Adsorption of Cu (II), Zn (II) and Ni (II) ions from aqueous solution by date stones

S. Khenchelaoui[1], A. Gherbia[2,3], Y. Medkour[1], A. Chergui[1,2*], A. R. Yeddou[2] , R. Kerbachi[1]

[1]Laboratoire des Sciences et Techniques de l'Environnement, Ecole Nationale Polytechnique, Département Génie de l'Environnement, 10 Avenue Hassen Badi, BP 182, El Harrach, Alger, ALGERIA

[2]Laboratoire d'étude et de développement des techniques de traitement et d'épuration des eaux et de gestion environnementale, LEDTEGE, Ecole Normale Supérieure Kouba, KOUBA BP 92, Alger, ALGERIA

[3]Université de Laghouat, Département des Sciences et Techniques, Faculté de technologie, Laghouat , ALGERIE

*Corresponding author: a_chergui@yahoo.fr; Tel.: +213 662 9587 34

ARTICLE INFO

ABSTRACT/RESUME

Abstract: The present study is concerned with the valorization of date stones for the waste water treatment. Date stones as adsorbent were characterized by X-ray diffraction, FT-IR and SEM, than tested for the adsorption of Cu (II), Zn (II) and Ni (II) from aqueous solotion. The effects of different parameters on the adsorption of metal metals such as the contact time, the initial concentration and the pH of the solution were investigated. The adsorption capacity was highest at pH5. Cu (II) had higher adsorption capacity than Zn (II) and Ni (II). The equilibrium data were fitted using Freundlich and Langmuir isotherm models.

I. Introduction

Considerable amounts of heavy metals released into aquatic systems from various sources such as municipal sewage, effluents garbage incineration, metallurgical industry, agricultural runoff, etc. Untreated effluents from these sources have an adverse impact on the environment which requires remedial action [1].Various innovative methods currently used to remove metal ions and dyes from waste water such as reduction precipitation, ion exchange, electrochemical reduction and adsorption [2,3].

In the recent years, there has been a wide realization of the importance of low-cost waste from numerous activities such as agricultural, there were few studies in the literature have been focused on the utilization of this naturally available adsorbents such as grape fruit peel [4],coconut shells [5], pine wood [6], orange peel [7], lentil husk [8],potato peel [9], coir pith [10], banana peel [11], apricot shell[12], mango peel waste [13], sugarcane bagasse [14], soy meal

hull [15], walnut shell [16], olive stone [17], grapefruit peel [18], agave bagasse[19].

In Algeria, date stones are abundant low cost by product from agricultural ,itcan be evaluated in many areas as feed for animals or combined with other feed preparation materials, additives in the pharmaceutical and food industries [20,21].

In this work date stones type Degla Beida were chosen as adsorbent to remove metal ions Cu(II), Zn(II) and Ni(II) from aqueous solution. The characterization of raw date stones is performed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Kinetics adsorption data were fitted to tow models pseudo first order and pseudo second order models, the experimental isotherms data were also fitted to Langmuir and Freundlich models.

II. Materials and methods

II.1. Adsorbent and reagents
The raw date stones (RDS) selected in this work were collected from locality of Tolga (Biskra), south east of Algeria.

The date stones were washed with distilled water to be completely free from dirt, dried at 105°C for 24 h, and finally crushed to obtain a powder with particles sizes in the range 200-300 µm. The Cu (II), Zn (II) and Ni (II) aqueous solutions were prepared by dissolving a known amount of (CuSO$_4$, 5H$_2$O), ZnCl$_2$, NiCl$_2$ salts in distilled water, and the pH of the solution was adjusted to the desired value by adding 0.1M of HCl and NaOH.All batch adsorption experiments were investigates at a constant speed of 300 rpm, temperature of 25°C and adsorbent dose of 3 g.L^{-1}.The adsorption of Cu (II), Zn (II) and Ni (II) ions was studied at different pH from 1.0 to 6.0.The effect of initial metal ion concentration was also studied at different concentrations from 100 to 600mg.L^{-1}. After adsorption process, the concentrations of Cu (II), Zn (II) and Ni (II) ions were determined using flam atomic absorption spectrometry (PERKIN ELMER A700) at a wave length of 249.2 nm, 213.9 nm and 323.3 nm, respectively.

