ORIGINAL ARTICLE

ADSORPTION KINETICS AND ISOTHERMS FOR THE REMOVAL OF ZN^{2+} AND CU^{2+} METALLIC IONS FROM LIQUID EFFLUENTS BY ACTIVATED CARBON PREPARED FROM DATES STONES

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ABSTRACT

Background: The technique of hot dip galvanizing is one of the most used techniques in the metallurgical industries. This technique requires a very large amount of water during its stages, which generates a considerable volume of effluents loaded with inorganic micro pollutants (heavy metals). These pollutants have the ability to concentrate along the food chain and accumulate in certain organs of the human body. In the last decades, adsorption is low-cost technology and one of best solutions for water and wastewater purification. Adsorption using activated carbon, a phase transfer process has been widely used in practice to remove contaminants in all their forms (organic and inorganic) from fluid phases because of the low investment in initial cost and design simplicity. **Objectives**: This Research aims to characterize activated carbon prepared from dates stones and to study its efficiency in removal of zn^{2+} and cu^{2+} metallic ions from liquid effluents. **Methods**: The activated carbon prepared was characterized by Fourier Transform Infrared Spectroscopy, and the assay of Cu^{2+} and Zn^{2+} ions was conducted by Flame Atomic Absorption Spectroscopy. The influences of the several operational parameters on the adsorption (mass of the adsorbent, pH and contact time) were examined. **Results:** As the dose increased, removal efficiency increased. The optimum pH for $Cu^{2+}$and Zn^{2+} removal was 6.The experimental sorption equilibrium followed both Langmuir (R^2=0.904 for $Zn^{2+}$and R^2=0.900 for Cu^{2+}) and Freundlich (R^2=0.959 for $Zn^{2+}$and R^2=0.934 for Cu^{2+}) relatively more of Freundlich. The experimental data fitted pseudo first (R^2=0.911 for Zn^{2+} and R^2=0.937 for Cu^{2+}) and second (R^2=0.998 for both ions) order kinetic models, being relatively better described by the pseudo-second-order. The thermodynamic parameters relating to the adsorbent/adsorbate system studied indicate that the adsorption process is spontaneous, exothermic and of the physical nature. **Conclusions:** The results obtained in this study showed that activated carbon prepared from dates stones can be used for the removal of heavy metals.

Keywords: *Adsorption, activated carbon, isotherms, Langmuir, Freundlich, thermodynamic, pseudo-first-order, pseudo-second-order, copper, zinc.*

1. INTRODUCTION

Effluents from industrial, agricultural and domestic origin are often charged with pollutants. Their impact on the environment is very harmful; they are sometimes recycled or quite simply rejected into nature which causes a capital problem and a major concern for local public authorities and international organizations [1]. Thus, all these encouraged the improvement of the existing techniques of depollution and the development of new processes, in accordance with the increasingly restrictive international standards. The industrial sector of the metal coating is a sector whose production is growing worldwide due to the use of metallic materials in different areas. Among which we find the automotive industry, aerospace, signs, etc… In the production of metal parts and their finishing, the metal industry uses surface treatment techniques, among the latter, there is that of the hot dip galvanizing. The latter is a series of steps: degreasing, rinsing, pickling, fluxing, steaming and cooling [2]. The implementation of these steps require a large volume of water, resulting in parallel a very large amount of waste water loaded with organic materials [3], inorganic[4] and organometallic[5]. This requires the treatment of this type of wastewater prior to discharge to receiving waters to not poison wildlife and aquatic flora and therefore the ecosystem and human health.

Indeed, many conventional methods have been used for wastewater treatment such as precipitation [6], oxidation [7] and coagulation-flocculation [8]. Even they appear effective, but they are limited to a variety of pollutants for technical reasons and high cost of exploitation or may not be capable of treating large volumes of effluent [9].

Among the mentioned methods for wastewater treatments that has drawn attention to many researchers in the last decades, adsorption using activated carbon, a phase transfer process has been widely used in practice to remove contaminants in all their forms (organic and inorganic) from fluid phases [10] because of the low investment in initial cost and design simplicity. Activated carbons for wastewater treatment are usually obtained from materials locally available such as natural materials, agricultural wastes and industrial wastes [11]. Adsorption isotherms which are usually used to determine the quantity of a given pollutant adsorbed are also used to describe adsorbent-adsorbate equilibrium relationship.

2. MATERIALS AND METHODS

2.1 Sampling: The experimental study was carried out using rejects from the company Galvacier (city of Kenitra, Morocco).The samples of these discharges were taken from two different points of the company's wastewater treatment plant, which are successively the entry and exit of the station, into bottles whose capacity is based on a high density of polyethylene (HDPE).

