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KINETIC, THERMODYNAMIC AND EQUILIBRIUM STUDIES ON ADSORPTION OF ALUMINA AND ZINC IONS ONTO ACTIVATED CARBON FROM HULL SEEDS OF MORINGA OLEIFERA

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The husk of Moringa will oleifera, agricultural solid waste was transformed into activated carbon for elimination of Alumina and zinc in aqueous solution. Adsorption equilibrium was obtained after 2 minutes. The yield of elimination of alumina and zinc is respectively 99.97% and 99.99%. Experimental data were analyzed by 4 isotherms (Langmuir, Freundlich, Temkin and Dubinin-Radushkevic). The value of constant non Freundlich model for zinc lies between 0 and 0.5, whereas alumina one lies between 0.5 and 1. Adsorption energies from the model of Dubinin-Radushkevic, were all lower than 8 kJmol^{-1}, which indicated that adsorption was physical and thermodynamic. Kinetic model of pseudo-second order is applicable to adsorption of alumina and zinc on activated carbon of husk of Moringa will Oleifera their R^2 is close to 1. Adsorption mechanism of metals ions was made according to this order kinetic model in two phases: the first was the diffusion of alumina and zinc ions towards the surface of the adsorbent and followed by interaction between molecules of adsorbates and adsorbent surface. Thermodynamic parameters proved the adsorption of aluminum and zinc into the activated carbon prepared from Moringa will oleifera is possible, spontaneous and exothermic in the ranges of temperature 298-333 K.

Keywords: Activated carbon, Husk of moringa will oleifera, Adsorption isotherms, Kinetics studies, Alumina, Zinc, Thermodynamic parameters

INTRODUCTION

The very diversified and very many human activities always generate significant rejections following the example residues of pesticides,

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dyes, gases, heavy metals, etc., which very often are poured without control in the environment. The presence of these elements in the area, the ground and water is in the beginning many problems of human health and environmental pollution. In the case of metals which are naturally present in the environment, the development of the industrial activities (mining, industries metallurgical and chemical) and agricultural (pesticides, manure) since last century entrained intensive contributions of these elements which became environmental pollutants. Therefore, many researchers of various horizons (chemistry, geology, agronomy, physiology plant, medicine etc.), were interested in the identification and elimination of these pollutants implied directly in imbalance of our ecosystem. As regards the elimination of heavy metals in water, several techniques already were implemented in particular precipitation, the oxidation/reduction, coagulation-flocculation, sedimentation, the exchange of ions, the biosorption and adsorption [1-4]. The elimination of heavy metals by adsorption on solid supports is a process less expensive and easy to implement. The adsorption is indeed the fixing of the particles (heavy metals) called adsorbates on solid supports called adsorbents [5, 6]. To this end several types of adsorbents were already tested in the elimination of heavy metals in water among which clays, silicon and alumina oxides [7-10]. However very few work concerning the use of the activated carbon for elimination of heavy metals in water were carried out until at the time. It will thus be a question in this work of using the activated carbon of seed hull of Moringa for the elimination of alumina and zinc in water of consumption. To this end, solutions of concentrations known out of alumina and zinc will be prepared at the laboratory and will be then treated using the activated carbon of seed hull of

Moringa in order to follow the evolution of their contents of these various heavy metals and to evaluate the capacities of adsorption of the new activated carbon.

EXPERIMENTAL

The material used in this work is primarily consisted of seeds of Moringa will oleifera and the aqueous zinc and alumina solutions prepared at the laboratory. These seeds of Moringa will oleifara were collected in the area of the Far-North of Cameroon, in the department of Mayo Tsanaga, the town of Mokolo.

Preparation of the Solutions

Stock Solution of Potassium Alumina with 1000 mg.L^{-1}

To dissolve 17.59 g crystals of sulphate doubles alumina and of potassium hydrated $(AlK(SO_4)_2,12H_2O)$ of molar mass 474.38 g.mol^{-1} in the water slightly acidified by sulphuric acid. To then adjust volume to 1000 mL. The solution obtained is preserved in a bottle out of glass. This stock solution will be used to prepare derived solutions of 25 and 500 mg.L^{-1} in alumina ion. The prepared solutions with different concentrations will be standardized.

