Copper (II) ions removal from aqueous solution using bentonite treated with ammonium chloride

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Abstract: A raw bentonite, obtained from Maghnia (Western Algerian) was impregnated into 1M ammonium chloride solution and thermally treated in a furnace at 200 °C during one hour. This treatment has improved its removal capacity of copper from aqueous solutions to about 30 %. The performances of the copper adsorption of this new material, after its physicochemical treatment, were evaluated by quantitative analysis on the copper remaining in the solution. The interface phenomena of bentonite- Cu2+ aqueous solution adheres to the Langmuir and Freundlich models. The adsorption energy, calculated by using Dubinin-Radushkevich equation, has proved that the removal of copper with this clay material is an ion exchange process. Nevertheless, the thermal treatment of this clay has inhibited the temperature effect on the retention of copper ions. Thus, the kinetic law governing the copper adsorption described here is following a second order model.

Keywords: Bentonite Activation, Ammonium Chloride, Removal Of Copper (II)

1. Introduction

Heavy metals are toxic substances present in the nature with tolerable quantities, but their accumulation due to the diverse rejections of agricultural and industrial activities has became a real threat to the environment. In order to treat the contaminated effluents of these inorganic pollutants, traditional physicochemical methods are, generally, used such as activated carbon molecular sieves, reverse osmosis, ion exchanging resin and electrodeposition have been applied. However, several difficulties which are essentially associated with the bad control of technology, availability and high cost of the methods. This situation has motivated some researchers to investigate other alternatives oriented to the use of natural materials as adsorbent that can eliminate toxic substance from aqueous solutions [1-4].

Among recent published works of this subject, the removal of copper (II) ions from the liquid rejections has attracted the attention in the literature [5-7]. The use of bentonites in the elimination of this pollutant appears to be the most studied methods [2,3]. The montmorillonite, which is considered as the main component of bentonites of Maghnia [8], is a clay of smectites family that have good adsorption properties due to its specific surface and cation exchange capacity (CEC) [9]. Many works have been devoted to improve above mentioned properties, for instance, [10-13]. The improvement can be brought by a chemical or thermal activation of this material. The activation technique by chemical ways should avoid the use of strong acids which can cause two major inconveniences:

Reduction of the cation exchange capacity (CEC) of the clay [14,15].

During the activation process, the effluents generated cannot be easily eliminated.

The ammonium chloride, which is a weak acid, may decomposes under the action of heat and release ammonia gas that shifts the equilibrium to the formation of hydrochloric acid in low concentration [16,17]. This decomposition, catalyzed in the presence of water, is almost total around 350°C [17]. The formed protons are responsible to the dissolution of crystalline carbonates impurities and also the attack of the octahedral layered alumina backbone that vulnerable to the strong acids. Consequently, the specific surface area and porosity of this material increase together with the increment in number of acid sites on the surfaces. These properties are accounted for the best adsorption properties of the material [14,16,18,19]. It is important to

note that the chloride ions did not bring any changes to the specific surface seeing that they did not attack the backbone of this material [20].

In a previous study [16], we had shown that the use of strong acids instead of ammonium chloride solution allows the control of the evolution kinetic of the exchange capacity and specific surface area of bentonite. Also, the use of the impregnation technique followed by a heating in the oven has increased the temperature of activation and meanwhile, reduced the heating duration, giving a very efficient material for the bleaching of crude edible oil [21].

In order to extend the range of applications of this new activation technique, we have attempted to study the adsorption of copper (II) ions on bentonite processed with this activation method. The objective of this work is to study the optimal conditions of activation of bentonite after its impregnation in a molar solution of NH4Cl by heating them in a muffle oven and investigate of the kinetic and thermodynamic phenomena governing the mechanism of the removal of copper (II) ions present in aqueous solutions.

2. Experimental

2.1. Material

The raw bentonite (BN) used in this study was gracefully offered to us by Bental society (Algeria). BN was collected from Maghnia region (west of Algeria). Its chemical composition is given in the Table 1. The cation exchange capacity (CEC) of raw bentonite was measured using the methylene blue and the capacity was 23.3 mmole.100 g-1 [22]. All chemicals are analytical grade RP. The copper (II) solutions were prepared by dissolving CuNO3 in distilled water. The pH of these solutions was measured by a pH-meter Schott CG711 equipped with a combined glass electrode. The heating of bentonite samples was carried out in a muffle oven (Nabertherm D-2804) consisting of a temperature control system (Tmax = 1200 °C). The analyses of Cu2+ were recorded on atomic absorption spectrophotometer (SP9 Pye Unicam) with flame generated by air–acetylene and a copper lamp, fixed at wavelength λ= 324.8 nm.