2.2. Adsorbent preparation: In this study, the carbon stones samples were chemically treated or activated with acid phosphoric. The latter is the most preferred because of the environmental and economic concerns.

After the date stones are separated, they are washed, and placed in an oven at 105°C for 24 hours and then ground and sieved. The ground material retained and kept protected from the air in well closed bottles. The carbonization is carried out in an electric four. The resulting carbon is put in closed porcelain capsules. The carbonization was between 400 and 800°C with a 1h to 3h. The samples are chemically activated with H_3PO_4 (40%) for 10h at 25°C. They are then washed with distilled water until the pH is neutral, and finally dried at 105°C for 24 hours. (Figure.1) the necessary steps for obtaining activated carbon.

Figure 1: The figure presents the activated carbon preparation.

2.3. Infrared spectroscopy: Fourier Transform Infrared Spectroscopy, SHIMADZU) FTIR8201PC whose frequency range is between 500 and 4000 cm^{-1}, was used to determine the functional groups responsible for the adsorption of metals.

2.4. Polarizing optical microscopy: Polarizing optical microscopy is an optical instrument with an objective and an eyepiece that magnifies the image of a small object and separates the details of the image so that it can be seen by human eye.

2.5. Metals Analysis by FAAS: Water samples were analyzed for metals using Flame Atomic Absorption Spectroscopy (FAAS). Operational parameters such as wavelength, energy, lamp and burner alignment and slit width for Zn^{2+} and Cu^{2+} were adjusted according to the working standards.

2.6. Adsorption isotherms: Both Langmuir and Freundlich models were tested for equilibrium description:

2.6.1. Langmuir isotherm: Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed molecules. It can be represented by the Eq. (1) [12].

$$\frac{ce}{qe} = \frac{1}{bq_m} + \frac{1}{q_m}ce \qquad (1)$$

Where qe corresponds to the amount adsorbed per gram of adsorbent at equilibrium (mg/g), Ce is the solute concentration (mg/L) in the aqueous solution at equilibrium, and qm is constant related to the maximum adsorption capacity (mg/g).

2.6.2. Freundlich isotherm: Freundlich equation is an empirical model based on heterogeneous adsorption over independent sites and is given by [13] Eq. (2).

$$\mathrm{Lnqe} = \ln k_F + \frac{1}{n}\ln ce \qquad (2)$$

Where, KF is related to binding energy and adsorption capacity and n is related to the intensity of adsorption-incorporating all the factors affecting adsorption capacity and intensity.

2.7. Kinetic studies: For analyzing the adsorption kinetics of zinc and copper ions two kinetic models were applied to the experimental data: pseudo-first order model and pseudo-second-order model:

2.7.1. Pseudo-first-order: The first-order rate equation is one of the most widely used equations for the adsorption of a solute from an aqueous solution and is represented as [14] Eq. (3).

$$\log(qe - qt) = \log qe - 0.4342k_1t \qquad (3)$$

Where qe and qt are the amounts of metal ions adsorbed per unit mass of biosorbent (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant for first-order adsorption (min^{-1}).

2.7.2. Pseudo-second-order: The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed as follows [15] Eq. (4).

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{1}{q_e}t \qquad (4)$$

Where, k_2 is the rate constant for the second-order adsorption kinetics ($g\ mg^{-1}\ min^{-1}$). The straight-line plots of log (qe-qt) against t and of t/qt against t were used to determine the rate constants.

2.8. Thermodynamic studies: In general, the adsorption phenomenon is always accompanied by a thermal process that can be exothermic or endothermic. Thermodynamic parameters such as the Gibbs free energy change, enthalpy change and entropy change can be used for the characterization of temperature effect. These parameters were calculated using the following equations [16] Eq. (5).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (5)$$

Where:

ΔG°: Gibbs free energy change (J/mol).
ΔH°: enthalpy change (j/mol).
ΔS°: entropy change ($J.mol^{-1}K^{-1}$).

The thermodynamic relation (5) associated with the Vant'Hoff relation (ΔG°=-RT lnKd) leads to the following Eq. (6):

$$\ln k_d = \frac{\Delta S^0}{R} - \frac{H^0}{R} * \frac{1}{T} \qquad (6)$$

Where:

Kd: Is the equilibrium constant obtained for each temperature from the Langmuir model.
R: Is the molar gas constant (8.314 J/mol K).
T: Is the absolute temperature (K).

3. RESULTS AND DISCUSSION

3.1. Characteristic of the physical-chemical parameters of the hot-dip galvanizing rejects

Table 1: The table presents the average values of the physical-chemical parameters of the liquid effluents taken at two different points and limit values retained.