Stock Solution of Zinc Sulphate of Concentration 1000 mg.L^{-1}

To dissolve 2.467g of zinc sulphate hydrated seven times of molar mass 287.55g.mol^{-1} $(Zn(SO_4)_2,7H_2O)$ in 1 liter of distilled water at ambient temperature. The solution obtained is preserved in a bottle out of glass. This solution mother will be used to prepare solutions from 25 to 500 mg.L^{-1} in zinc ions.

Batch Equilibrium Studies

For the experiments of adsorption, one introduces into a series of reagent bottles of 250 ml, solutions

of 50 ml of aluminium or zinc to the concentration of 200 mg.L^{-1}. The pH of the solution is adjusted by using the sulphuric acid or the hydroxide of sodium 2 N. The unit is maintained with 25 °C under magnetic stirrer at a constant speed of 180 tr/min. Then, one will introduce into the bottles 0.2 g of activated carbon. The mixture is maintained under magnetic agitation the time of instruction; then filtered using paper wattman N°1 in order to separate the liquid phase from the solid phase. With the exit of filtration, the filtrate is then analyzed by UV-VISIBLE spectroscopy, against the white made up of filtrate obtained by filtration of a suspension of active coalin distilled water. The metal quantity of ion adsorbed per unit of activated carbon mass is calculated by the relation:

$$Q_0 = \frac{(C_0 - C_e)V}{m} \qquad ...(1)$$

with V is the volume of adsorbate (L); m activated carbon mass (g); and C_O and C_e (mg.L^{-1}) are respectively the initial concentration of metal ions and concentration of metal ions at the moment [11-13].

RESULTS AND DISCUSSION

Adsorption Kinetics

In order to determine the kinetics of Al^{3+} and Zn^{2+} by modified clay, 200 mg of pillared clay was mixed with 50 mg/L of three ions solution in centrifuge tubes. The dispersions were shaken for amount 5 min at 30 min on a shaker. Figure 1 shows the results of the kinetics studies of Alumina and Zinc ions uptake by activated carbon at 50 mg/L in ions initial concentration. As shown in Figure 1, the amount of heavy metal ion adsorption increases with increased time, Adsorption equilibrium was obtained after 2

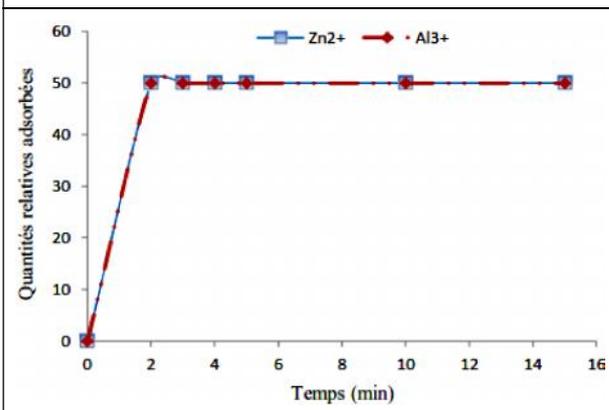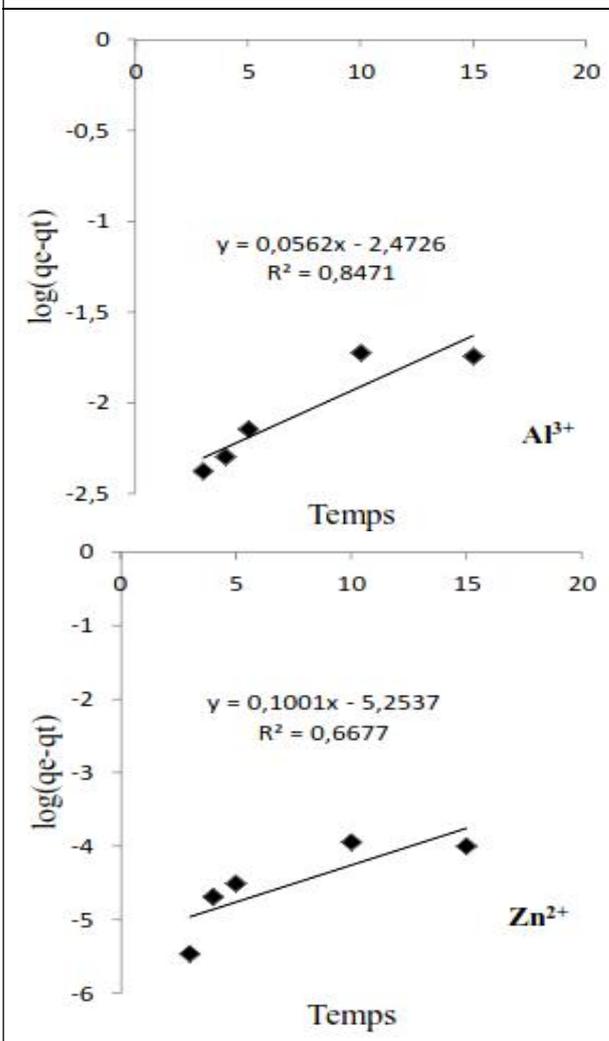Figure 1: Kinetics Study for Al^{3+} and Zn^{2+} ions Uptake by Activated Carbon

