Kinetics and isotherms studies on Cu^{2+} Adsorption unto PANa bead form from aqueous solutions

I. Ismi, H. Elaidi, E. H. Rifi, A. lebkiri, A. Skalli

Abstract— The equilibrium sorption of copper (II) into the sodium polyacrylate bead form was studied. The experimental data were fitted into following kinetic models: Lagergren pseudo-first order, the chemisorptions pseudo-second order and Elovich kinetic model. It was observed that chemisorptions pseudo-second order kinetic model described the sorption process with high coefficients of determination (R^2) better than any other kinetic models. The experimental data for the sorption of copper on the PANa bead form to different concentrations of the metal solution were fitted into Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms. Of the three adsorption isotherm, the R^2 value of Langmuir isotherm model was the highest. The maximum monolayer converge (q_m) from Langmuir isotherm model was determined to be 58.82 mg/g, the separation factor (R_L) indicating a favorable sorption experiment is $0<R_L<0.6$. The free energy value is -5.245 Kj/mol indicating that sorption is exothermic. The mean free energy was estimated from D-R isotherm model to be 707.2 KJ/mol which vividly proved that the adsorption is made by chemisorption.

Index Terms— Copper sorption, Isotherms, Kinetic models, Sodium polyacrylate.

---

1 Introduction

Heavy metals Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes) [1-6], high ambient air concentrations near emission sources, or intake via the food chain. Heavy metals are dangerous because they tend to bioaccumulate [7-8]. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Therefore, it is necessary to design feasible processes to minimize the pollution caused by Cu^{2+} discharges and reduce the risks associed to its presence in the environment.

A wide range of various treatment techniques such as ion exchange, biodegradation, oxidation, solvent extraction [9-10] and adsorption have been reported to be used for removal of heavy metal ions from industrial effluents [11-14]. However, adsorption has been universally accepted as one of the most effective pollutant removal process, with low cost, ease in handling.

The ability of this sorbent (PANa bead form) to remediate water contaminated with copper dye was investigated. The sorption capacity of PANa was evaluated using three equilibriums isotherm models (Langmuir, Freundlich, and D-R isotherm models) and the sorption dynamics were analyzed using pseudo first order, pseudo second order, and Elovich kinetic models.

Ilham Ismi, Laboratory of Organic Synthesis and Extraction Processes, Department of Chemistry, Faculty of Sciences, University Ibn Tofail, Kénitra, Morocco. E-mail: ilham123ismi@yahoo.com

2 Experimental Methods

2.1 Used materials

The sample used in this work is superabsorbent polymer which is present in spherical beads transparent, the diameters ranging between 2 and 3.5 mm. They introduce oneself in many colors from which the name: SEVEN COLOR CRYSTAL BOLL, reference SJQ-007, supplied by the company Xinchang Chengtan Magic Bean & Grass Doll Artware Factory of Origin: Zhejiang, China (Mainland).

2.2 Preparation of sorbent

Sodium polyacrylate has the drawback of being hygroscopic. This poses a problem for stability weighing especially when using very small quantities. To remedy this, we worked with gels (PANA swolled with distilled water).

We introduce a mass of gel equivalent to 0.035 g of dry poly mer in a filter bag (bag made filter paper) to avoid breaking the bead swelled by stirring the metal solution. This bag is closed with a wire which can also maintain the above has magnetic bar. Thus the gel is protected and levies can be made directly in the solution without problem drive from the gel grains in the samples assayed.

2.3 Preparation of aqueous solution

We prepared different solutions of known concentrations of copper metal from salt of copper nitrate ($Cu(NO_3)_2$), concentration at 6.8, 19.5, 49.5 and 103 ppm. The pH of each solution was adjusted by adding nitric acid or sodium hydroxide (pH = 5.5).

2.4 Sorption dynamics

They are used to model the much system kinetics and determining certain parameters such as the kinetic rate constant and the adsorbed amount at equilibrium as a function of operating conditions. Those constants are significant for designing an effective process. In this study we used the first, pseudo second order [15] and Elovich models [16].
The adsorption capacity was calculated using the following relation (1):

$$q_e = (C_o - C_e).\ V/m \quad (1)$$

With: q_e: adsorbed amount of copper on the sodium polyacrylate at equilibrium ($mg.g^{-1}$),
C_o: Initial concentration of copper in solution ($mg.L^{-1}$),
C_e: concentration of copper in solution at equilibrium ($mg.L^{-1}$),
V: volume of solution (L).

