

Biosorption of heavy metals (Cooper, Nickel) and dye (methylene bleu) from aqueous solution onto southern Algerian carob shells

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Abstract

raw carob shells was used as biosorbent for removal of copper, nickel and methylene blue from aqueous solution. The adsorbent was characterized by thermal gravimetric analysis (TGA), The Brunauer-Emmett-Teller (BET) surface area, and the point of zero charge (pH_{PZC}). Biosorption experiments were carried out as function of solution pH, biosorbent dosage, contact time and initial ions concentration. Experimental results show that maximum biosorption capacity of 4.0, 3.91 and 13.17, mg/g for Cu (II), Ni (II) and MB respectively, occurred at an initial concentration of 100 mg/L, and temperature of 20 °C. Kinetic data were best fitted with pseudo-second-order. Biosorption isotherms were best correlated with Langmuir model for MB and Freundlich model for Cu (II) and Ni (II).

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Received 30 Dec 2019,

Revised 13 May 2020,

Accepted 26 Jun 2020

Keywords: Biosorption; Copper; Nickel; Methylene blue; Isotherms.

1. Introduction

Organic compounds as well as dyes and heavy metal are important pollutants in water, causing environmental problem to human beings and aquatic animals. These contaminants are non-biodegradable and highly toxic. In heavy metals Copper and nickel cause a serious case of pollution to the human body [1]. Copper and nickel ions Concentrations of 0.001 mg/L for Ni (II) and 0.1 mg/L for Cu (II) will fatal and cause illness in humans [2]. Methylene blue (MB) is selected as a model compound to evaluate the capacity of adsorbents for the removal of basic dyes from aqueous solutions. The presence of dyes in water, even at very low concentrations, is highly visible and undesirable. Wastewater from the textile and dyeing industries contains dye stuffs, suspended solids, other soluble organic substances, and heavy metals. In this way, the removal and recovery of heavy metals and dyes from wastewater before disposal in the environment is required [3]. Several methods have been used to remove heavy metals and dyes ions such as chemical precipitation [4], membrane filtration [5], ion exchange [6], solvent extraction [7], flotation [8], and electrochemical treatment [9]. Among all these mentioned methods adsorption is an effective method and attractive processes for the treatment of dyes and heavy metal bearing wastewaters [10-11]. Activated carbons are used as adsorbents in wastewater treatment because of their high surface area, but their high cost inhibits sometimes their use [12]. Recently low-cost biomaterials have become the focus of researchers such as, chitosans [13], bark of *Pinus elliottii* [14], starch [15], rice husk [16], *Eichornia crassipes* [17], and coconut [18]. This is due to their availability, environmental compatibility, cost effectiveness, renewability, and biodegradability. One of the low-cost natural is carob (*Ceratonia siliqua*). The aim of the present work is to evaluate the potential of carob shells for the removal Cu (II), Ni (II) and methylene bleu from aqueous solution. The effect of operating variables such as solution pH, adsorbent dose, contact time, initial ion concentration, on the percentage removal of metals and dye ions by raw carob shells were investigated.). Biosorption kinetic data were tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich models.

2. Materials and methods

2.1. Preparation of the RCS

The raw carob shells (RCS) were collected in the southern part of Algeria from Laghouat region. Firstly it was cut into small pieces and washed several times with distilled water in order to remove the impurities such as the sand and dust and then dried at 105°C for 120 min to evaporate the humidity. The obtained material was ground to improve its specific area. Finally, the powder was sieved at different diameters.

2.2. Characterization of the RCS

In order to study thermal behavior of the RCS by weight loss in the determined temperature ranges, thermo gravimetric analysis was carried out with TGA STA 504 instrument. A sample of the RCS was heated from the room temperature to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The Brunauer-Emmett-Teller (BET) surface area of the RCS was measured from N₂ adsorption/desorption isotherms at 77 K, using a Micromeritics ASAP 2020 instrument. The pH_{pzc} (point of zero charge) of RCS adsorbent was determined by mixing 0.05 g of RCS adsorbent with 50 mL of distilled water. The pH of the starting solutions (2.0 to 12.0) was adjusted using HCl or NaOH (0.1M). The containers were shaken for 24 hours. After filtration, the final pH was measured. The pH_{pzc} were determined by the curve intersect of graph ($\Delta\text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{final}}$) vs pH_{initial}.