Figure 2: Pseudo-First Order Kinetics for Adsorption of Al^{3+} and Zn^{2+} ions onto Activated Carbon

minutes. The yield of elimination of alumina and zinc is respectively 99.97% and 99.99%. This stage could be attributed to the instantaneous monolayer adsorption of heavy metals at the surfaces of the investigated samples.

Several kinetic models are used to examine the controlling mechanism of the adsorption processes and also to test the experimental data obtained [12, 14].

The experimental data was fitted with pseudo-first-order differential equation as follows:

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

where, q_e and q_t are the amounts of heavy metal ions absorbed (mg/g) at equilibrium and time, t (min), respectively, k_1 is the rate constant of first–order adsorption (min^{-1}). The first-order-rate k_1 can be obtained from the slope of the plot of $\log(q_e - q_t) = f(t)$ (Figure 2).

A pseudo-second-order equation can be expressed in the form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad ...(3)$$

where, is the rate constant of the second–order adsorption (min^{-1}). The second-order-rate k_2 can be obtained from the slope of the plot of t/q_t vs t as showed in Figure 3. A good agreement of the experimental data with these cond-order kinetic model was obtained (Table 1). The correlation coefficients, R^2 are greater than 0.98, which suggests a strong relationship between the parameters and also explains that the process follow spseudo–second–order kinetics.