Table 1. *Chemical composition of raw bentonite (BN) (Bental source).*

Component	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO	TiO_2	P. F.	Total
% mass	57.8	19.7	1.6	3.56	1.5	1.26	2.1	0.04	0.13	12.2	99.9

2.2. Methods

2.2.1. Characterization of the Porous Texture of Raw Bentonite

The porous texture of bentonite was characterized by using Micromeritics ASAP2010 for nitrogen gas adsorption analysis at 77 K. This step was achieved after degasification of the clay samples under continuous vacuum for twelve hours at 160 °C. The BET equation was developed in the relative pressures ranging between 0.039 and 0.200. The results of the relative pressure based on the volume of nitrogen adsorbed allowed us to calculate various parameters of texture (Table 2) by using the BET (Brunauer-Emmet-Teller) and BJH (Barret-Joyner-Halenda) equations.

Table 2. *Porous texture of raw bentonite(BN).*

Para-meters	S_S (m^2g^{-1})	V_P (cm^3g^{-1})	S_P (cm^2g^{-1})	D_P $(A°)$	V_{mic} (cm^3g^{-1})	S_{mic} (cm^2g^{-1})
Value	57.9	0.11	99.2	60.8	0.004	9.34

S_S: specific surface area; V_P: pore volume; S_P: pore surface ; D_P: pore diameter;

V_{mic}: micropore volume ;S_{mic}: micropore surface.

2.2.2. Thermal Treatment of Bentonite Impregnated by NH$_4$Cl (1M)

The raw bentonite was crushed and sieved several times over 50 μm screen. This no-treated solid was noted as BN. A part of this pre-treatment BN was impregnated into 1M NH$_4$Cl solutions with the bentonite / NH$_4$Cl solutions ratio of 1:1 w/w. The suspension was left overnight at the ambient temperature under constant stirring, then dried in an oven at 60 °C for several days without washing. The dried material, after a fine crushing, was put in porcelain crucibles and heated in a furnace with controlled temperature values ranging between 100 and 500°C at fixed period of times. The BN clay samples, heated at 100°C, were placed in the furnace for the different exposition times: 0.5; 1; 2; 3; 4; 5 and 6 hours. This operation was repeated, in the same manner at 200, 250, 300, 350, 400, 450 and 500 °C. After cooling, each bentonite sample was washed with distilled water until all chloride ions were removed (confirmed with silver nitrate test). These materials were crushed and sieved over 0.05 mm screen. The bentonite obtained was noted as BA and used to investigate its Cu^{2+} removal ability.

2.2.3. Removal of Copper (II) by Bentonite

In a 250 mL polyethylene bottles, a mass of m (g) activated bentonite (BA) or raw bentonite (BN) was dispersed into 100 mL of copper solution with initial concentration C_0 (mg L^{-1}). The pH of suspensions varies between 5.5 and 6 (natural pH of suspensions). The suspensions were centrifuged after continuous stirring and the concentration of Cu^{2+} at the equilibrium state, C_e (mg L^{-1}), where the supernatant was measured, was obtained.

2.2.4. Effect of the Physicochemical Parameters

The determination of optimum experimental conditions, for bentonite treatment and metal removal, were systematically through the study of following parameters:

Temperature and duration of heating in oven.
Contact time of bentonite-copper (II) solution mixture.
The effect of clay titration (g bentonite / 100 mL copper

(II) solution).