2.4.1 Pseudo- First Order Kinetics Model

The simple form of first order model by applying the boundary conditions, qt = 0 at t= 0 and qt = qt at t = t, is shown in Eq.(2).

$$\log(q_e - q_t) = \log q_e - k_1.t/2.303 \quad (2)$$

Where k_1 is the rate constant, q_e is the copper equilibrium concentration (mg/g); qt (mg/g) is the amount of adsorbed copper at any time t(min).

2.4.2 Pseudo Second Order Model

The general form of the model is given as Eq.(3).

$$dq/q_t = k_2.(q_e - q_t)^2 \quad (3)$$

By integration and linearization of Eq. (4) gives:

$$1/q_t = 1/Kq_e + t/q_e \quad (4)$$

In which, k_2 is the equilibrium rate constant (g/mg.min) of pseudo-second-order chemical sorption; q_e is the amount of adsorption sorbed at equilibrium (mg/g); q_t is the amount of adsorbate sorbed at t (min). The straight line plots of (t/q_t) vs t have been tested to obtain rate parameters [14].

2.4.3. Elovich Kinetic model

Elovich kinetic equation is presented as follows:

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln(t) \quad (5)$$

If the sorption of Cu^{2+} on PANa fits the Elovich Model, a plot of q_t versus ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ).

5.2 Sorption Isotherms

Equilibrium isotherm equations are used to describe experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent. The symbols and coefficients used in the equations are defined in the Nomenclature section.

2.6.1 Langmuir Isotherm Model

This model deals with monolayer and homogeneous adsorption because the adsorbed layer is one molecule in thickness, with adsorption occurring at fixed sites, which are identical and equivalent [17]. Linear form of this model is given in Equation (2):

$$C_e/q_e = (C_e/q_m) + 1/(1 + K_L.q_m) \quad (6)$$

Where C_e is the equilibrium concentration of copper in solution and q_e is the amount of copper in PANa surface, q_m is the monolayer adsorption capacity, and K_L is the constant of the Langmuir isotherm.

2.6.2 Freundlich Isotherm Model

Freundlich isotherm is related to the non-ideal and reversible adsorption, not limited to monolayer formation. Therefore is applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [17]. Linear form of this model is given as in Equation (7).

$$\log q_e = \log k + (1/n)\log C_e \quad (7)$$

Where *k* is multilayer adsorption capacity and *n* is adsorption intensity.

2.6.3 Dubinin-Rudeshkevich Isotherm Model

This isotherm is generally expressed as follows (Dubinin, 1960) [18]:

$$\ln q_e = \ln q_s - B\varepsilon^2 \quad (8)$$

With q_s ($mg.g^{-1}$) is the theoretical monolayer saturation capacity of the adsorbent and ε is Polanyi potential is given as follows:

$$\varepsilon = RT\ \ln(1 + (1/C_e)) \quad (9)$$

Radushkevich (1949) and Dubinin (1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant *B* is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship (Hasany and Chaudhary, 1996):

$$E = \sqrt{1/2B} \quad (10)$$

3 RESULTS AND DISCUSSION

3.1 Effect of initial Cu^{2+} concentration

Concentration values of 6.8, 19.6, 49.2 and 103 ppm which is equivalent to 10^{-4}, 3.10^{-4}, $7.7.\ 10^{-4}$ and $1.57.10^{-3}$ M, were considered. The extraction tests are performed under the same conditions: 25°C, pH value equal to 5.5, mass of gel equal to 7.5 g (equivalent to 0.035 g dry PANa) and fixed agitation speed (200 rpm). Only the metal concentration varies.
The effect of initial concentration on the sorption of copper on PANa bead form is presented in Figure 1.