II.2. Characterization of adsorbent
The morphology of raw date stones were examined using scanning electron microscopy FET Quanta 600, before and after adsorption process. Chemical functional groups were analyzed by an infrared spectrometer type (thermo scientific nicolet-6700 FT-IR), using KBr pellet method, at a wave number range from 500 to 4000 cm^{-1}. Crystalline phases eventually present in the adsorbent material were analyzed by powder X-ray diffraction (ADP 2000), using monochromatic copper radiation (Cu/k$_\alpha$, λ= 0.1541 nm) at 40 kV and 30 mA over the 2θ range 0-70°. Thermal stability of raw date stones (9.23 mg) was studied with TGA (Mettler Tolido) in the range of 25-1000°C.

III. Results and discussion

III.1. Thermogravimetric analysis (TGA/DTA)
Figure 1 shows the thermogravimetric and the derivative thermogravimetry analysis (TG/DTG) of the raw date stones. Three peaks can be observed in DTG curve present and suggest that the composition of dates stones is similar and comparable to other lignocellulosic adsorbents whose mainly constituted of cellulose, hemicelluloses and lignin [22,23]. From TG curve,it can be seen three stages, the first weight loss (~ 6%) engendered by heating the materials up to 150°C corresponding to the moisture elimination, followed by a considerable weight loss (~ 65%) due

to the combustion of volatile matter until 380°C and the last weight loss (~23%) attributed to the combustion of char until 550°C [24].
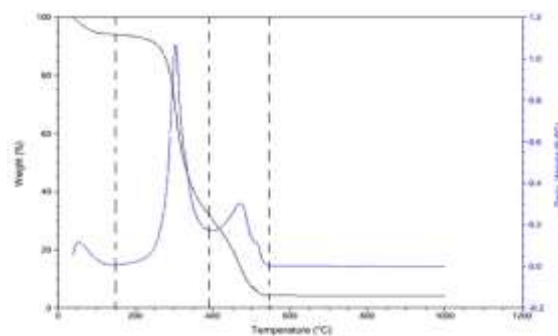

Figure 1. *TGA-TDA curves of raw date stones.*

III.2. FTIR spectroscopy
Figure 2, revealed the presence of a various groups on the raw date stones, (a) before and (b) after adsorption of copper ions, the broad band at 3418 cm^{-1} attributed to the O-H bond of elongation vibration, but after adsorption of Cu(II), this peak was displaced to wave length less than that obtained before adsorption. The sharp peak of average intensity observed in the range 2950-2800 cm^{-1} corresponds to the vibration of asymmetric and symmetric stretching of C-H bond present in cellulose [25]. The band at 2360 cm^{-1}due to the presence of (C≡N) groups, while, after adsorption of Cu(II), this peak was almost disappeared, may be due to the adsorption of Cu(II) on the surface of the adsorbent. The peak around 1745 cm^{-1} is ascribed to the C=O of a carboxylic acids present in hemicelluloses [26,27]. The vibration at 1616-1517 cm^{-1} attributed to the deformation of (C=C) aromatic in lignin [28]. The band at 1450 cm^{-1} due to the deformation (C-H) in cellulose. The bands at about 1088-1375 cm^{-1} attributed to the C-O-C stretching of (alcohols, ethers or phenols) and O-H deformation vibration [29], whereas, after adsorption of Cu (II), these peaks were displaced to wave lengths higher than those obtained before adsorption. A similar observation has been observed for the various groups on the raw date stones after adsorption of Zn (II) and Ni (II).