Analyzed Parameters	**Measured values downstream of the neutralization station**	**Measured values upstream of the neutralization station**	**Limit values retained**
pH	4.01	3.56	6-9
Zn^{2+} (mg/L)	11.75	11.19	10
Cu^{2+}(mg/L)	6,25	6.12	4

From the table 1 we noticed that the liquid effluents of hot-dip galvanizing provide values of major physical-chemical parameters that relatively exceed the general values limits for the "hot-dip galvanizing" branch [17].

3.2. Characterization of the adsorbent by Infrared spectroscopy

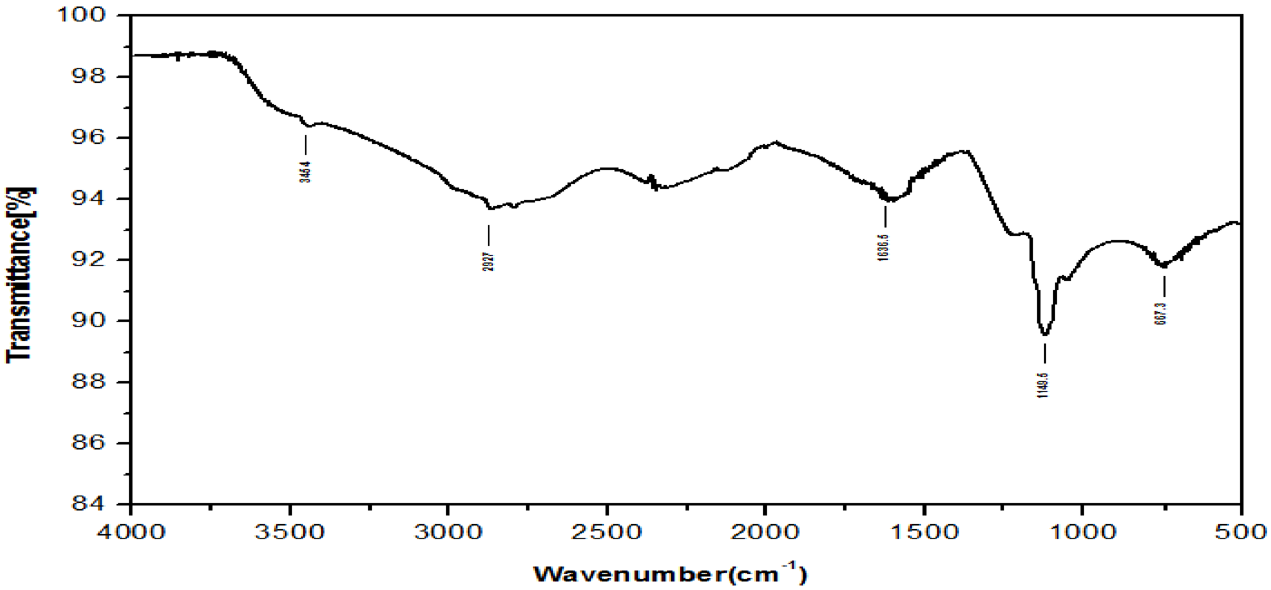

Figure 2: The figure presents the IRTF Spectrum of activated carbon.

From the spectrum of FTIR we found that the main peaks found at 3454cm^{-1} for activated carbon were attributed to the hydrogen stretching vibration of the O-H hydroxyl groups (of carboxyl's, phenols or alcohols) and adsorbed water [18]. It also corresponds to the O-H elongation vibration of cellulose, pectin and lignin [19]. The 2927cm^{-1} band was attributed to the C-H elongation vibration of aliphatic molecules. The band observed in the 1636.5cm^{-1} region is attributed to the C=C bond of groups of pyrones [20], the peak at1149.5cm^{-1} is assigned to the vibration of the C-O bonds [18]. The band of 667.3cm^{-1} corresponds to the vibration of the S-C bonds [21-22].

3.3. Characterization of the adsorbent by polarizing optical microscopy

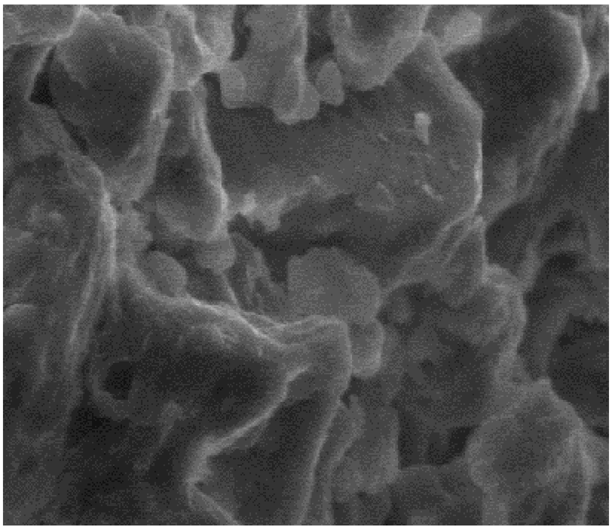

Figure 3: The figure presents the morphology of activated carbon seen by polarizing optical microscopy at (x100).