The adsorption process involves transportation of the solute molecules from the

Figure 3: Pseudo-Second Order Kinetics for Adsorption of Al^{3+} and Zn^{2+} ions onto Activated Carbon
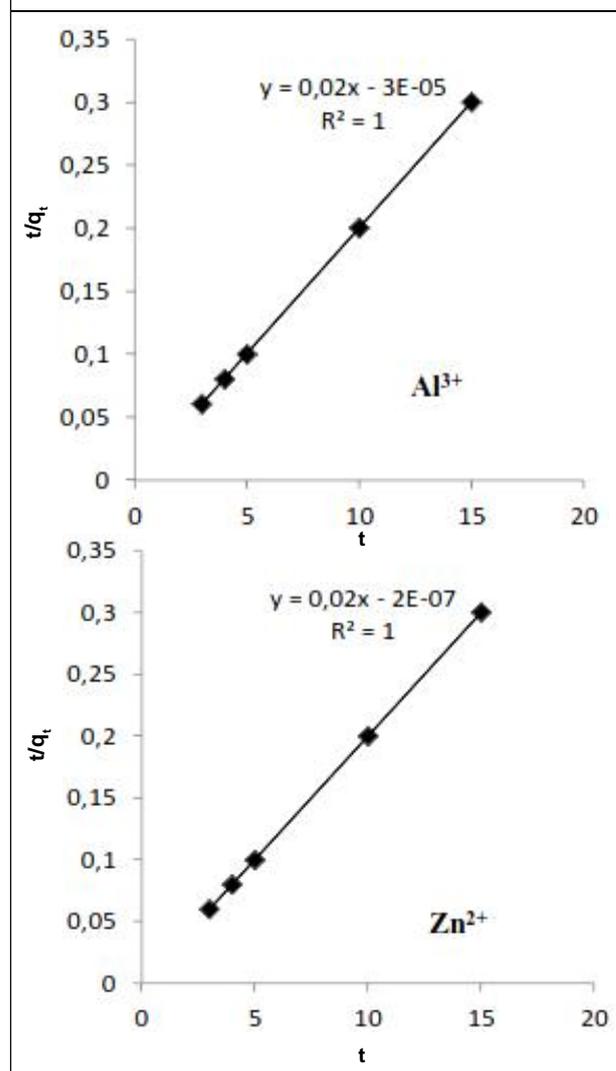
aqueous solution to the surfaces of activated carbon followed by intraparticle diffusion/transport process [15]. The constants k_{int} and C are calculated from the plot of qt vs t$^{1/2}$ shown in Figure 4.
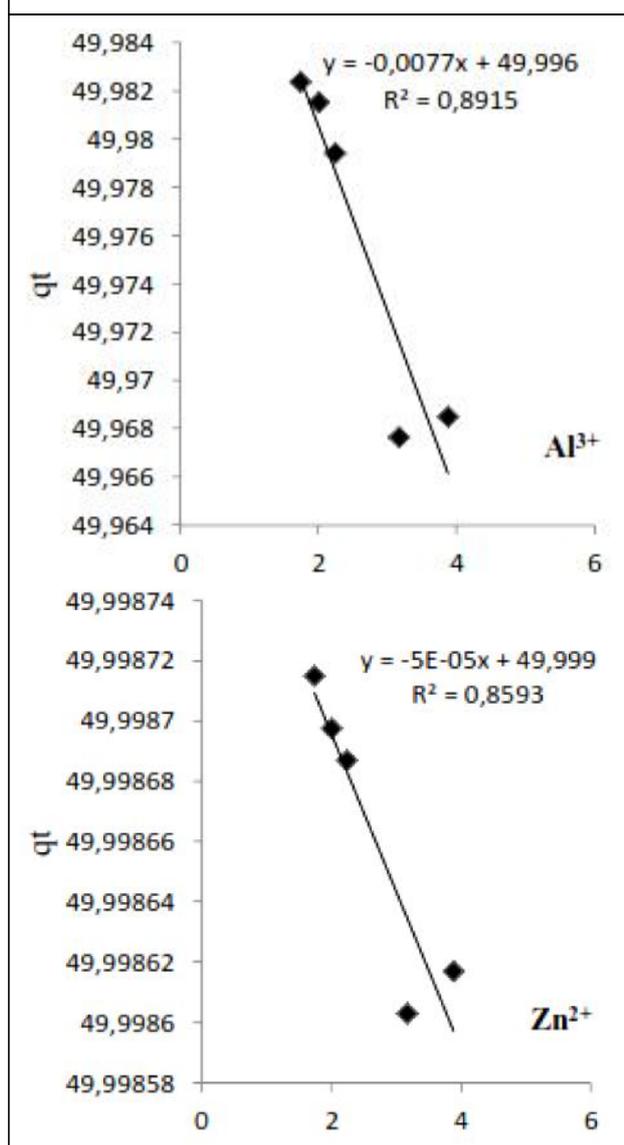
Effect of Solution pH onAl^{3+} and Zn^{2+} ions Adsorption

The adsorption of these both ions is a phenomenon that is highly influenced by solution pH; this is due to the implication of mechanisms that are pH dependent, through reactions such

Ions	First Order Kinetics			Second Order Kinetics			Intraparticle Diffusion		
	$q_e(cal.) \times 10^{-3}$ (mg.g^{-1})	K^1 (min^{-1})	R^2	$q_e(cal)$ (mg.g^{-1})	K_2 (mg.g^{-1}.min^{-1})	R^2	$k_{int} \times 10^{-2}$ (mg.g^{-1}.min$^{-1/2}$)	C (m^2.S^{-1})	R^2
Al^{3+}	3.372	0.129	0.847	50	13	1	-0.7	49.99	0.891
Zn^{2+}	0.005	0.23	0.667	50	2000	1	-0.005	49.99	859

Table 1: Constants of the Three Kinetics Models


Figure 4: Intraparticle Diffusion Kinetics for Adsorption of Al^{3+} and Zn^{2+} ions onto Activated Carbon

this figure the variation of pH showed that the maximum of elimination of alumina was obtained 5 and 9 (99.97%); in the case of zinc, each value of pH used gave a yield of elimination of 99.99%. These ions (H$^+$) are then more adsorbed than the three ions, considering their easy mobility in solution.