III.3. Scanning electron microscopy (SEM)
The morphologies of the raw date stones (a) before and (b) after adsorption of copper ions were observed by scanning electron microscopy (SEM). As shown in Figure 3, there is a difference between the surface morphology of the samples, the adsorbent surface before the adsorption exhibits a clear porous structureand a rough surface with pores compared to the RDS after adsorption. This difference is due to the deposition of the pollutant on the cavities observed on the surface of the adsorbents before adsorption.
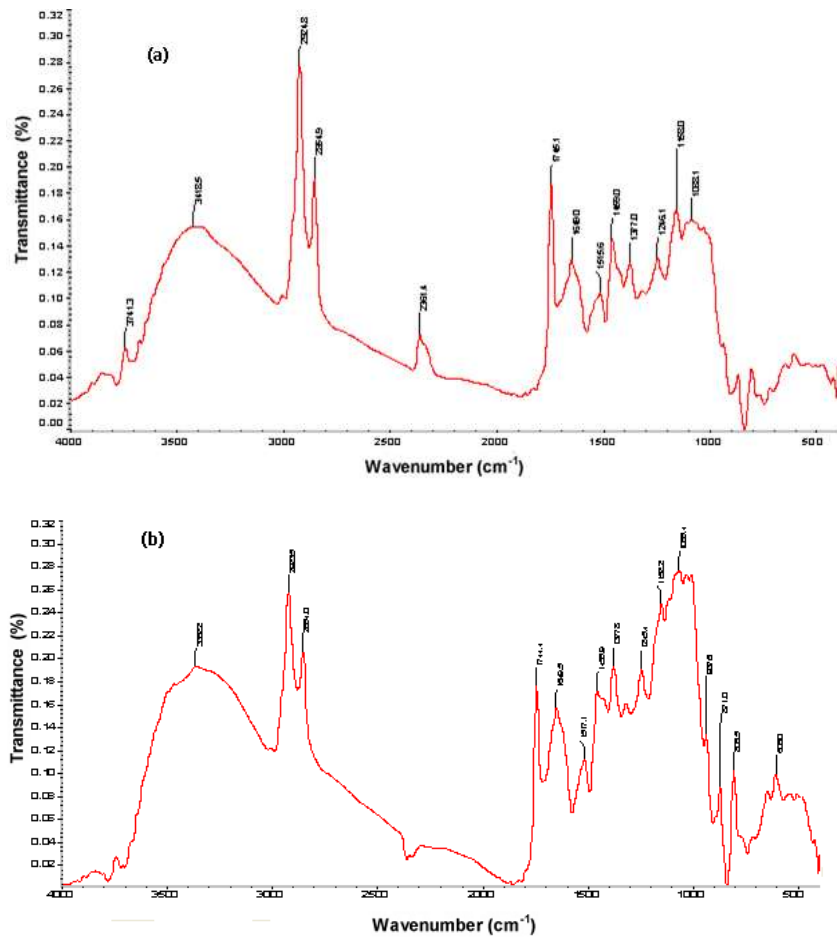
Figure 2. *FTIR spectrum of the raw date stones: (a) before and (b) after adsorption of copper ions.*
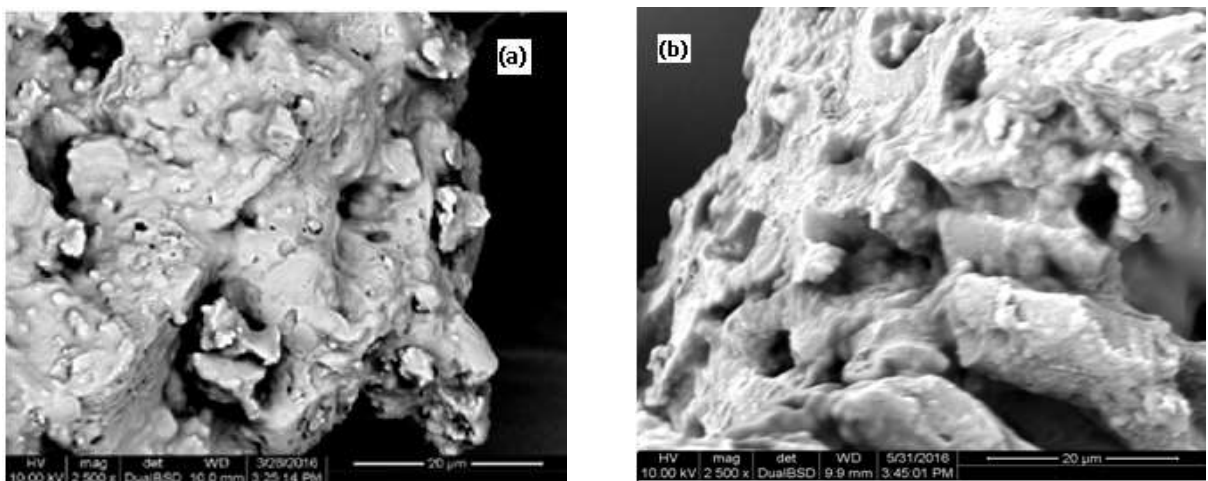

Figure 3. *SEM images of Raw date stones: (a) before and (b) after adsorption of Cu(II).*

