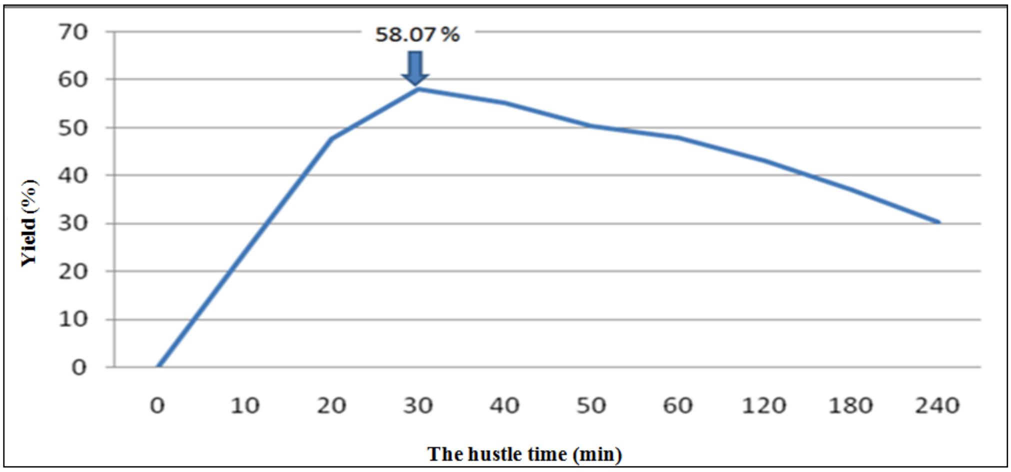


Fig.4.Zn (II) adsorption kinetics (5mg/L) by El Menia clay

Pseudo-second-order kinetics

Fig. 5 shows the application of the pseudo-second-order kinetics model to the results obtained for the adsorption of Zn (II) by crude clay. The pseudo-second-order is expressed by equation [11]:

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

After integration between t = 0 and t, on the one hand, and qt = 0 and qt, we obtain the linear form:

$$\frac{t}{q} = \frac{1}{k q_e^2} + \frac{t}{q_e} \quad (3)$$

The constants can be determined by drawing the line $1/q_t$ v.t

Where:

q_t and q_e: the quantities adsorbed at times t and equilibrium; k: rate constant of the pseudo-second-order adsorption process. The adsorbed quantity values q_e, the pseudo-second-order constant k, and the regression coefficient R^2 are given in Table 3. The other kinetic models studied (first order, pseudo-first-order, and second-order) are not validated for this study because they have too low correlation coefficients (the results of these three kinetic models are not presented in the article).

Given these results, it appears that the quantity fixed at equilibrium q_e(0.2 mg / g) is close to the values found experimentally and the value of R^2 is very high is of the order of 0.974; these findings lead us to believe that the adsorption process does indeed follow the pseudo-second-order model.

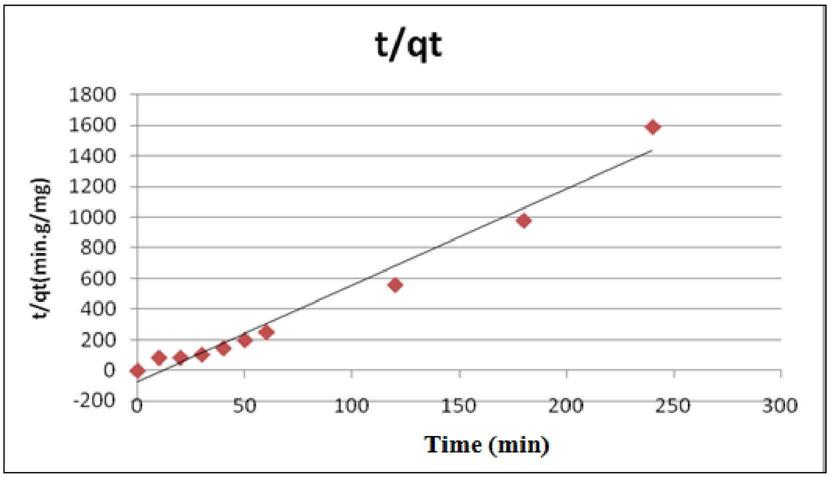


Fig.5.Determination of pseudo second order rate constant of Zn (II) adsorption by El Menia clay

Table3

Zn (II) adsorption kinetic constants in El Menia clay

Pseudo-second-order			
C_0(mg/L)	K(g.min^{-1}.mg^{-1})	q_e(mg/g)	R^2
5	0.27	0.2	0.974

Zinc adsorption isotherms

The adsorption isotherm experiments were carried out by varying the initial concentration of zinc in contact with a fixed mass of 1 g of clay for 30 min. Fig.6 shows the concentration variation of Zn (II) at equilibrium (C_e) as a function of the quantity of zinc adsorbed (x) by the adsorbent (m = 1 g). The results mean that for initial concentrations below 18 mg/L, removal efficiencies are greater than 50%.