Temperature influence on the adsorption of copper (II) ions

3. Results and Discussions

3.1. Effect of the Temperature and Heating Times

0.2 g bentonite (BN or BA) was introduced into a polyethylene bottle containing 100 mL of aqueous solution of Cu^{2+} with an initial concentration, C_o of 50 mg L^{-1}. The suspensions were maintained under constant stirring at room temperature overnight. The supernatant of each bottle was analyzed and the results were represented on the Fig. 1.
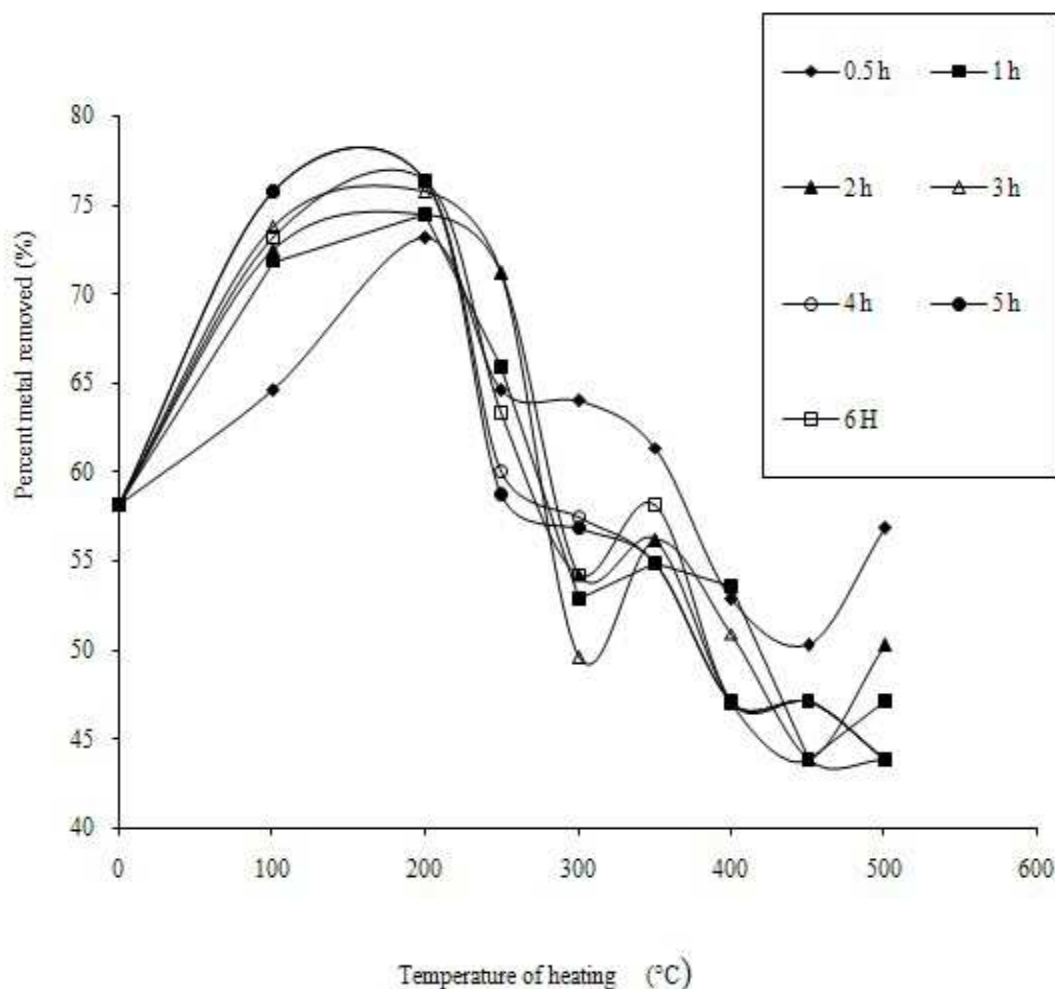

Figure 1. Effect of the temperature (°C) and heating duration (h) on the removal efficiency of Copper (%) from aqueous solution.

Raw bentonite BN (non- heated), possesses adsorption properties towards elimination of copper (II) ions from its aqueous solutions. The Cu^{2+} removal efficiency of BN was approximately 58 %. The curves of Fig. 1 show two distinct shapes, before and after the heating at 200 °C respectively. Below 200 °C, the removal efficiency of this material increases with as heating temperatures of bentonite increases. This can be explained as the result of increasing specific surface area that inducing an increment in number of adsorption sites [11]. When this material is heated at temperature higher than 200 °C, corresponding to the second shape, it loses more and more its adsorption properties.

It was literately reported that Cu^{2+} ions exist in diverse cation forms, such as $Cu(OH)^+$ and of $Cu_2(OH)_2^{2+}$, when

the pH of reaction medium near to 6 [6,10,11,23]. The reaction of decomposition of NH_4Cl by heating between 100 °C and 200 °C produces protons that are sufficient to dissolve the mineral elements of the clay structure which is vulnerable to acid attack. This causes the formation of significant mesoporosity in the clay. It must also be noted that the water molecules adsorbed in the interlayer space of bentonite begins to desorb at 200 °C. The combination of both of these factors agrees with the creation of new Lewis and Bronsted acid sites that are responsible for the adsorption phenomena [10,11]. These factors increase the ion exchange capacity of BA induce a real improvement in the absorption properties of this material.

When the temperature is fixed at above 200 °C, the decomposition kinetic of NH_4Cl is accelerated by the forma-

tion of strong acidity and meanwhile, causing the destruction of adsorption sites [11,16]. Consequently, this directly reduces the Cu^{2+} ions removal capacity of bentonite [10,11,23].

It is also important to note that when heating the NH_4Cl impregnated material at temperature below 200 °C the number of adsorption increased significantly whereas destruction of the same sites was noted at temperature higher than 200 °C. This behavior suggested us to fix the working temperature strictly at 200 °C for one hour for the continuation of this study.

3.2. Effect of Contact Time Bentonite – Solution of Copper(II)

0.2 g bentonite (BN or BA) was added to 100 mL of Cu^{2+} aqueous solution (C_o = 50 mg L^{-1}) to form a suspension. This suspension is maintained under constant stirring at room temperature for a fixed period of times [10-250 min]. The supernatant is then analyzed by spectrophotometer atomic adsorption at 324.8 nm, and the results obtained are represented in the Fig. 2.