III.4. X-ray diffraction

The results of X-ray diffraction of RDS before (a) and after (b) adsorption are presented in Figure 4, two diffraction peaks at 2θ=16.7° and 21° for RDS before and after adsorption of Copper respectively which are attributed to the presence of cellulose [30]. The raw material constituted of an amorphous material generally produces a signal of intensity negligible compared to another crystalline substance.
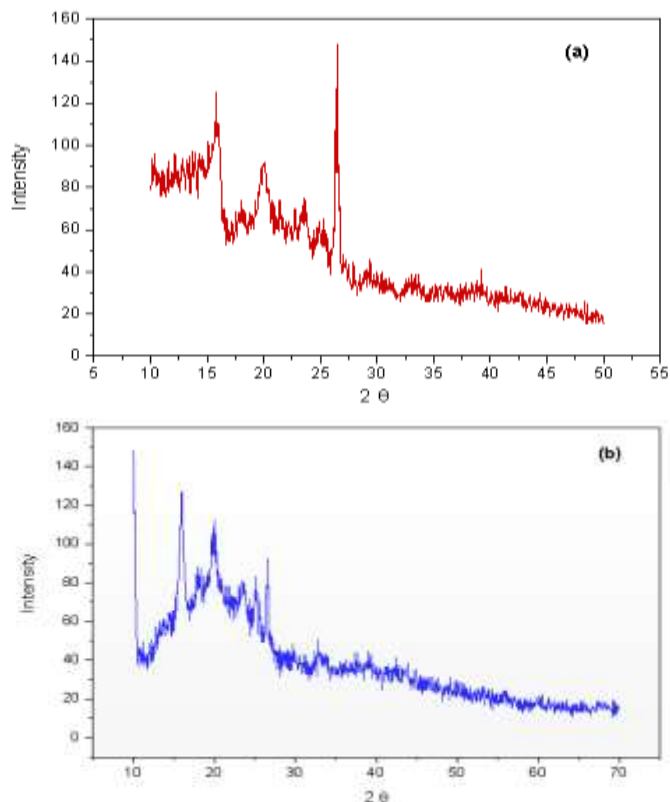

Figure 4. XRD pattern of raw dates stones (a) before and (b) after adsorption of copper.

III.5. Effect of pH

Figure 5 shows the effect of pH on the adsorption of Cu, Zn and Ni by raw date stones (RDS), the adsorption capacity increased as the pH increased from 1.0 to 5.0, then decrease for all metals ions, the maximum equilibrium value was found as 9.14 mg of Cu(II), 6.57 mg of Zn(II) and 5.10 mg of Ni(II) per g of RDS at pH=5. Similar results have also been reported for the adsorption of Cu (II) onto tea waste in the pH range (5 to 7) [31]. Lower adsorption of metals at low pH values is probably due to the presence of excess H^+ ions competing with the metal cations for the adsorption sites. Also, at low pH, the overall surface charge on the adsorbent surface became positive, which inhibited the approach of positively charged metal cations [32].
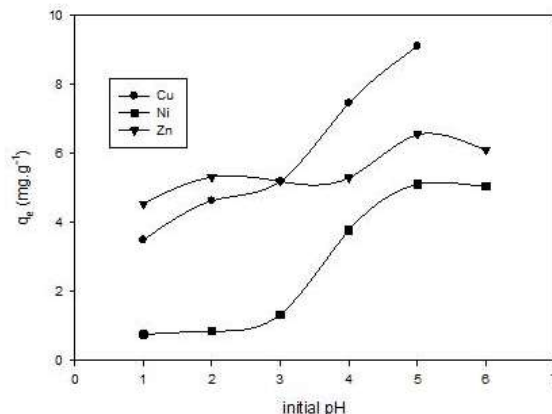

Figure 5. Effect of initial pH on the adsorption of Cu(II), Zn(II) and Ni(II) onto RDS.

III.6. Effect of contact time

Adsorption capacity of Cu (II), Zn (II) and Ni (II) onto RDS was measured as a function of time (Figure 6). It was noted that the capacity of all metals ions adsorbed per unit of weight of the adsorbent at equilibrium (q_e), increased quickly with time and slowed gradually as equilibrium was approached. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of metals ions to the surface of RDS and the availability of the uncovered surface area and active sites on the adsorbent.The sufficient time to reach the adsorption equilibrium for Cu(II), Zn(II) and Ni(II) were 100, 140 and 160 min, respectively, and the amount of Cu(II), Zn(II) and Ni(II) adsorbed onto RDS at equilibrium were 9.29, 6.47 and 5.49 mg.g^{-1}, respectively.