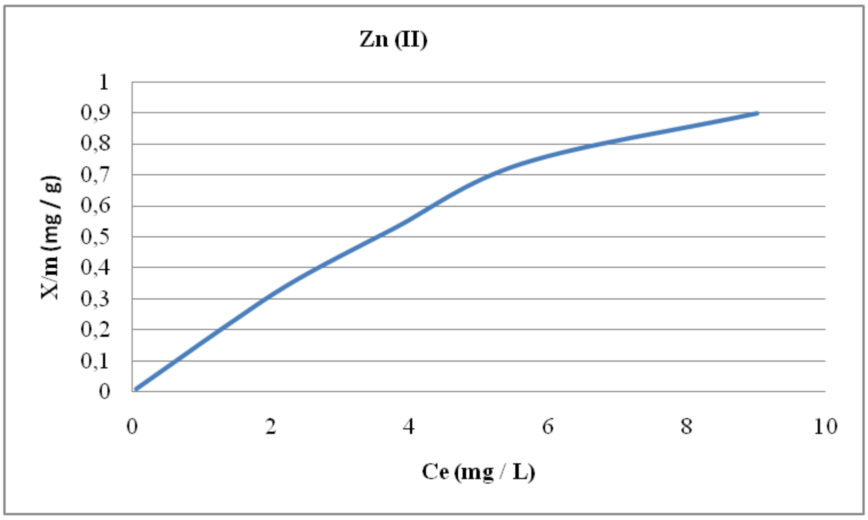


Fig.6. Adsorption isotherm of Zn (II) by the bute clay of El Menia

Application of adsorption isotherm models

We have adopted the classic models of Langmuir and Freundlich adsorption isotherms; which allow linear regression to obtain the values of the constants (q_m, K, 1/n, K_L, q_e)

The exploitation of the results according to the laws of Freundlich and Langmuir is presented in Fig.7. These laws are expressed by [12]:

Freundlich law:

$$\text{Log}\, q_e = \log K + \frac{1}{n} \log C_e \quad (4)$$

Langmuir Law:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{(K_L \cdot q_m)} \quad (5)$$

Where:

C_e: equilibrium concentration (mg/L); q_e: equilibrium adsorption capacity (mg/g); q_m: is the ultimate adsorption capacity (mg/g); K, K_L and n,: are adsorption constants. Fig.7 presents the application of the Freundlich and Langmuir model for the adsorption of Zn (II) by the raw clay of El Menia; Table 4 summarizes the parameters calculated by the two models as well as the correlation coefficient R^2.

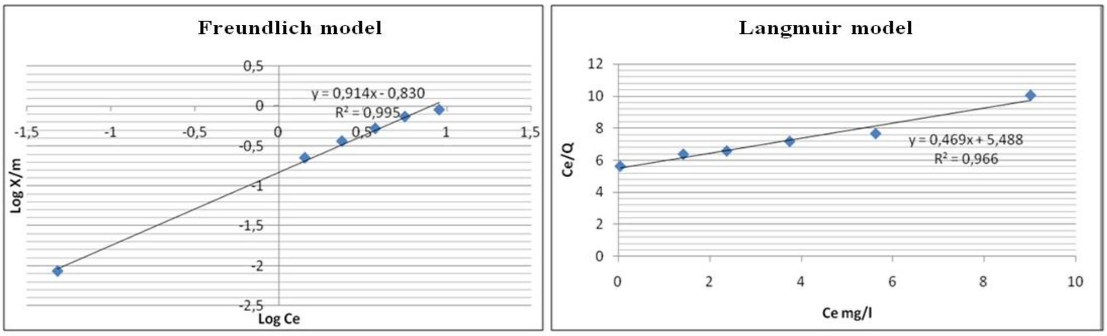
Based on the latter, we see that the Freundlich model gives good results where the R^2 coefficient values are 0.995. This result is similar to that found in a study concerning the elimination of Zn (II) pollution by the bentonite from Mostaganem [13].

The value of n obtained, which is greater than 1, shows that the clay studied is an excellent adsorbent. According to the values of 1/n, we notice that this parameter is lower than 1 suggests that the isotherm is convex of type L [14]. Concerning the Langmuir model, we notice from Fig.7 that the variation curve is linear, it shows a good agreement. Indeed, the correlation coefficients found are greater than 0.900; which confirms that the adsorption of Zn (II) responds to the Langmuir isotherm model.