The shapes of the curves in Fig. 2 show that the rate of elimination of Cu^{2+} increases rapidly until it reached an equilibrium state after 45 min. The maximum values reached 62 % for a non-treated bentonite (BN) and 69 % for an activated bentonite (BA) (as shown in Fig 2). However, according to Fig 1, the Cu^{2+} removal efficiency by raw bentonite BN is approximately 58 % overnight.
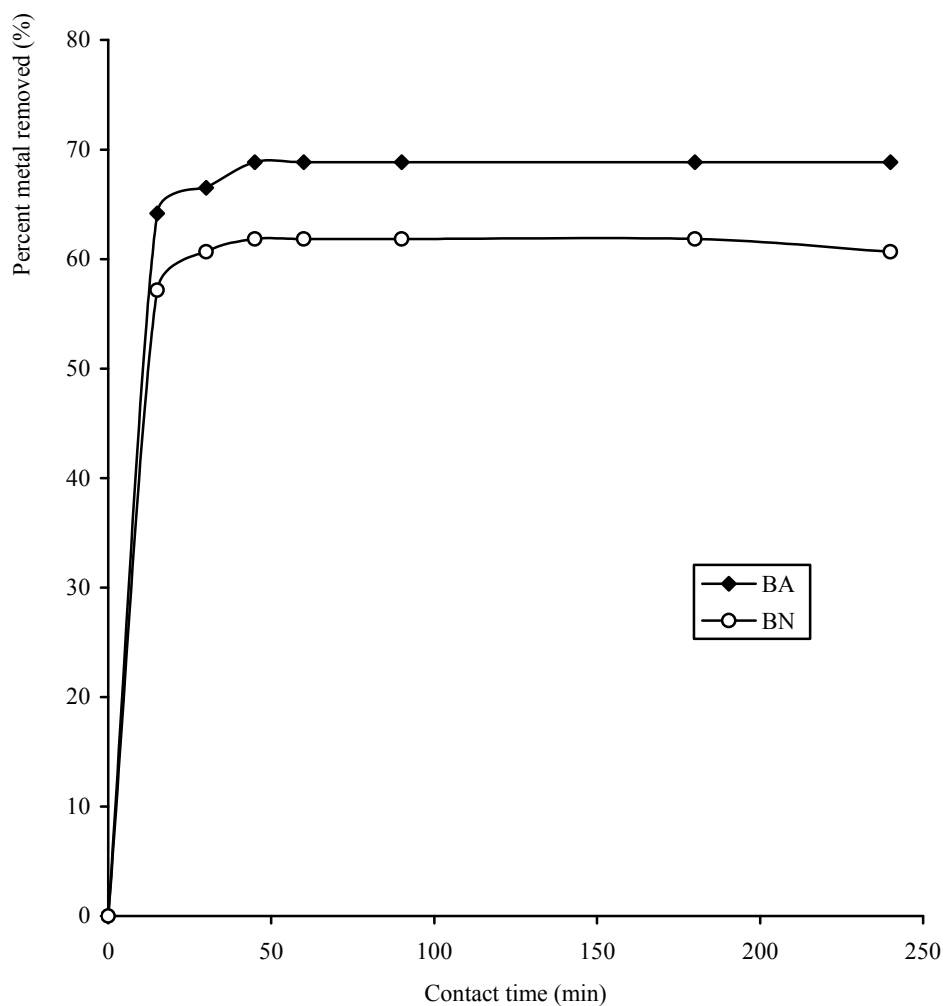

Figure 2. Effect of contact time on the efficiency of copper (II) removal by bentonite.

In order to improve the accuracy of results, the contact time of bentonite-copper (II) solution was set at 120 min.

3.3. Effect of Clay Dosage

A mass m (g) (m ranging between 0.1 and 0.6 g) of bentonite was added to 100 mL of aqueous solutions of copper (II) ions that the initial concentration, C_o= 50 mg L^{-1} and

the suspensions was maintained under constant stirring at room temperature for 120 min. The results obtained are summarized in Fig. 3.

The curves of Fig. 3 show that the maximum removal efficiency of Cu^{2+} by BN is 74.6 %. This percentage of Cu^{2+} removed was significantly increased to 90 % by a simple thermal treatment of the same material (BN). These maxi-

mum values of rate were obtained when the dosage of bentonite (either BN or BA) is 0.4 g/ 100 mL. Beyond this ratio, the curves reach a level in which the quantity of Cu^{2+}