The images of the polarizing optical microscopy of the carbon surface show a relatively heterogeneous surface rich of pores with large size situated in the mesoporous range, as well as the presence of cavities, which result from the reaction of the activating agent on the surface of the activated carbon as in the studies of Enaime al., (2017) [12].

3.4. Effects of adsorbent mass: The analysis results of the samples of treated water ions as a function of the increasing masses of the adsorbent (activated carbon) are represented in the following figure.

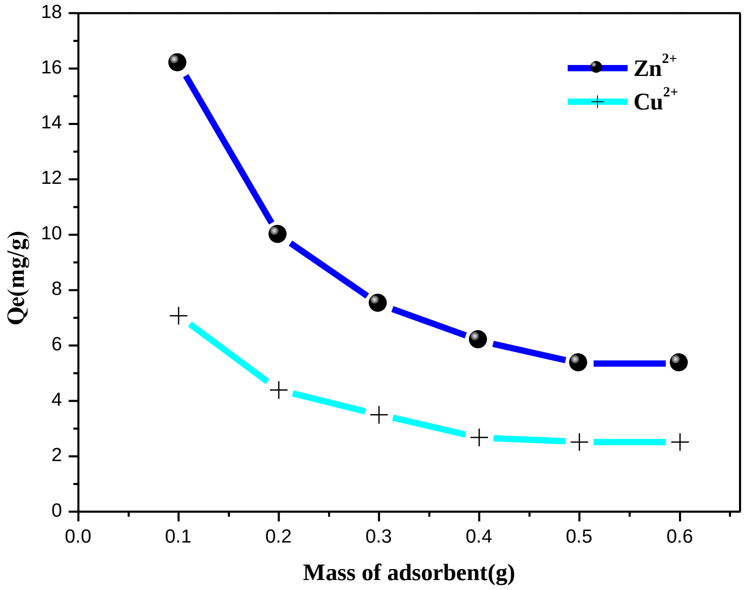

Figure 4: Influence of the mass of activated carbon on the adsorption of Zn^{2+} and Cu^{2+} ions.

The results the influence of the mass the activated carbon on the adsorption ions has shown that the removal efficiency increased as adsorbents mass increased (R^2=0.889) from 0.1 to 0.5g. These results may be explained by the increases the number of specific sites on the adsorbent surface in view of the activated carbon powder increased mass.

3.5. Effects of Contact Time

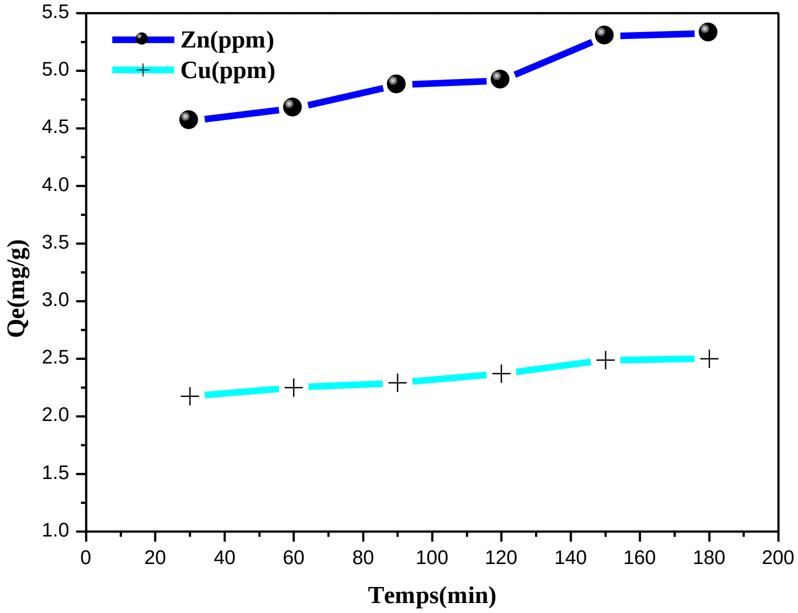

Figure 5: The figure presents the influence of the contact time of activated carbon on the adsorption of Zn^{2+} and Cu^{2+} ions.

The results obtained show that the adsorption capacity of the zinc and copper ions increases as a function of the contact time until reaching a saturation plateau and then becomes stable after 180minutes. This is positively and linearly correlated (R^2=0.972). This phenomenon can be explained by the molecular diffusion of the ions towards the adsorption sites until reaching an adsorption equilibrium where all the sites become occupied and reveal a similar behavior vis-a-vis the Zn^{2+} and Cu^{2+} ions.