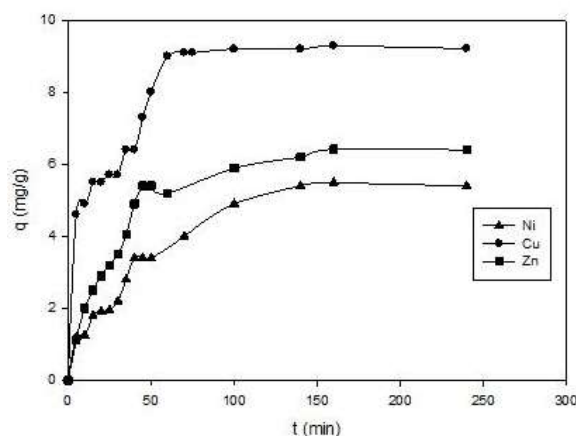*Figure 6. Effect of contact time on the adsorption of Cu(II), Zn(II) and Ni(II).*

III.7. Effectof initial metal ion concentration

The adsorption capacity of Cu(II), Zn(II) and Ni(II) ions as a function of initial concentrations are shown in Figure 7. As seen in the figure, an increase in initial concentration of metals leads to an increase of adsorption capacity, similar results reported by other researchers [33-34].

The maximum adsorption was found at 600 mg.L^{-1} for all metals ions, at higher concentrations, the maximum adsorption was 23.39 mg.g^{-1} for Cu(II) compared to Zn (II) 17.80 mg.g^{-1} and Ni (II) 16.91 mg.g^{-1}, corresponding to the saturation of active sites on the adsorbent. An increase in metal sorption could be due to an increase in electrostatic interactions, involving sites of progressively lower affinity for metal ions.
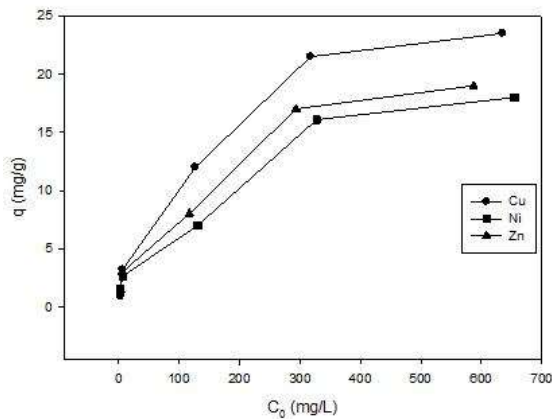
Figure 7. *Effect of initial concentration of Cu(II), Zn (II) and Ni(II).*

III.8. Kinetic study
In order to determine the adsorption rate constant and to examine the mechanism of Cu(II), Zn(II) and Ni(II) adsorption on RDS two models were applied to experimental data, pseudo-first-order and pseudo-second-order models. The linear form of pseudo-first-order is expressed as follows:

$$log\,(q_e - q_t) = logq_e - \frac{K_1}{2.303}t \qquad (1)$$

Where q$_e$ (mg.g^{-1}) and q$_t$ (mg.g^{-1}) are the amounts of metals adsorbed at equilibrium and at any time, respectively, K$_1$ is equilibrium rate constant of pseudo-first-order sorption (g.mg^{-1}.min^{-1}), t is time (min).The pseudo-second-order kinetic model rate is expressed:

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

Where K$_2$ is the equilibrium rate constant of pseudo-second-order adsorption (g.mg^{-1}.min^{-1}).

The values calculated from the related plots (Figure 8) and (Figure 9), are given in table1. The validity of the exploited models is verified by the correlation coefficient R^2. The value of R^2 was found to be in the range of 0.8964-0.9346 for