Figure 5: Effect of Solution pH
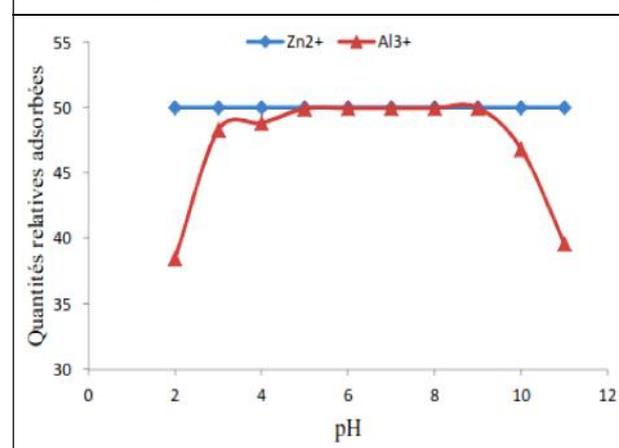
Effect of Solution Concentration on these Both ions Adsorption

In order to examine the changes of pillared clay and non-pillared clay, concerning the Al^{3+} and Zn^{2+} when the latter change the initial concentration without any condition, six concentrations in Al^{3+} and Zn^{2+} ions have been chosen. Figure 3 bellows represent the percentage of Al^{3+} and Zn^{2+} ions elimination from the initial ion concentration.

These figures show that the rate of elimination at equilibrium on the modified clay for both ions increases as the initial heavy metal ion concentration increases. This may be justified by the fact that the more the solution is

as ions exchange, complexation reactions, or by the retention of electrostatic forces [16]. The adsorption of the both ions Al^{3+} and Zn^{2+} on pillared clay at different pH is showed in the Figure 5. On

Figure 6: Effect of Initial Concentration on Adsorption of Al^{3+} and Zn^{2+} onto Activated Carbon
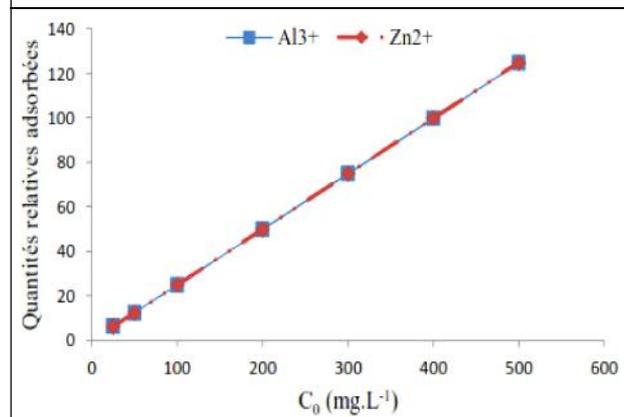
concentrated, the more the heavy metal ions will go through the surface active sites the pillared clay and consequently, the retention becomes more important. Influence of the initial zinc and alumina concentration on the adsorption capacity of activated carbon showed that the quantities of alumina and zinc were equivalent for the both ions. It was also observed that the quantities of alumina and zinc adsorbed per unit of activated carbon increased with the increase in the initial concentration. This same phenomenon has been observed by Kalavathy and Lima (2010) on the adsorption of Copper, Zinc and Nickel activated carbon of husk of Moringa Oleifera (temperature 303K, time 4 hours, pH 6 [2,8].

Adsorption Isotherm Studies

Adsorption isotherms indicate distribution of adsorbate between solution and adsorbent at the equilibrium state of the adsorption process [17]. The type of adsorption isotherm model is very important in order to understand the adsorption behavior for solid–liquid adsorption system. In the present study, Langmuir, Freundlich, Temkin and Dubinin-Raduschovich models were tested to study the adsorption behavior of Al^{3+} and Zn^{2+}.