adsorbed remains constant. Thus, it can be concluded that the activation of bentonite is able to improve the removal rate of copper (II) ions.
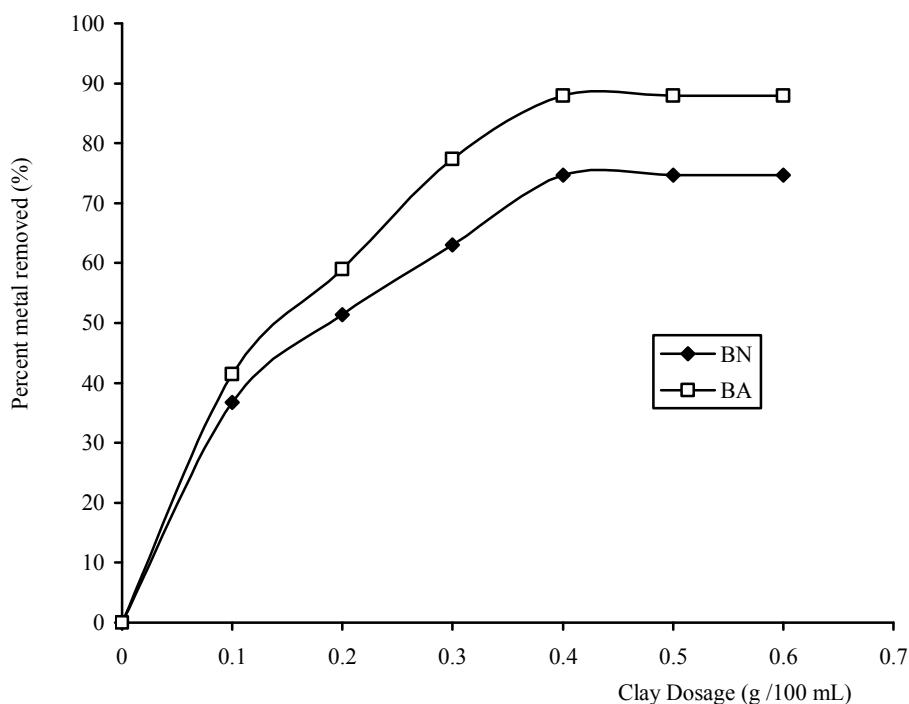

Figure 3. Effect of clay dosage (g/100 ml) on removal efficiency (%) of Cu (II)

3.4. Adsorption Isotherms

The adsorption isotherms are, in general very significant in describing the phenomena of different interactions existing at the solid - solution interface. Nevertheless, the reaction mechanism in aqueous solution seems to be very complicated. The adsorption phenomenon is always correlated with theoretical equations which can be described by isotherms as shown by equations below [11,12,23,24].

Freundlich isotherm is used as the model to describe the adsorption on heterogeneous surfaces [23]. This isotherm can be expressed by the following equation:

$$\frac{X}{m} = K \, C_e^{\frac{1}{n}} \tag{1}$$

Whereas, C_e is the equilibrium concentration of the solution (mg L⁻¹), X/m is amount of adsorbed copper (II) ions per unit of clay mass (mg g⁻¹), K is Freundlich constant and 1/n represents the adsorption intensity. This equation was linearized as following:

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log C_e \tag{2}$$

The curve representing logX/m agains logCe allows us to calculate the parameters of Freundlich isotherms. Thus, the results obtained are shown in Table 3.

Table 3. Parameters of Langmuir, Freundlich and Dubinin-Radushkevich isotherms.

Bentonite	Langmuir				Freundlich			Dubinin-Radushkevich			
	b dm³g⁻¹	Q° mmole g⁻¹	r²	R_L	n	k	r²	β mol² J⁻²	q_DR mmol g⁻¹	r²	E kJ mol⁻¹
BN	0.04	0.12	0.98	0.32	1.5	0.46	0.995	10⁻⁹	0.21	0.98	10
BA	0.31	0.18	0.99	0.04	3.2	3.74	0.982	10⁻⁹	0.57	0.98	15.8

Langmuir isotherm model describe the systems that having a simple monolayer adsorbed on the surface. This model has supposed that the adsorption takes place at a specific adsorption sites. The interaction forces between molecules and adsorption sites decreased as these molecules become further from the same surfaces [23]. So, Langmuir isotherm can be defined according to the following equations:

$$\frac{X}{m} = \frac{Q_o \, b \, C_e}{1 + b \, C_e} \tag{3}$$

While Q_0 is the monolayer capacity (mg/ g) and b is the equilibrium constant (dm³ g⁻¹).

$$\frac{C_e}{\frac{X}{m}} = \frac{1}{Q_0 \, b} + \frac{C_e}{Q_0} \tag{4}$$

The curve representing Ce/X/m versus Ce allows calculating the parameters of Langmuir isotherms. The results obtained are shown in Table 3.

The main characteristic of the Langmuir equation is the dimensionless constant called equilibrium parameter, R_L [5]. The Parameter gives information on the type of equilibrium which takes place between two phases (eg. liquid-solid). The R_L can be expressed by equation (5):

$$R_L = \frac{1}{1 + b\, C_o} \qquad (5)$$

The C_o is the highest initial concentration (mg L^{-1}). The value of R_L indicates that the type of isotherm is: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$) or linear ($R_L = 1$). In this study, the results (see Table 3) of R_L show that adsorption on both BN and BA surface are favorable.