pseudo-first-order kinetic model for Cu(II), Zn(II) and Ni(II) by using RDS compared to pseudo-second-order kinetic model has the highest correlation coefficient (R^2=0.9523-0.9935).
Pseudo-second-order kinetic model implies that the predominant process here is chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbate and the surface of the adsorbent [35-36].
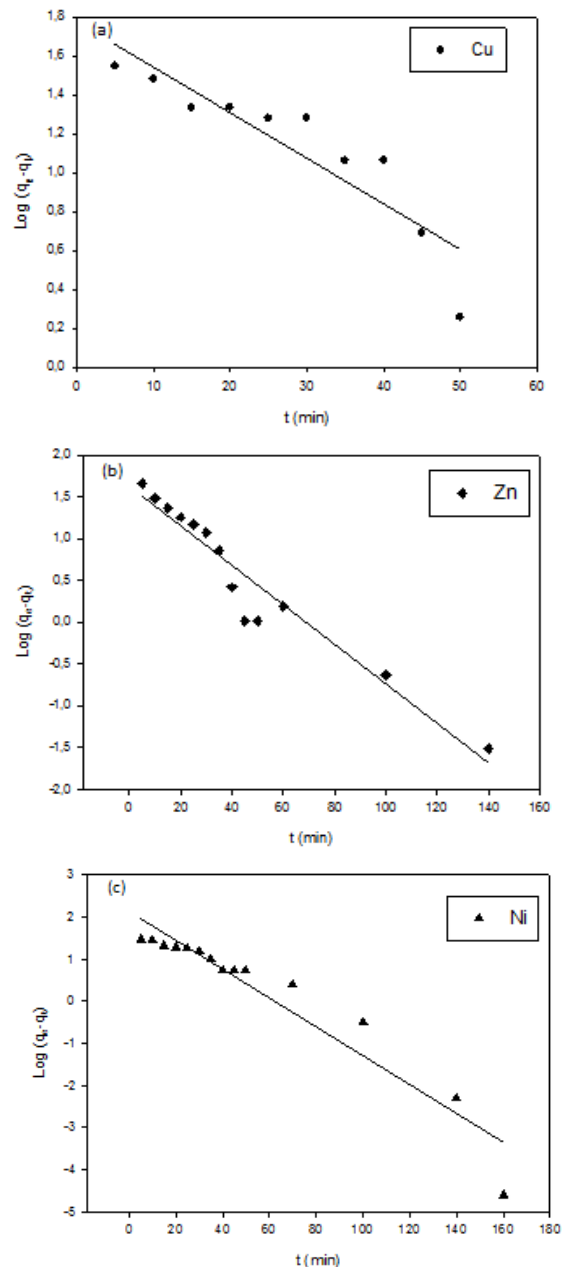
Figure 8. *Pseudo-first-order plots for the adsorption of Cu (II) (a), Zn (II) (b) and Ni (II) (c) onto RDS*
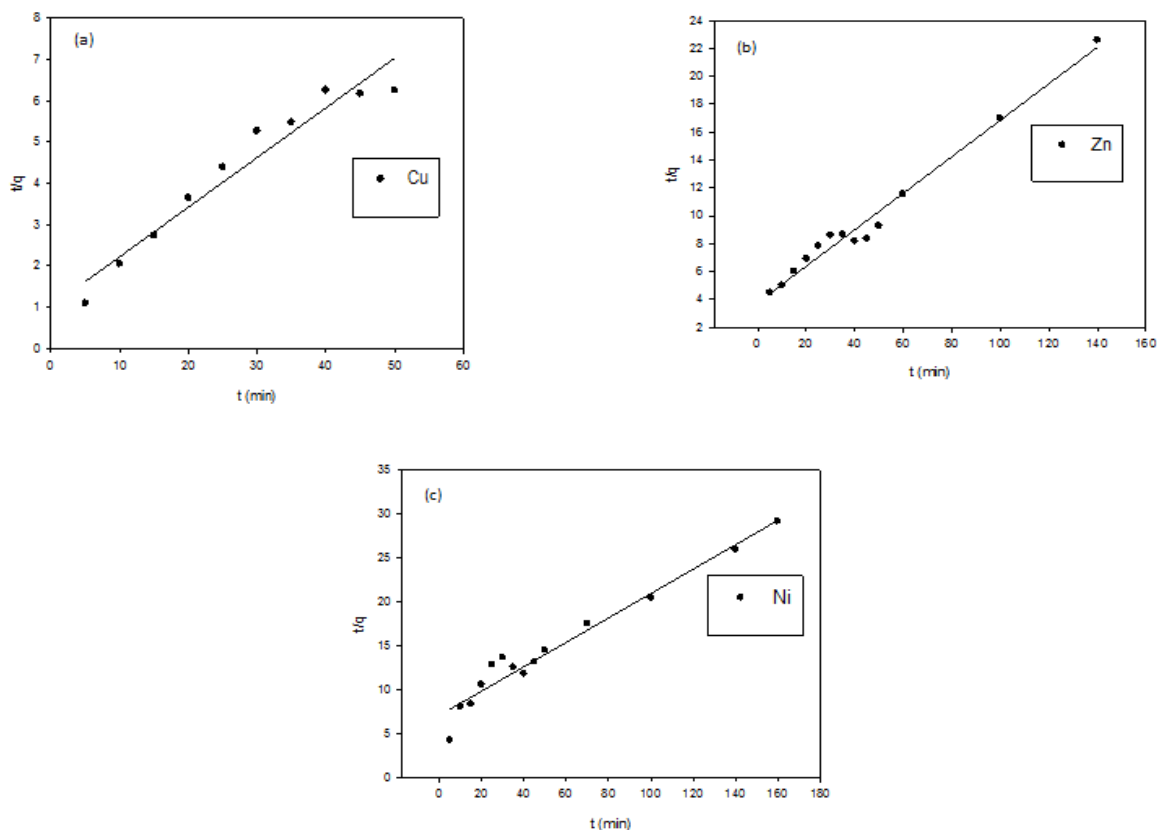
Figure 9. Pseudo-second-order plots for the adsorption of Cu (II) (a), Zn (II) (b) and Ni (II) (c) onto RDS.