Table 4

Parameters of the Freundlich and Langmuir isotherms

Adsorbate	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	1/n	K	R^2
Zn^{+2}	2,132	0,085	0,966	0,914	0.15	0,995



A **B**

Fig.7. A/ Freundlich model for the adsorption of zinc by clay. B/ Langmuir model for the adsorption of Zn (II) by El Menia clay.

c. Application of removal of Zn (II), Pb (II) and Cu (II) from wastewater by crude clay of El Menia

Regarding wastewater the pH value is 7.84; from wastewater treated with clay, the pH values are narrowly between 8.02 and 8.27. There's a slight increase in wastewater, this may be justified by lower Ca^{+2} and Mg^{+2}levels, which will cause an equalizing effect and increase pH [15].

The pH value of the wastewater complies with the limits of the Algerian discharge standards [16]; even clay treatment values comply with Algerian standards for the protection of the receiving environment and irrigation, which is below the pH value of 8.5 [17, 18].

The results show that the Zn (II) level in wastewater is 0.19 mg/L. Values of zinc are not natural due to the release of zinc from human activities. The primary sources of zinc in the environment are the manufacture of copper and bronze alloys and galvanization. It is also used for paints, rubber, plastics, cosmetics and pharmaceutical products [18]. According to Fig. 8 processing with crude clay allows reducing the concentration of Zn (II) under the effect of adsorption and this is observed by the study on graphite and Maghnia bentonite [20] and by another study on the removal of organic compounds by local clay [21]. The clay removal yields are 32% after 3 days.

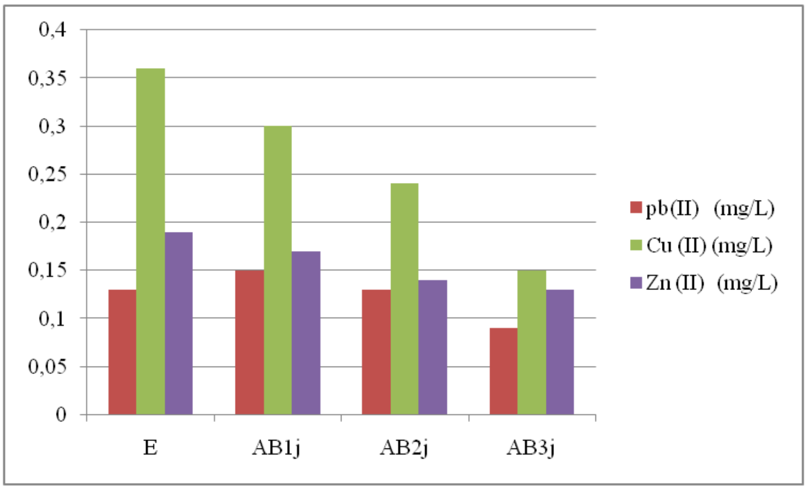


Fig.8. Variation of Zn (II), Pb (II), and Cu (II), of all samples (Raw wastewater (E): Raw wastewater treated with raw clay for one day (AB_{1D}); two days (AB_{2D}); three days (AB_{3D}))

The value of Pb (II) is 0.13 mg / L for raw water and varied between 0.09 and 0.15 mg / L for water treated crude clay we note that the concentration has declined with a reduction rate of 31%, these concentrations meet national and international water quality standards for irrigation on the long-term effect of 5 mg/L [18, 22].

The Cu (II) value of wastewater is less than 0.4 mg/L, this value is due to discharges from industrial textile, tannery and battery industries [23]. As regards the crude clay treatment, it yields a reduction in copper under the effect of adsorption, with a reduction rate of 47%, based on these results, the effect of clay is remarkable, and this is confirmed in another study concerning the removal of organic compounds by local clays [21]. The values recorded by clay are still lower than Algerian and international irrigation standards

4. Conclusion

The study was initially conducted to assess the removal of heavy metals from wastewater by El Menia crude clay. The results of the analysis of urban wastewater show the existence of pollution characterized by a strong organic load and made us conclude from the results of heavy metals that the raw water is not domestic wastewater; it is a mixture of urban and industrial water. The kinetic study of Zn (II) of raw clay shows that the equilibrium is established after 30 minutes and that the adsorption mechanism can be described by the pseudo-second order kinetics. The graph of the adsorption isotherms shows that the Freundlich model perfectly represents the adsorption of Zn (II) with clay coefficients R^2 of 0.995, it shows multilayer adsorption. The El Menia clay thus has an important adsorption capacity for the removal of Zn (II). According to the results of Zn adsorption (II); El Menia clay has an important adsorption capacity for the removal of heavy metals, a reduction rate ranging between 58% and 40% for Cu (II) and Pb (II), respectively.

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