3.6. Effects of pH

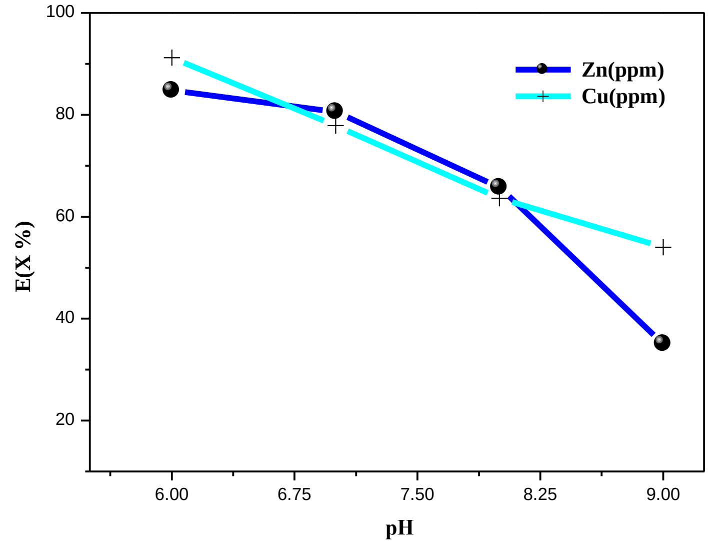

Figure 6: Effects of the pH of activated carbon on the adsorption of Zn^{2+} and Cu^{2+} ions.

From the results obtained we observed that the effect of pH on uptake of metal is significant (R^2=0.9398). The results presented show excellent removal capacities for both Zn^{2+} and Cu^{2+} by powdered activated carbon.

From these results, the pH equal to 6 is considered as an optimal pH giving the best results of adsorption of zinc and copper ions.

3.7. Adsorption isotherms: The results of the zinc and copper adsorption isotherms by activated carbon from date stones according to the Langmuir and Freundlich model are shown in the Figure 7 and 8.

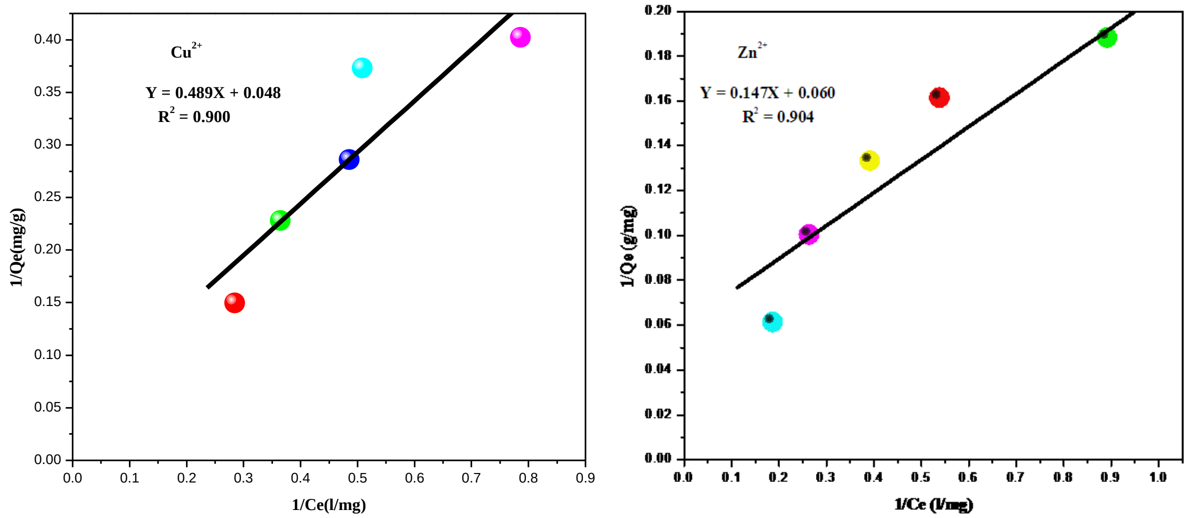

Figure 7: The linearized Langmuir adsorption isotherms of Zn^{2+} and Cu^{2+} ions by activated carbon

From the figure we found that the correlation coefficients of the Langmuir model are between 0 and 1 (R^2=0.904 for Zn^{2+} and R^2=0.900 for Cu^{2+}) with an adsorption energy b equal to 0.408 to Zn^{2+} and b equal to 0.098 to Cu^{2+}.The maximum capacities (qmax=16.66mg/g of Zn^{2+} and 20.833mg/g of Cu^{2+}) are close to the calculated results, which means that the Langmuir model is adequate for modeling the zinc and copper adsorption isotherms. The mechanism involved is therefore a monolayer adsorption involving identical and independent sites, in a limited number [23]. Thus, it appears from these results that the Langmuir isotherm is favorable for the adsorption of copper zinc on the material studied.