Table 1. Kinetic parameters of Cu (II), Zn (II) and Ni (II) adsorption onto RDS.

Metal	q_{exp}(mg.g⁻¹)	Pseudo-first-order			Pseudo-second-order		
		q_e(mg.g⁻¹)	K_1(g.mg⁻¹.min⁻¹)	R^2	q_e (mg.g⁻¹)	K_2(g.mg⁻¹.min⁻¹)	R^2
Cu (II)	9.29	10.2410	0.1121	0.8964	10.7758	0.0052	0.9523
Ni(II)	5.50	5.3811	0.0792	0.9126	6 .6577	0.0034	0.9758
Zn (II)	6.47	8.3977	0.0545	0.9346	7.2621	0.0054	0.9935

III.9. Adsorption isotherms

The study of adsorption isotherm is a very important to obtain information about the mechanism and the interaction between the adsorbent and the adsorbate. The equilibrium adsorption experiments were analyzed by fitting them to Langmuir and Freundlich isotherm models. The linear form of the Langmuir and Freundlich isotherm equation are expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Where C_e (mg.L⁻¹) is the equilibrium concentration of the adsorbate, q_e (mg.g⁻¹) correspond to the amount of adsorbate adsorbed at equilibrium, q_m (mg.g⁻¹) is the maximum capacity (mg.g⁻¹) and b is Langmuir constant related to adsorption capacity and rate of adsorption. The intercept and the slope are obtained from the slope of the linear plot of $\ln q_e$ against $\ln C_e$ and provide the value of K_F and $1/n$. The essential characteristics of the Langmuir isotherm can be described by a distribution factor, defined as follows:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

Where R_L is the dimensionless equilibrium parameter and C_0 (mg.L⁻¹) is the initial adsorbate concentration, the value of R_L indicates the type of

isotherm, favorable when ($0<R_L<1$), unfavorable ($R_L>1$), linear ($R_L=1$) or irreversible ($R_L=0$).

Figure 10 and Figure 11 exhibited the comparison of linear form of Langmuir and Freundlich isotherm models for the adsorption of Cu(II), Zn(II) and Ni(II) onto RDS. According to the table 2, the maximum adsorption capacity was 26.74, 21.01 and 20.04 to mg.g^{-1} for Cu(II), Zn(II) and Ni(II) respectively; these results indicate a higher adsorption of Cu(II) compared to Zn(II) and Ni(II) under the same experimental conditions.
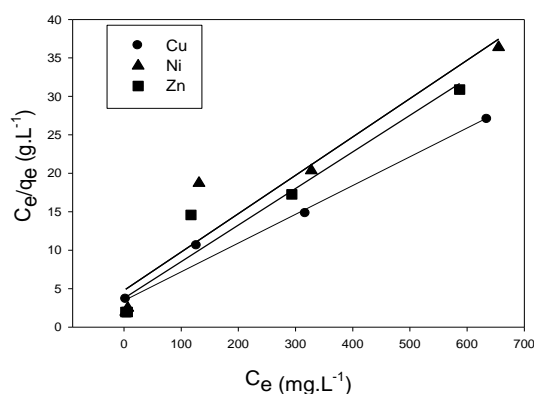