Langmuir Isotherm

The Langmuir isotherm is based on the assumptions that adsorption takes place at specific homogeneous sites within the adsorbent, there is no significant interaction among adsorbed species, and the adsorbent is saturated after the formation of one layer of adsorbate on the surface of adsorbent [13,16,18-20]. The Langmuir isotherm equation can be written as follows:

$$q_e = \frac{bK_LC_e}{1+K_LC_e} \qquad ...(4)$$

where, C_e is the equilibrium concentration of the remaining solute in the solution (mg/L), qe is the amount of the solute adsorbed per mass unit of adsorbent at equilibrium (mg/g), $q_{max} = bK_L$ is the amount of adsorbate per mass unit of adsorbent at complete monolayer coverage (mg/g), and b (L/mg) is a Langmuir constant. The K_L and b values were calculated from the slopes and intercepts of linear plots of $\frac{q_e}{C_e}$ versus C_e. The deducted parameters of adsorption of Langmuir isotherms are summarized in Table 2. The plots were found to be linear with good correlation coefficients ranging from 0.991 to 0.995. This indicates the applicability of Langmuir model in the present study.

Freundlich Isotherm

Freundlich isotherm model can be used to describe the non-ideal adsorption of a heterogeneous system and reversible adsorption. The isotherm is expressed by the following equation:

$$q_e = K_FC_e^{1/n} \qquad ...(5)$$

This expression can be linearized to give the following equation:

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

where, K_F (mg/g) and n are Freundlich adsorption isotherm constants. The values of K_F and 1/n are determined from the intercept and slope of the linear regressions. The value of 1/n for higher than 1/n for Al^{3+} and Zn^{2+} ions suggests that the link of adsorption is fragile. The Freundlich enponents K_F and 1/n can be determined from the plot of $\ln(q_e)$ vs. $\ln(C_e)$ (Figure 5). The plots were found to be linear with good correlation coefficients ranging from 0.826 to 0.892. This indicates the applicability of Freundlich model in the present study. The values of n for the studied samples are more than unity and therefore, adsorption is favorable [19, 20]. The deducted parameters of adsorption of Freundlich isotherm are summarized in Table 2.

Temkin Isotherm

One admits in the model of Temkin that the energy of adsorption of any molecule decreases linearly with the covering of the surface of the Adsorbent by the adsorbed species [19, 20]. The isotherm of Temkin is given by the relation:

$$q_e = B \ln A + B \ln X_e \qquad ...(7)$$

$B = R_T$ is the constant of Temkin comparable to the energy of adsorption and expressed in J.mol^{-1}, R the constant of perfect gas (8.314×10^{-3}Kj. mol^{-1}.K^{-1}. The plots were found to be linear with good correlation coefficients ranging from 0.92 to 0.99.

Dubinin-Radushkevich Isotherm

Its theory of filling of the volume of the micropores rests on the fact that the potential of adsorption is variable and that the free enthalpy of adsorption is connected to the degree of filling of the pores [1, 2]. The isotherm of Dubinin-Radushkevich is given by the equation:

$$q_e = q_m \exp(-K\mathrm{v}^2) \qquad ...(8)$$

The linear expression of the equation can be on the following form:

$$\ln q_e = \ln q_m - K\mathrm{v} \qquad ...(9)$$

where q_e is the quantity of the metal ion adsorbed with balance, K is a constant related to the average free energy of adsorption, q_m is the theoretical capacity in the micropores, ε is the potential of Polanyi, equalizes in $RT \ln\left(1 + \frac{1}{C_e}\right)$.

The deducted parameters of adsorption of Dubinin-Radushkevich isotherm are summarized in Table 2.

Thermodynamic Studies

Thermodynamic parameters have been determined for the qualification of adsorption phenomenon of Al^{3+} and Zn^{2+} ions on pillared clay of Karewa. The deducted estimates of $\Delta G°$, $\Delta H°$ and $\Delta S°$ of the experimental data are found in Table 2. As illustrated from the results in Table 3, the negatives values of standard energy of Gibbs ($\Delta G°$) of Al^{3+} and Zn^{2+} ions indicate that the adsorption is thermodynamic possible and