Langmuir and Freundlich isotherms appear to be insufficient to express all the physical and chemical characteristics of the adsorption. The Dubinin-Radushkevich (D-R) isotherm is commonly used to study the adsorption of metallic ions on clay materials [24]. The D-R isotherm is expressed by the following equation:

$$\frac{X}{m} = q_{DR}\left[\exp(-\beta\,\varepsilon^2)\right] \qquad (6)$$

Where X/m is the amount of heavy metal that was removed per mass unit of clay (mg/g), q_{DR} is the D-R adsorption capacity (mg/g), ε is the Polanyi potential which is related to the concentration at the equilibrium state and expressed by equation (7).

$$\varepsilon = RT \ln(1 + \frac{1}{Ce}) \qquad (7)$$

Where R is the constant (kJ K^{-1} mol^{-1}) of perfect gases and T the absolute temperature (K), β is the constant related to the adsorption energy E. The main energy of adsorption is calculated by using E = $(2\beta)^{-1/2}$ where, E gives information about the physical and chemical features of the adsorption. The numerical value of sorption energy varies in the range of 1.00 – 8.00 and 9.00- 16.00 kJ mol^{-1}, for physical and chemical adsorption respectively. For some authors, the adsorption energy of an ion-exchange mechanism is within the range of 9-16 kJ mol^{-1} [5]. However the equation of D-R can give an estimation for the maximum capacity of adsorption by a solid-solution system. Its expression is given by the linearization of the following equation:

$$\ln \frac{X}{m} = \ln q_{DR} - \beta\,\varepsilon^2 \qquad (8)$$

The curve representing ln X/m versus ε^2 allows us to calculate the D-R parameters. So, the results obtained are gathered in Table 3.

The study of the isotherms of Freundlich, Langmuir and

Dubinin-Radushkevich was carried out using suspensions of 0.4 g bentonite in 100 mL of solutions. The initial concentrations vary between 15 and 70 mg/L of Cu^{2+}. These suspensions were maintained at room temperature under constant stirring for 120 min. The results obtained for the three isotherms studied are given in Table 3.

The examination of the results given in Table 3 shows a sharp increase in the parameters of Freundlich and Langmuir after thermal treatment of the bentonite.

After treating at 200 °C for one hour, the molecular monolayer of Langmuir and their adsorption capacities have shown an increment from 0.12 to 0.18 mmole g^{-1}. This has caused an increase in the adsorption capacity of BN without reaching its CEC value of 0.23 mg/g. This behavior is in agreement with the mechanism involving the copper (II) adsorption thru cationic exchange [11]. The dissolution of the mineral substances under the effect of strong acidity implies a high level of division of clay that allows the access to more exchange sites this leads to an improvement of exchange capacity [16]. In connection to this, it must also be noted that additional effect of hydrochloride acid, resulting from the decomposition of NH$_4$Cl at 200 °C, which cannot be excluded. During the decomposition process, the edges of clay sheets could be opened to increase its surface area and pores diameter [11].

The values of R_L constitute a good illustration for a favorable adsorption of copper (II) ions by this bentonite. Moreover the R_L value of BA is close to zero (0.04), indicating that the adsorption phenomenon is spontaneously produced [11,25].

It was noted that the Freundlich parameters increase as expressed by the constant K and n, which increased from 0.46 to 3.74 and 1.51 to 3.21, respectively. The adsorption intensity given by the Freundlich coefficient (1/n) is smaller than the unity: these values are 0.66 and 0.31 for BN and BA respectively. These results indicate that the adsorption of Cu^{2+} onto the bentonite samples under the studied experimental conditions is favorable, confirming the previously mentioned conclusions about R_L parameter [26].

However, the Dubinin-Radushkevich (D-R) isotherm results obtained have shown that energy, E varies from 10 kJ mole^{-1} to 15.8 kJ mole^{-1}. These values are compatible with the mechanism of elimination of copper (II) ions by bentonite thru ionic exchange process as reported in the literature [5,24,25].

3.5. Adsorption Kinetics

Two models were used to interpret the experimental results obtained during the examination of the adsorption kinetic of copper (II) ions onto the bentonite, that is, the pseudo-first-order and the pseudo–second–order models [10-12,23,27,28].

The adsorption rate constant proposed by Lagergren and Ho [29] obeys the first order reaction kinetic as expressed by the following linearized equation:

$$\log{(q_e - q_t)} = \log{q_e} - \frac{k_1}{2{,}303}\, t \qquad (9)$$

Where k_1 is the first order adsorption rate constant (min^{-1}), q_t is the amount of heavy metal adsorbed at time t (mg/g) and q_e is the amount of heavy metal adsorbed at saturation (mg/g).

The kinetic model of the second order adsorption reaction [28] can be expressed by the following linearized equation:

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}\, t \qquad (10)$$

Where k_2 is the second order reaction constant, q_e is the amount of heavy metal adsorbed at saturation (mg/g).