Figure 11. *Freundlich isotherm for Cu(II), Zn(II) and Ni(II) adsorption by RDS.*
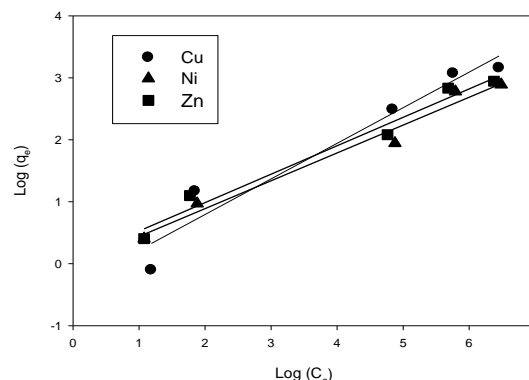

Figure 10. *Langmuir isotherm for Cu(II), Zn(II) and Ni(II) adsorption by RDS*

The adsorbent RDS had better applicability for Langmuir isotherm model than Freundlich isotherm model for the case of Cu ions, which confirmed monolayer adsorption and indicates surface homogeneity of the adsorbent. In addition, the values of R_L between 0.3 and 0.5 indicate favorable adsorption on RDS. The values of the adsorption capacity of other adsorbents from the literature are given in Table 3 for comparison.

Table 2. *Equilibrium model parameters for adsorption of Cu(II), Zn(II) and Ni(II) onto RDS.*

Adsorbent	Ion metal	Langmuir isotherm			Freundlich isotherm		
RDS		q_m(mg.g^{-1})	b (L.mg^{-1})	R^2	K_F(mg.g^{-1})	N	R^2
	Cu(II)	26.74	0,011	0,978	0,702	1,7412	0,942
	Zn(II)	21.01	0,013	0,937	1,072	2,1810	0,976
	Ni(II)	20.04	0,010	0,912	0,974	0,9735	0,976

IV. Conclusion

Raw date stones were used to remove Cu(II), Zn(II) and Ni(II) ions from aqueous solutions. SEM examination of raw material shows a very developed porosity before adsorption. Date stones used for this work were not treated chemically or thermally. Cu(II) showed higher adsorption capacity compared to Zn(II) and Ni(II), the maximum adsorption capacity was found to be 26.74, 21.01 and 20.04 mg.g^{-1} were observed for Cu(II), Zn(II) and Ni(II), respectively. Langmuir model fitted better the equilibrium adsorption data of Cu(II). The adsorption capacity was highest at solution pH 5. However, the results show that the raw date stones *Degla Beida (DB)* are an effective adsorbent for the removal of heavy metals from aqueous solution.

These preliminary batch experiments must therefore be followed by additional tests in a continuous system (column reactor) with improved adsorption/desorption rates to confirm the technical and economic interests of this adsorbent. Such tests are being performed and results will be published in the near future.

Table 3. *Comparison of the maximal adsorption capacities Cu (II), Zn (II) and Ni (II) ions obtained from various adsorbents.*

Adsorbent	Metal ion	pH	Adsorbant capacity(mg.g^{-1})	Reference
Raw date stones	Cu (II)	5	9.29	This work
Date stones	Cu (II)	6	31.25	[1]
Tea waste	Cu (II)	5.5	9	[37]
Rice husk	Cu (II)	6	29	[38]
Olive waste cakes	Cu (II)	4.79	12	[39]
Apricot stone	Cu (II)	6	22.85	[40]
Raw date stones	Zn (II)	-	6.47	This work
Activated carbon C	Zn (II)	-	4.01–18.53	[41]
Bentonite	Zn (II)	-	52.91	[42]
Red mud	Zn (II)	-	12.59	[43]
Peat	Zn (II)	-	9.28–12.1	[44]
Lignin	Zn (II)	-	95	[45]
Chitosan	Zn (II)	-	58.83	[46]
Raw date stones	Ni (II)	5	5.50	This work
Waste tea	Ni (II)	4	8.24	[47]
Sphagnum moss peat	Ni (II)	7	9.18	[48]
Melon seed husk	Ni (II)	-	5.9	[49]
Fly ash	Ni (II)	-	0.03	[50]

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Please cite this Article as:
Khenchelaoui S.; Gherbia A.; Medkour Y.; Chergui A.; Yeddou A.R.; Kerbachi R., Adsorption of Cu (II), Zn (II) and Ni (II) ions from aqueous solution by date stones, *Algerian J. Env. Sc. Technology*, *7*:1 (2021) 1750-1759