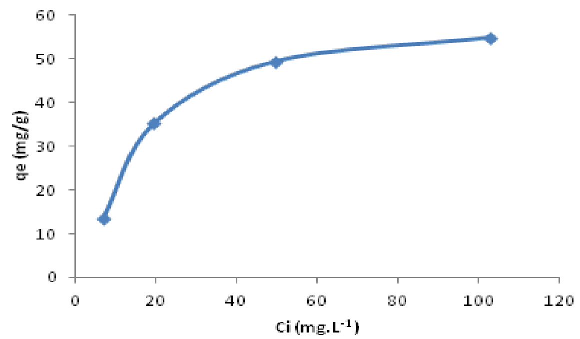


Figure 1. Effect of initial concentration (mg/l) and time on the sorption of Cu^{2+} byPANa beads form.

Generally speaking, the kinetics curves obtained show a rapid increase in the adsorption area of high concentrations (103 and 49.2 ppm). Then, the resulting saturation carboxylate sites involved in the adsorption process.

3.2 Effect of contact time

A quantity equal to 7.5 g of gel (equivalent to 0.035g of dry PANa) was contacted with a solution of copper nitrate at a concentration of 6.8 ppm (≈10^{-4} M), the pH of the solution was adjusted to 5.5. The mixture was agitated. We realized the kinetics of complexation of copper in solution, taking samples at regular intervals in order to know the time at which there is saturation of the gel of metal.
The effect of contact time on the sorption of copper on PANa bead form is presented in Fig.2.

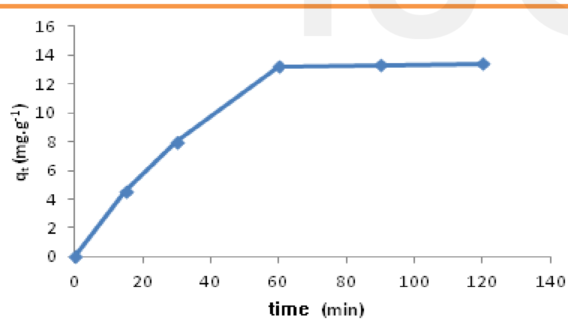


Figure 2 : Effect of contact time on Cu (II) adsorption by PANa bead form

Under these conditions, the gel reaches its saturation metal. After some time t, he settled a plateau for a value of q_e where the gel extraction reaches its equilibrium. To a 6.8 mg/L of copper concentration in the supernatant, the extraction equilibrium is reached after 60 minutes

3.2 Kinetic Adsorption Study

3.2.1 Pseudo first order model

First order rate constant was calculated by Equation (1) and by the plot in the figure 3. This model was not followed by adsorption of copper. The results are shown in table 1.

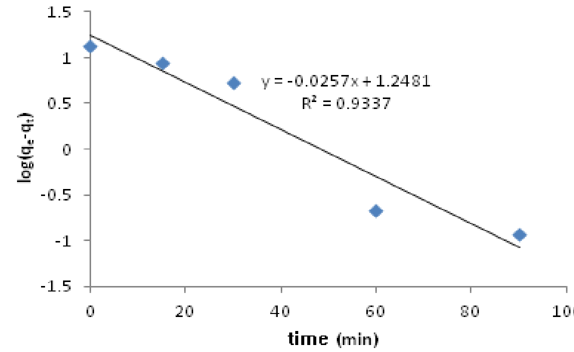


Figure 3 : Pseudo-first-order sorption kinetics of Cu(II) onto PANa bead form

3.2.2 Pseudo second order model

q_e (exp) values for the first-order-rate expression do not agree with the calculated ones obtained from the linear plots. In contrast, qe (calc) values for the second-order-model are close to qe (exp) which suggest the process of adsorption is chemisorption. In chemisorption process, the pseudo second order is superior to pseudo-first order model because it deals with interaction of adsorbent-adsorbate through their valency forces. The correlation coefficients and other parameters calculated for the Pseudo-first order model and pseudo-second order model are listed in Table 2. From the table, it is clear that the relative difference values of the pseudo-first order model for copper greater than those obtained for the pseudo-second order model.

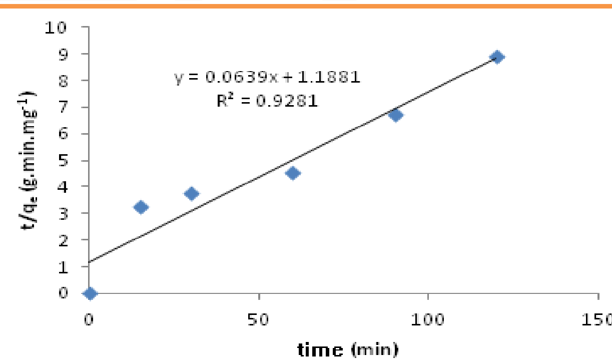


Figure (4) : Pseudo-second order sorption kinetics of Cu(II) onto PANa bead form

TABLE 1

PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC MODEL PARAMETERS FOR COPPER ADSORPTION ONTO PANA BEAD FORM.