In order to calculate the adsorption rate constants of copper removal, the first order kinetic was applied. The curves representing $\log(q_e - q_t)$ versus t did not shown any linearity for both BN and BA samples. Meanwhile, the pseudo-second-order kinetic, when it was applied for the same samples, the curves plotted t/q_t against t are, here, rather linear. Thus, the rate constants k_2 can be calculated from the slope of these curves (Fig. 4). The values of $q_{e,\ were}$ calculated for the both samples from the intersection of the straight line of the second order kinetic curves with the ordinates (y-axis) (See Table 4).
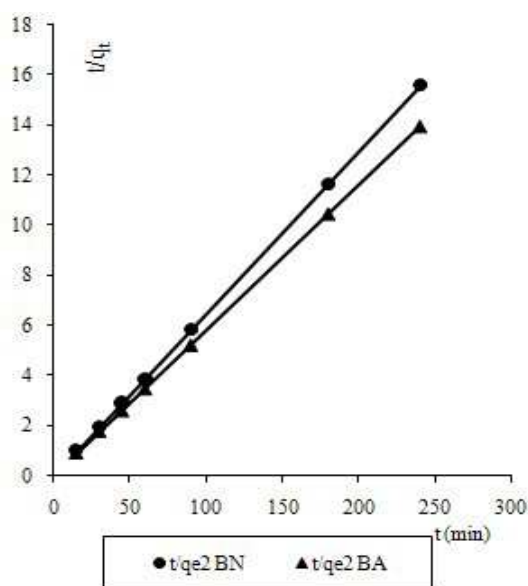
Figure 4. *Pseudo–second–order reaction kinetics for the adsorption of copper ions by bentonite.*

The results given in Table 4 shows that the values of qe, calculated and qe, experimental are equal. Moreover, all the correlation coefficients of second order kinetic are exalted, suggesting a high compatibility of this model with the removal of copper (II) ions by bentonite. The values of qe, given in Table 4, have shown that the thermal can improve the removal efficiency of copper (II) ions.

Table 4. *Parameters of second order kinetic of removal copper by bentonite*

Para-meters	$q_{e,\ experimental}$ (mmole g^{-1})	K_2 (g mmole^{-1} mn^{-1})	$q_{e,\ calculated}$ (mmole g^{-1})	r^2
BN	243.3	0.145	243.77	0.99
BA	271.02	0.089	271.98	1

The examination of the results given in Table 4 shows that the values of qe,calculated and qe, experimental are equal. Moreover, all the correlation coefficients of second order kinetic are exalted suggesting a high compatibility with the second order model governing the removal copper ions by bentonite. The values of qe, given in Table 4, show that the thermal treatment expresses an improvement in the removal efficiency of copper ions.

3.6. Thermodynamic Study

The thermodynamic parameters of the adsorption process as enthalpy (ΔH^o, kJ mol^{-1}), entropy (ΔS^o, J K^{-1} mol^{-1}) and Gibbs free energy (ΔG^o, kJ mol^{-1}) are estimated using the following equations:

$$\Delta G^0 = -\, RT \ln K_d \qquad (11)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R\, T} \qquad (12)$$

Where K_d is the distribution coefficient of the adsorption sites on the adsorbate, T absolute temperature and R is perfect gases constant. The plot $\ln K_d$ against $1/T$ should be linear with the slope (- $\Delta H^o/R$) and its intersection with ordinate (y-axis) will give rise to $\Delta S^o/R$, ΔH^o and ΔS^o values. In this case, it seems to be important to note that the free energy of Gibbs ΔG^o constitutes the fundamental criterion of the adsorption spontaneity.

The copper ions removal efficiency (% rate) by these materials (BN or BA) can be deduced from K_d values using the following relation:

$$\%\ rate = \frac{100 K_d}{K_d + \dfrac{V}{m}} \qquad (13)$$

Where V is the volume of solution (mL) and m is mass of clay (g).

The Cu^{2+} removal rate percentage have been calculated for solutions maintained at constant temperatures of 25, 35 and 45 °C using suspensions with initial concentration of 15, 25 and 35 mg L^{-1}.These suspensions were constantly stirred for 120 min. The Gibbs free energy ΔG^0 is calculated using the following thermodynamic equation:

$$\Delta G^0 = \Delta H^0 - T\, \Delta S^0 \qquad (14)$$

The obtained results were given in Table 6. The values of K_d vary from 42.2 to 230.8 for BN and from 1000.44 to 3916.67 for BA. The removal rate of copper ions varies from 47.4 to 49.7 % for BN and from 81.8 to 94 % for BA. We can conclude that the thermal treatment has exalted the K_d values and therefore the removal rates of copper ions.

However, when the activated bentonite BA is used, there are no significant variations in the K_d values and in the removal rates for copper ions in spite of the rising of the temperature for the Cu^{2+} aqueous solutions. So, it seems possible to deduce that there is no significant influence of the temperature on the adsorption process of copper ions by BA material in the range of the temperatures investigated. This, do not allow us to calculate the thermodynamic parameters. In this case, it is probably possible to think to an establishment of a spontaneous equilibrium at the contact of copper ions with the surface particles of clay BA. This phenomenon is resulted from the thermal treatment of the bentonite. Thus, the thermal activation of this bentonite has allowed to adsorption phenomena to overcome only a small energetic barrier in the BN material. This treatment has facilitated the adsorption of Cu^{2+} ions on the surface of bentonite BA [10-12].

The results given in Fig. 5 were obtained with bentonite BN and they have shown that, for an initial concentration of 15 mg L-1, no effect was observed for Kd values (slope zero) whereas for initial concentrations of 25 et 35 mg L-1, an increase of the temperature influences advantageously the Kd values and removal rates (% rate), enable the calculation of the thermodynamic parameters given in following Table 6.