Ions	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm			Dubinin-Radushkevic Isotherm			
	a (mg.g^{-1})	K$_L$ (L/mg)	R^2	K$_F$ (mg.g^{-1})	n	R^2	B	A (L/g)	R^2	K	q$_m$ (mg/g)	R^2	E (KJ/mol)
Al^{3+}	7.042	9.467	0.999	615.177	0.634	0.99	184.2	4.273	0.992	0.071	232.525	0.992	2.654
Zn^{2+}	0.014	495.99	0.998	6.607×10^{32}	0.072	0.977	6×10^9	2.356	0.999	0.22	2.109×10^{17}	0.957	1.507

Table 2: Parameters of the Langmuir, Freundlich, Dubinin and Temkin Isotherms

Figure 7: Freundlich Adsorption Isotherm of Al^{3+} and Zn^{2+} ions onto Activated Carbon

Figure 8: Dubinin-Radushkevich Adsorption Isotherm of Al^{3+} and Zn^{2+} ions onto Activated Carbon
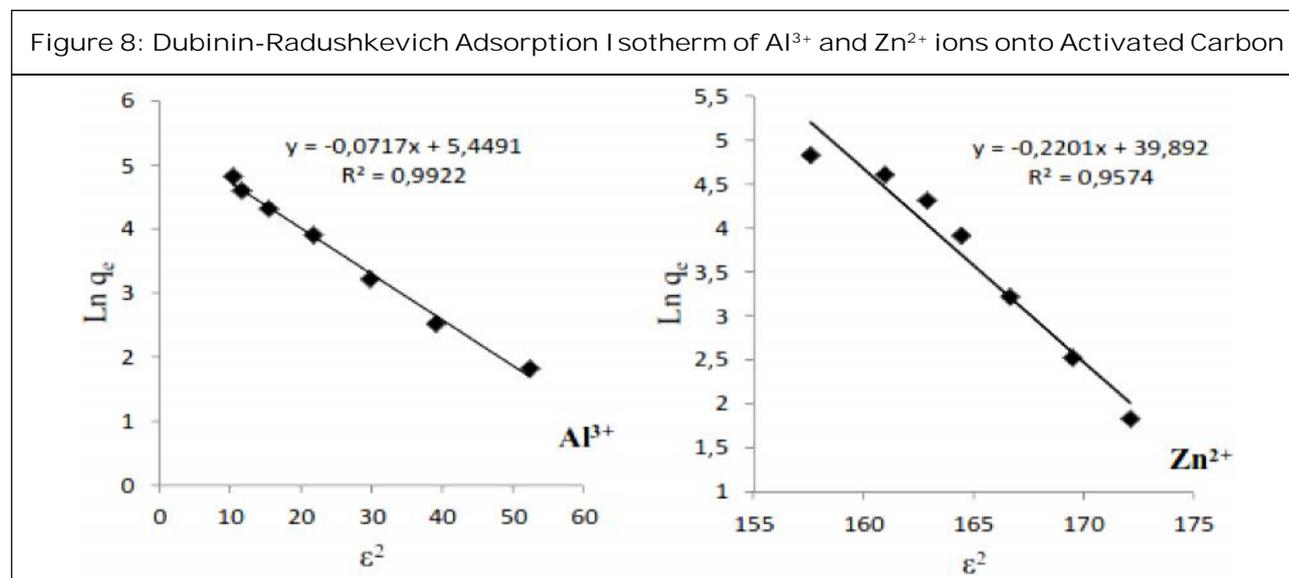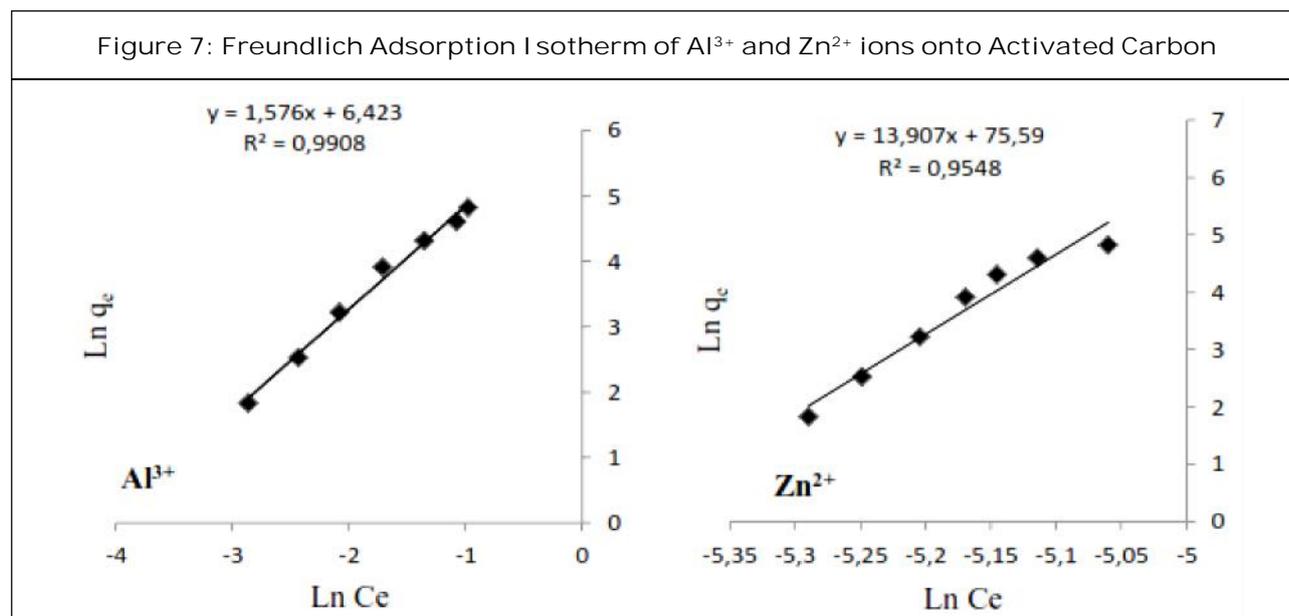
Table 3: Thermodynamic Parameters of Adsorption of Al^{3+} and Zn^{2+} on Activated Carbon at Different Temperatures