Model	*Pseudo-first order*				*Pseudo-second order*			
Adsorbate	*Parameters*				*Parameters*			
Copper	q_e (calc)	K_1	R^2	Relative diffèrence (%)	q_e (calc)	K_2	R^2	Relative diffèrence (%)
	13.43	17.10	0.933	24.12	15.64	0.0344	0.928	14.13

3.2.3 Elovich Kinitic model

The Elovich kinetic model was also applied to the experimental results. The results are shown in Figure (4). The constants α, β and R^2 are summarized in Table (III).

R^2 values are close to unity, $R^2 > 0.91$. This probably means that the adsorption is chemisorption types. The initial rate of adsorption on the PANa in the form of bead is 2.1. While the constant desorption of copper for the PANa is equal to 0.328.

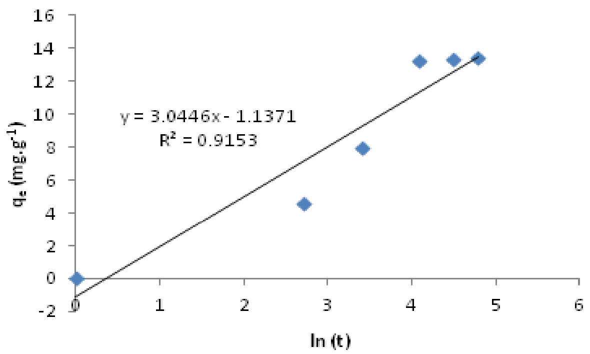


Figure (5) : Elovich sorption kinetics of Cu(II) onto PANa bead form

TABLE 2

ELOVICH KINETIC MODEL PARAMETERS

Prameters	*α*	*β*	*R²*
PANa bead form	2.1	0.328	0.9153

3.3 Equilibrium Isotherms

Figure (2) shows the variation of the adsorption capacity q_e as a function on the initial concentration of the copper in metallic solution.

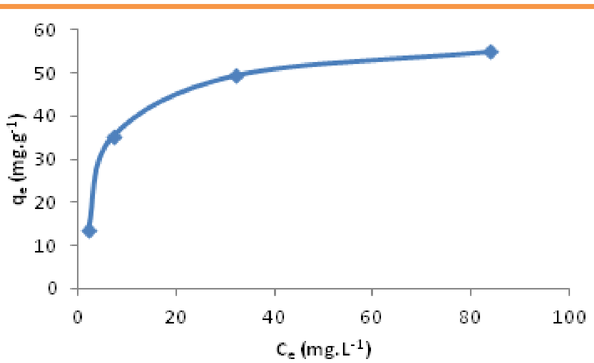


Figure 6 : Adsorption isotherms of copper on the PANa bead form

The parameters of Langmuir and Freundlich models are shown in Table 3.

TABLE 3

LANGMUIR AND FREUNDLICH MODEL PARAMETERS OF COPPER ADSORPTION ON PANA BEAD FORM.

Isotherm	*Langmuir*					*Freundlich*			
Adsorbate	*Parameters*					*Parameters*			
Copper	q_m	K_L	$\Delta G°ads$	R^2	R_L	K_f	1/n	n	R^2
	58.82	0.149	-5.245	0.9993	$0<R_L<0.6$	12.34	0.37	2.7	0.87

Adsorption tends to have n between 1 and 10. Larger value of *n* implies stronger interaction between the PANa and the copper. The *n* values were 2.7, showing that adsorption process was favorable. The multilayer capacities factor of copper (K_f) shows the good interaction between the PANa and the copper. The Freundlich equation for the adsorption of copper on the PANa bead form (11) is:

$$q_e = 12.34.\ C_e^{2.7} \quad (11)$$

The Langmuir adsorption isotherm is commonly applied to monolayer chemisorptions of gases. This isotherm is mainly applied when no strong adsorption is expected and when the adsorption surface is uniform. The Langmuir isotherm shows that adsorption will increase with increasing copper concentration up to a saturation point, in which all of the sites are occupied (Fig. 8).