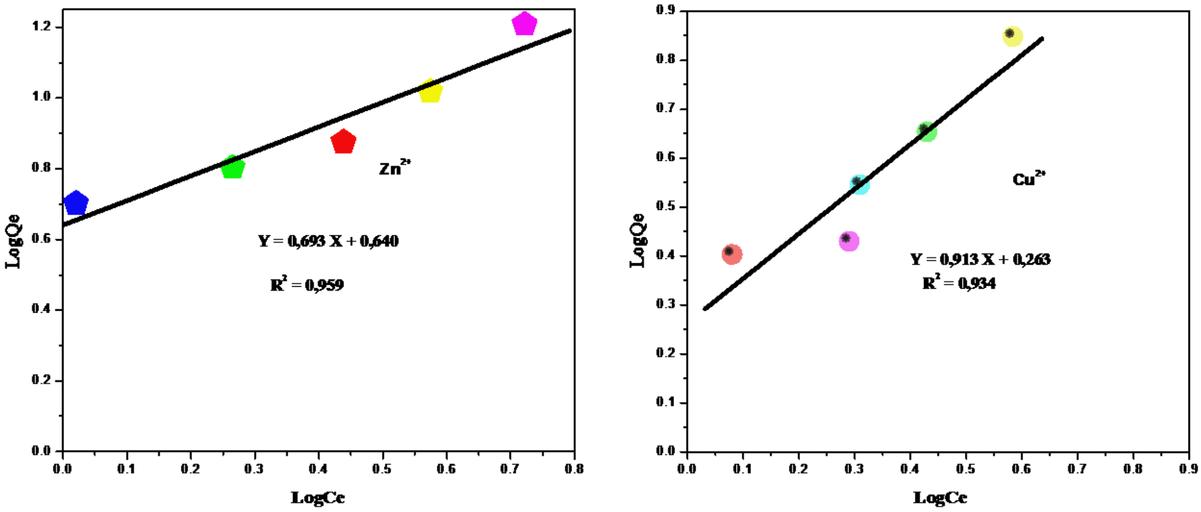

Figure 8: The linearized Freundlich adsorption isotherms of Zn^{2+} and Cu^{2+} ions by activated carbon.

From the curve presented in Figure 8 we noticed that the correlation coefficients of the experimental results obtained by applying the Freundlich equation are close to 1 (R^2=0.959 for Zn^{2+} and R^2=0.934 for Cu^{2+}), which seems that the model is representative of the adsorption reaction of the zinc and copper on activated carbon. K_F constant values correspond to the maximum adsorption capacities of zinc and copper are equal 1.896 and 1.300 successively respond to the empirical model of Freundlich and intensity parameter values, 1/n <1 (1/n=0.693 and 0.913) means good adsorption obtained for the ions and indicate that the adsorption intensity is favorable at high range of the studied concentrations [24]. These values are between 0 and 1 which means good adsorption [25].

The values of the equational parameters of the two models as well as the correlation coefficient R^2 are collated in the table.

Table 2: Langmuir and Freundlich constants for sorption of metals by Activated carbon.

	LANGMUIR			**FRUNDLICH**		
	R^2	**qm (mg/g)**	**b (1/mg)**	**R^2**	**1/n**	**K_F**
Zn^{2+}	0.904	16.66	0.408	0,959	0,693	1,896
Cu^{2+}	0.900	20.833	0.098	0.934	0.913	1.300

From the results presented in the table we observed that experimental data for zinc and copper ions provided a good fit with the Langmuir and Freundlich models.

3.8. Adsorption kinetics: The results of the adsorption kinetics of zinc and copper by activated carbon according to the pseudo-first order model and the pseudo-second order model are shown in the figures and the values of the parameters are collated in table 3.