Table 5. *Effect of the temperature on the removal rate and K_d values.*

Co (mg/l)	Temperature (°C)	25	35	45
15	Kd(BN)	225.6	230.8	225.6
	% rate. (BN)	47.4	48	47.4
	Kd(BA)	3916.67	3916.67	3916.67
	% rate. (BA)	94	94	94
25	Kd (BN)	187.0	216.4	242.1
	% rate. (BN)	42.8	46.4	49.2
	Kd(BA)	1766.13	1770.60	1792.09
	% rate. (BA)	83.12	83.64	83.8
35	Kd (BN)	183.2	205.7	247.2
	% rate. (BN)	42.2	45.1	49.7
	Kd (BA)	1000.44	1036.75	1052.56
	% rate. (BA)	81.8	82.22	82.4

The results mentioned in Table 6 show that the initial concentrations 25 and 35 mg L-1 are in agreement with an endothermic adsorption process for the copper ions removal on bentonite seeing that $\Delta H^0 > 0$ [3,27]. Also, the positive values of the entropy attest of an affinity between the Cu^{2+} ions and the clay material [2, 27]. Thus, the positive

entropy favors the complexation and the stability of adsorption. The ΔG^0 values (absolute value) increase with the increasing of the temperature have indicated the spontaneity in the adsorption process of Cu^{2+} ions by bentonite [3,27].
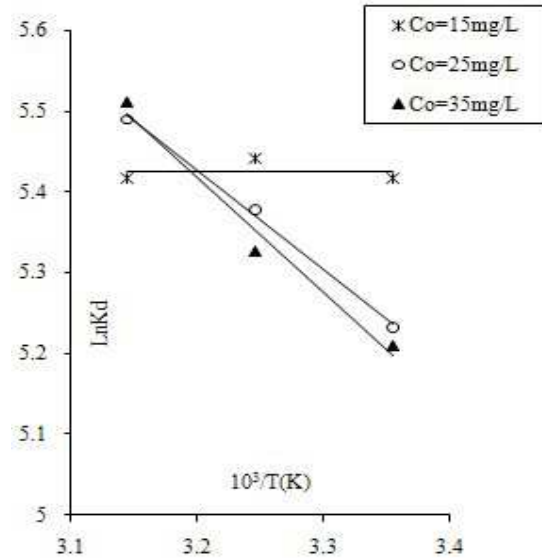
Figure 5. *Effect of the temperature on LnK_d versus 10^3/T for raw bentonite BN.*

Table 6. *Energetic data obtained from thermodynamic parameters of Cu^{2+} adsorption by BN.*

Co (mg l-1)	R2	ΔH^0 (KJ mole1)	ΔS^0 (J/K mole-1)	$-\Delta G^0$ (KJ mole -1)		
				298	308	318
25	0.99	10.17	77.63	12.96	12.96	13.74
35	0.97	11.77	82.67	12.87	12.87	13.69

The results given in Fig.5 are obtained with bentonite BN and show that, for an initial concentration of 15 mg l-1, anyone effect was observed for K_d values (slope zero) whereas For initial concentrations of 25 et 35 mg l-1, an increase of the temperature influences advantageously the K_d values and removal rates (%rate) rendering enable to calculate the thermodynamic parameters given in following Table 6.

The results mentioned in Table 6 show that the initial concentrations 25 and 35 mg l-1 are in agreement with an endothermic adsorption process for the copper ions removal on bentonite seeing that $\Delta H^0 > 0$ [3,27]. Also, the positive values of the entropy attest of an affinity between the Cu^{2+} ions and the clay material [2, 27]. Thus, the positive entropy favors the complexation and the stability of adsorption, while the ΔG^0 values (absolute value) increase with the increasing of the temperature indicating the spontaneousness in the adsorption process of Cu^{2+} ions by bentonite[3,27].

4. Conclusion

The heating of raw bentonite impregnated in 1 M ammonium chloride solutions in the oven renders it possibility to create from new sites of ion exchange and this leads to an increase of the adsorption capacity of copper (II) ions from their aqueous solutions with pH=6 using bentonite, obtained from Maghnia (west Algeria). This thermal treatment improves the affinity of this material towards the copper ions adsorption while, a process of a spontaneous equilibrium is established as soon as the contact is made between the copper (II) ions on the surface of clay particles in aqueous solutions. The study of adsorption isotherms shows that the removal efficiency of Cu^{2+} ions is governed by the two traditional models; Langmuir and Freundlich, with which the adsorption mechanism of Cu^{2+} ions by bentonite is a phenomenon of ionic exchange. This thermal treatment of bentonite inhibited the temperature effect of the aqueous solutions towards the removal rate of Cu^{2+} ions and also the improving of the K_d values. Owing to this new activation technique, applied for the clay materials, a rational use of bentonite could be envisaged in the treatment of wastwaters often polluted by the heavy metals. Thus, this work may be considered as a modest contribution to minimize the quantities of sludge during the decontamination of industrial effluents containing the heavy metals such as the family of copper (II).

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