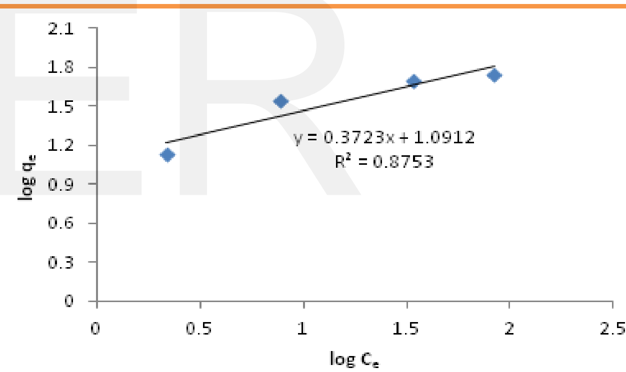


Figure 7 : Model Freundlich isotherm

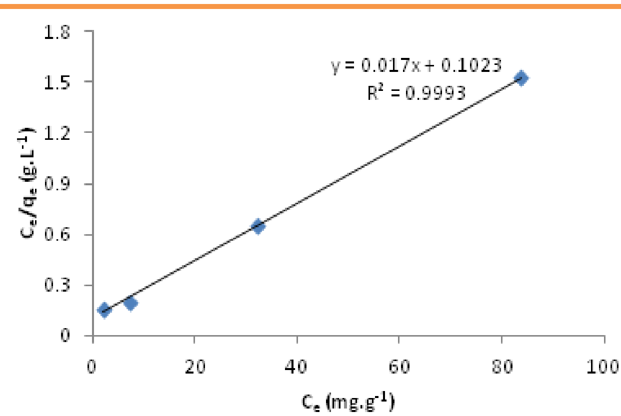
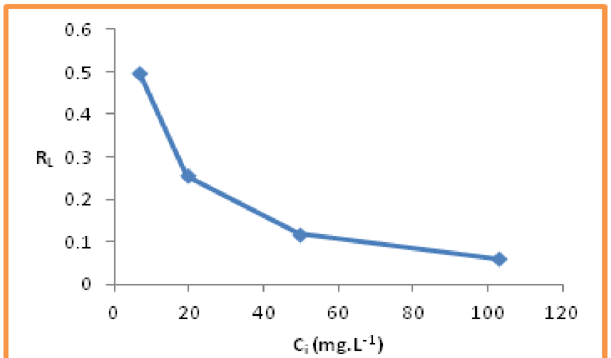


Figure 8 : Model Langmuir Isotherm

The essential feature of the Langmuir isotherm can be expressed by means of the dimensionless constant separation factor [19] which is calculated using:

$$R_L = 1/(1+K_L.C_o) \qquad (12)$$

Where K_L is the Langmuir constant and C_o is the initial concentration.
The R_L for adsorption of copper on PANa bead form is shows in figue 9.



Figur 9 : Separation factor profile

A R_L value less than unity represent a favorable adsorption and a value greater than unity represents an unfavorable adsorption. For an initial concentration of 6.8 mg.L^{-1}, are the value of R_L is 0.13. These estimated values of R_L that are less than unity and do not exceed 0.5, clearly show a very favorable copper adsorption on the PANa bead form. Adsorption becomes more favorable as the initial concentration of Cu^{2+} ions increases. The increased presence of Cu^{2+} ions in the supernatant solution favors adsorption on PANa.
A temperature studied, the free energy of adsorption $\Delta G°_{ads}$ can be calculated by the following equation:

$$\Delta G°ads = - RT(\ln K_L + 4.02) \qquad (13)$$

$\Delta G°_{ads}$, R, K_L and T represent the free energy of adsorption, the ideal gas constant, the absolute temperature and the Langmuir constant, respectively. The free energy of adsorption of the PANa bead form will:
$\Delta G°ads$ =-5.24565 Kj/mol
Adsorption is exothermic, since the energy of the reaction is negative. In this case, the solution balances its temperature by yielding heat in the environment. The value of the free energy of adsorption demonstrates spontaneous nature of the process involved.
When C_o increases to 103 ppm, the separation factor approaches 0. All sites are saturated and there are almost no vacant sites. The molecules located near a vacant site are more likely to be desorbed, as they are agitated and not compacted in the adsorbed layer. In the case of 103 ppm concentrations, the layer is uniform and has only occupied sites.
The Langmuir equation for copper adsorbed on the PANa bead form (14) is:

$$q_e = 8.76\, C_e/1+0.149C_e \qquad (14)$$

All the Langmuir, Freundlich adsorption isotherms showed linear relationship on the present results shown in Figs. 8 and 9 for the Langmuir, Freundlich adsorption isotherms, respectively, but R^2 for the Langmuir adsorption isotherms is larger than that in Freundlich adsorption isotherms and close to 1.
q_s and B isothermal constants of the Dubinin-Radushkevich model (Table 4) were obtained from the intercept and the slope of the curve depending on ln(qe) and ε^2, respectively (Figure 10).

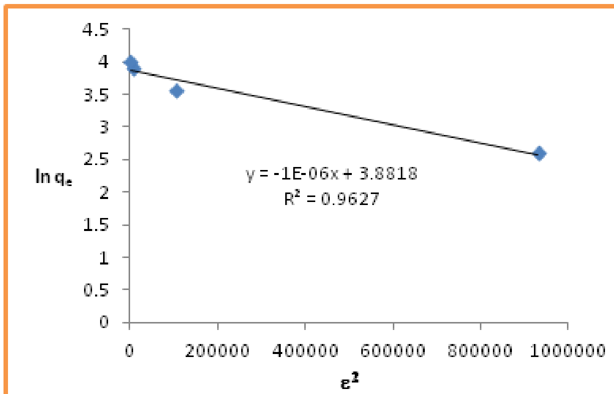


Figure 10 : Model Dubinin-Rudeshkevich Isotherm

Table 4
D-R isotherm model parameters and correlation coefficient of copper adsorption on PANa bead form.

Isotherm	*Dubinin-Radushkevich*				
Adsorbate	*Parameters*				
	q_s	*DR(%)*	*B*	*E*	R^2
Copper	48.51	13.2	10^{-6}	707.2	0.963

The magnitude of E is useful for estimating the type of adsorption process. The resulting value is 707.2 KJ.mg-1, which is greater than the energy range of the adsorption reactions (16 KJ.mg-1), knowing that the energy value ranging from 8-15 KJ mg^{-1} shows the ion exchange. Thus, the type of adsorption of the copper on the sodium polyacrylate has been defined as a chemical adsorption (chemisorption), which is proved by the kinetic study. The D-R equation for copper adsorbed on the PANa bead form (15) is:

$$q_e = 48.51 \exp(-10^{-6}\, \varepsilon^2) \qquad (15)$$

4 Conclusion

The results for the different models of adsorption are found that the adsorption of copper on the PANa bead form follows the Langmuir model because it has the highest linear regression. All adsorption sites are equivalent and the ability of copper to adsorb at a given site is independent of the occupation of neighboring sites. It seems that a specific adsorption of copper ions on the charged sites PANa bead form occurs. There continues to be involved with compatibility between the copper and an inclusion in the pores. The inclusion in the pores occurs after all the surface sites are occupied. The adsorption is monolayer. In addition, the adsorption is made by chemisorption (pseudo-first and Elovich kinetic model).

ACKNOWLEDGMENT

Sample Types analysis was performed using the ICP in the national center for scientific and technical research of morocco.

REFERENCES

[1] PB. Tchounwou, CG. Yedjou, AK. Patlolla, DJ. Sutton. "*Heavy metal toxicity and the environment*", US National Library of Medicine National Institutes of Health, EXS, 2012;101: pp. 133-64. doi: 10.1007/978-3-7643-8340-4_6.

[2] L. Järup. "*Hazards of heavy metal contamination*", US NATIONAL LIBRARY OF MEDICINE NATIONAL INSTITUTES OF HEALTH, BR MED BULL, 2003;68:pp. 167-82.