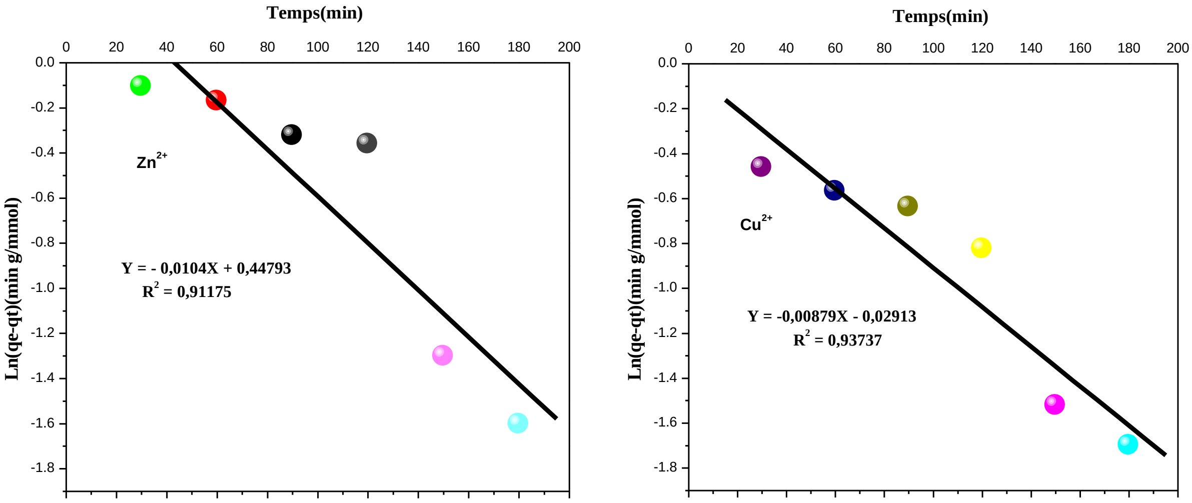

Figure 9: Kinetic model according to the pseudo-first order

The coefficients of determination R^2 are 0.911 for Zn^{2+} and 0.937 for Cu^{2+} and theoretically determined equilibrium adsorption capacity values are lower than experimental values (qe,exp=5.350 mgg^{-1}> qe,cal=1.565 mgg^{-1}) for Zn^{2+} and (qe,exp=2.52 mgg^{-1}> qe,cal=0.971 mgg^{-1}) for Cu^{2+}, showing that the Lagergren model is not applicable for description of the adsorption of ions by the adsorbent used.

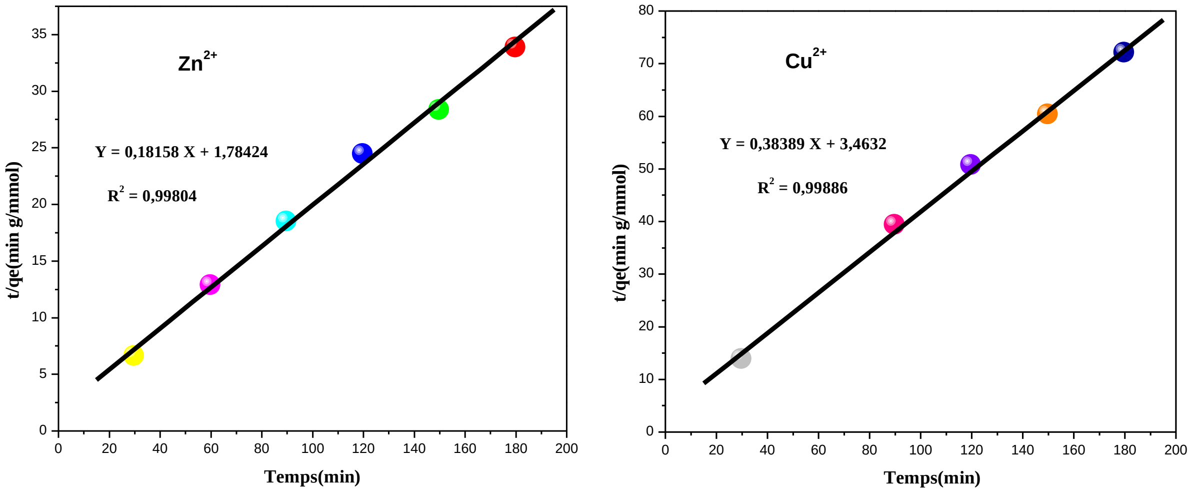

Figure 10: Pseudo-second order sorption kinetics of Zn^{2+} and Cu^{2+} onto actived carbon.

The coefficients of determination are good (R^2=0.998 for the two ions), which shows that the linearization is of good quality, and the theoretical values la of the equilibrium adsorption capacity qe obtained from this equation are similar to experimental ones (qe,exp=5.350 mgg^{-1}, qe,cal=5.507 mgg-1) for Zn^{2+} and (qe,exp=2.52 mgg^{-1}, qe, cal=2.604 mgg^{-1}) for Cu^{2+}, which suggests that the adsorption of zinc and copper on the adsorbent is better represented by the kinetic process of the pseudo - second order.

The kinetic parameter values of the two models as well as the correlation coefficient R^2 are collated in table 3.

Table 3: Pseudo first and second order kinetic parameters for the adsorption of zinc and copper ions by activated carbon from date stones.