T(K)	Al^{3+}				Zn^{2+}			
	$\Delta G°$ (KJ.mol^{-1})	$\Delta H°$ (KJ.mol^{-1})	$\Delta S°$ (KJ.mol^{-1}K^{-1})	R^2	$\Delta G°$ (KJ.mol^{-1})	$\Delta H°$ (KJ.mol^{-1})	$\Delta S°$ (KJ.mol-1K^{-1})	R^2
298	-17.374	-0.498	0.038	0.992	-26.206	-0.0431	0.0861	0.934
308	-16.227				-26.863			
318	-15.953				-27.682			
333	-15.439				-28.954			

spontaneous. The positives values of standard entropy (∆S°) show the crescent aspect to interface this solid/liquid during the adsorption of copper, of manganese and of the phosphate ions on active carbon. The negative value of ∆H° indicates the positive nature of the present adsorption phenomenon. Also, the negative value of ∆H° proves the exothermic and physical nature of this retained phenomenon of ions [16, 21]. These results are in agreement with the above studied model.

CONCLUSION

This work had for object the study of retention of alumina and zinc ions on active carbon by Moringa oleifera. The study of the adsorption of alumina and zinc ions by active carbon is a contribution to the water treatment. This present study aimed at, the application of active carbon in the adsorption of some micropolluants (heavy metals and organic molecules) present in water. The study in particular of the influence of certain parameters (pH, thermodynamic concentrations, parameters, isotherms) on the retention of these adsorbates held our attention. Adsorption equilibrium was obtained.

After 2 minutes. The yield of elimination of alumina and zinc is respectively 99.97% and 99.99. Experimental data were analyzed by 4 isotherms (Langmuir, Freundlich, Temkin and Dubinin-Radushkevic). The value of constant non Freundlich model for zinc lies between 0 and 0.5, whereas alumina one lies between 0.5 and 1. Adsorption energies from the model of Dubinin-Radushkevic, were all lower than 8 kJmol^{-1}, which indicated that Adsorption was physical and thermodynamic. Kinetic model of pseudo-second order is applicable to adsorption of alumina and zinc on activated carbon of husk of

MoringaOleifera their R2 is close to 1. The variation of pH showed that the maximum of elimination of alumina was obtained 5 and 9 (99.97%); in the case of zinc, each value of pH used gave a yield of elimination of 99.99%. The nature of the retainment phenomenon of both ions is exothermic, spontaneous and physical. The active carbon is more practical and efficient than natural clay for the retainment of metallic ions.

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