[3] GF. Nordberg, RA. Goyer, TW. Clarkson. "*Impact of effects of acid precipitation on toxicity of metals*", US NATIONAL LIBRARY OF MEDICINE NATIONAL INSTITUTES OF HEALTH, ENVIRON HEALTH PERSPECT, *1985 Nov;63:pp. 169-80.*

[4] EJ. Tokar, L. Benbrahim-Tallaa, MP. Waalkes, "*Metal ions in human cancer development*". US NATIONAL LIBRARY OF MEDICINE NATIONAL INSTITUTES OF HEALTH, MET IONS LIFE SCI. *2011;8:pp.375-401.*

[5] M. Corradi, A. Mutti,, "*Metal ions affecting the pulmonary and cardiovascular systems*". US NATIONAL LIBRARY OF MEDICINE NATIONAL INSTITUTES OF HEALTH, MET IONS LIFE SCI. *2011;8:pp. 81-105.*

[6] M. Valko, H. Morris, MT. Cronin, "*Metals, toxicity and oxidative stress*". US NATIONAL LIBRARY OF MEDICINE NATIONAL INSTITUTES OF HEALTH, CURR MED CHEM. *2005;12(10):pp. 1161-208.*

[7] A. Kumar, SK. Maiti, "*Translocationand Bioaccumulation of Metals in Oryza sativa and Zea mays Growing in Chromite Asbestos Contaminated Agricultural Fields, Jharkhand, India*". Bull Environ Contam Toxicol. 2014 Aug 2. [Epub ahead of print]

[8] G. Bidar, C. Pruvot, G. Garçon, A. Verdin, P. Shirali, F. Douay. "*Seasonal and annual variations of metal uptake, bioaccumulation, and toxicity in Trifolium repens and Lolium perenne growing in a heavy metal-contaminated field*". Environ Sci Pollut Res Int. 2009 Jan; 16(1):pp. 42-53, doi: 10.1007/s11356-008-0021-4.

[9] RW. Peters. "*Chelant extraction of heavy metals from contaminated soils*". J Hazard Mater. 1999 Apr 23; 66(1-2): pp. 151-210.

[10] E. H. Rifi, D. Lakkis, J.F. Maurice Leroy." *Extraction of silver by gels of sodium polyacrylic-polyacrylate acid. Application: elimination of chloride anions*". Comptes rendus - Chimie. 2005 , 8(5): pp. 917-921

[11] L. Di Palma, R. Mecozzi,"*Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents*". J. Hazard Mater. 2007 Aug 25; 147(3):pp. 768-75.

[12] S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack. "*Extraction of heavy metals from soils using biodegradable chelating agents*". Environ Sci Technol. 2004 Feb 1; 38(3):pp. 937-44.

[13] CS. Lee, MM. Kao. "*Effects of extracting reagents and metal speciation on the removal of heavy metal contaminated soils by chemical extraction*", J Environ Sci Health A Tox Hazard Subst Environ Eng. 2004;39(5):pp. 1233-49.

[14] S. Babel, D. del Mundo Dacera." *Heavy metal removal from contaminated sludge for land application: a review*". Waste Manag. 2006;26(9):pp. 988-1004. Epub 2005 Nov 17.

[15] A. Abdellah, I. Abdelkader, S. O. Mohand. "*Hg(II) Sorption from Aqueous Solution by Blast-furnace Slag*", Water qual.Res. J. Canada 2007, vol 42. No 1.

[16] Y.S. Ho, G. McKay. "Application of Kinetic Models to the Sorption of Copper (II) on to Peat". Adsorption Science & Technology Vol. 20 No. 8, 2002.

[17] H. Chafai, H. Lotfi , M. Bazzaoui , A. Albourine. "*Adsorption du salicylate de sodium et du Cr(VI) par le polypyrrole*", *J. Mater. Environ. Sci. 4 (2) (2013), pp.285-292.*

[18] A. U. Itodo, H. U. Itodo. "*Sorption Energies Estimation Using Dubinin-Radushkevich and Temkin Adsorption Isotherms*". Life Science Journal, Volume 7, Issue 4, 2010.

[19] S. Jodeh, O. Khalaf, A. Abu Obaid, B. Hammouti, T. B. Hadda, W. Jodeh, M. Haddad, I. Warad. "*Adsorption and Kinetics Study of Abamectin and Imidacloprid in Greenhouse Soil in Palestine*", J. Mater. Environ. Sci. 5 (2) (2014), pp. 571-580.