Ions	**qe,exp (mgg^{-1})**	**Pseudo-first order**			**Pseudo-second order**		
		K_1	**qe,cal (mgg^{-1})**	**R^2**	**K^2**	**qe,cal (mgg^{-1})**	**R^2**
Zn^{2+}	5.350	0.023	1.565	0.911	0.018	5.507	0.998
Cu^{2+}	2.52	0.020	0.971	0.937	0.042	2.604	0.998

From the results obtained, we notice the correlation coefficients R^2 of the pseudo first order are relatively weak compared to those found in the case of the pseudo-second order model and the experimental qe values clearly deviate from the theoretical values of the second order model. It can be concluded that the kinetics do not respond to the Lagergren model (pseudo first order).

3.9. Thermodynamic study of adsorption: In order to complete the study of the adsorption of zinc and copper by activated carbon, it is advisable to carry out a thermodynamic adsorption study. The results obtained are shown in table 4:

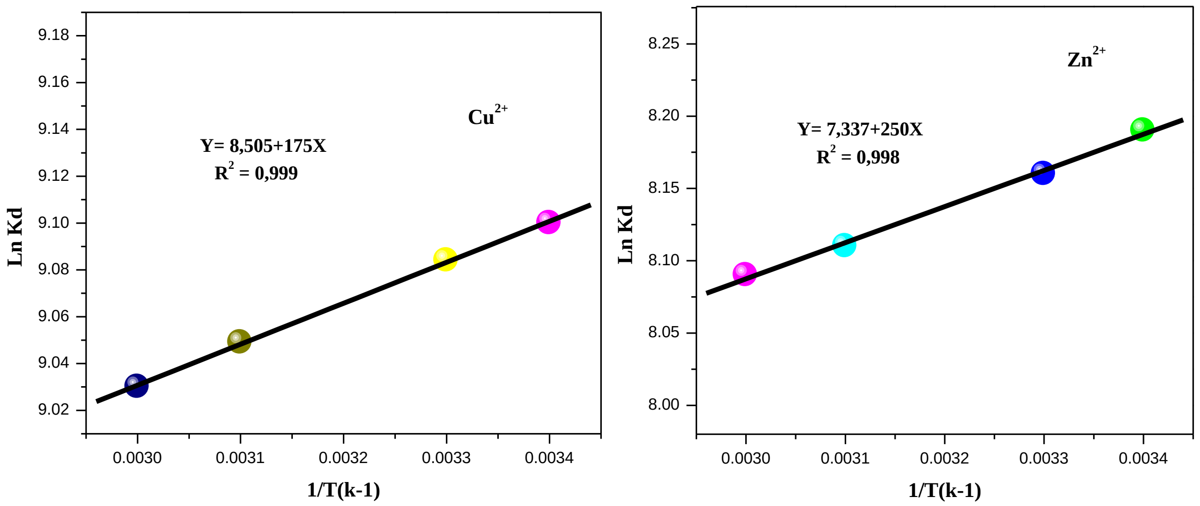

Figure 11: Linearization curve of the distribution constant as a function of temperature for Zn^{2+} and Cu^{2+}.

Tableau 4: Thermodynamic parameters for the adsorption of zinc and copper.

Ions	**ΔH (kj.mol^{-1})**	**ΔS (j.K^{-1}.mol^{-1})**	**ΔG (kj.mol^{-1})**			
			303K	313K	323K	333K
Zn^{2+}	-2,078	60,99	-20,55	-21,16	-21,77	-22,38
Cu^{2+}	-1,454	70,71	-22,87	-23,58	-24,29	-24,99

According to the quantities mentioned in this table 4, it is found that the values of Gibbs free energy are negative ($\Delta G < 0$), this shows that the process of adsorption of zinc and copper by activated carbon from nuclei of dates is spontaneous and the degree of spontaneity increases with increasing temperature. The effect that the adsorption becomes greater depends on the temperature, can be attributed to the increase of active sites on the surface of solids and less important for activated carbon. The negativity of the enthalpy values indicates that the process is exothermic. The values of the heat of adsorption obtained for our systems confirm that the interactions with zinc and copper are of a physical nature (physical adsorption ($\Delta H < 50$ KJ/mol) it is noted that the entropy values are low.

4. CONCLUSIONS

A study of using activated carbon for the removal of metal ions from effluent liquid was successfully carried out. The biosorption efficiency was higher for both zinc and copper ions at pH 6. Biosorption kinetics was described by both a pseudo-first-order model and a pseudo-second-order model, but betterment is to pseudo-second-order model. Equilibrium was attained after 3 hours of contact time for both ions. Sorption isotherms were described by both Langmuir and Freundlich models but more is by Langmuir. As the dose increased removal efficiency increased with statistical significance. The thermodynamic study indicates that the process is exothermic and of the physical nature .The experimental data demonstrated activated carbon from date stones to be a suitable candidate for use as biosorbent in the removal of heavy metals from effluent liquid.

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