2.3. Biosorption studies

Stock solutions of heavy metals and dye (1 g/L: Cu (II), Ni (II), MB) were prepared by dissolving desired weight in distilled water .The necessary concentrations were obtained by gradually diluting of the stock solutions. The batch

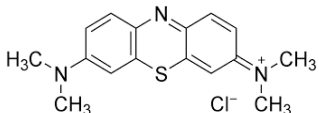
tests were conducted in 250 mL con-ical flasks containing 100 mL of Cu (II) or Ni (II) or MB solutions. To obtain the optimum conditions, the adsorption experiments were carried out by varying the adsorbent dosage (0.05-3 g) and pH of the solutions (from 2 to 6 for Cu (II), from 2 to 8 for Ni (II), and from 2 to 10 for dye), the contact time from 5 to 180 min. The solutions were shaken at 300 rpm at room temperature. The pH of the solutions was adjusted prior to the adsorption (time “zero”) by using 0.1 M solutions of HCl or NaOH. Adsorption isotherms were studied with different initial concentrations of metal ions and dye. The RCS was separated from the solution by filtration .The concentration of metal ions was measured by using AAS. The concentration of dye were analyzed by UV-vis spectrophotometer at the maximum absorption intensity of the corresponding wavelength max = 667 nm. The removal percentage and the equilibrium adsorption capacity Q_e , (mg/g) of the metal ions and dye were calculated by using Eq. (1) and Eq. (2), respectively.

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where C_0 and C_e (mg/L) are the initial and equilibrium metal ion and dye concentrations, respectively. V (L) is the volume of the solution and m (g) is the weight of dried adsorbent.

Table 1. Characteristics of MB.

Chemical formula	$C_{16}H_{18}N_3S\text{Cl}$
Chemical structure	
Molar mass (g /mol)	319.85
λ_{max} (nm)	667

3. Results and Discussions

3.1. Characterization of the RCS

TGA-DTG analysis

TGA and their first derivative DTG thermograms of RCS adsorbent are shown in figure 1. The TGA curve gives a mass loss in the range of 25-800 °C, which can be divided into several stages. The initial mass loss (5, 85 wt %) observed at temperature up to 150 °C can be ascribed to the dehydration of the sample [19]. The degradation of lignin and hemicelluloses occurs at temperatures from 150 °C to 450 °C [20].

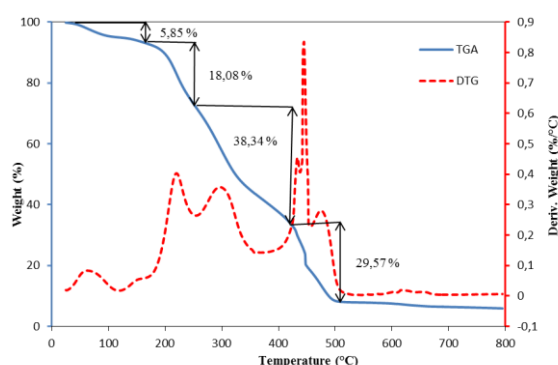


Figure 1. TGA-DTG curves of the RCS under argon atmosphere.

The mass loss (18, 08 wt %) between 150 °C and 240 °C corresponds to organic substances decomposition. The degradation of cellulose and hemicelluloses in this study observed at temperatures from 240 °C to 400 °C and lignin above 400 °C with mass loss increases drastically (67,91 wt %). The carob shell has an average fiber content of (67, 91 wt. %) including cellulose, hemicelluloses, lignin, followed by stabilization of the biomaterial was observed above 510 °C, in the TGA and DTG.

BET surface area:

Figure 2 shows the adsorption-desorption isotherms of N₂ by RCS. The obtained isotherms follow the patterns of type II based on IUPAC classification [21], which is characteristic for the macroporous or no porous materials, The BET surface area and pore volume were calculated as 0.9464 (m²/g) and 0.005048 (cm³/g) respectively.

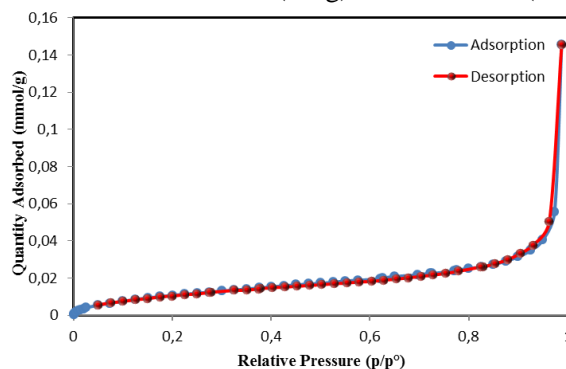


Figure 2. Nitrogen physisorption of the RCS adsorption-desorption isotherm.

Point of zero charge (pH_{pzc})

The pH_{PZC} is an important parameter in the adsorption corresponds to the pH value for which the net charge on the surface of the adsorbent is zero. The pH_{pzc} is found to be 6.3 which mean the surface is positively charged for pH values below the pH_{pzc} and negatively charged for higher pH values.

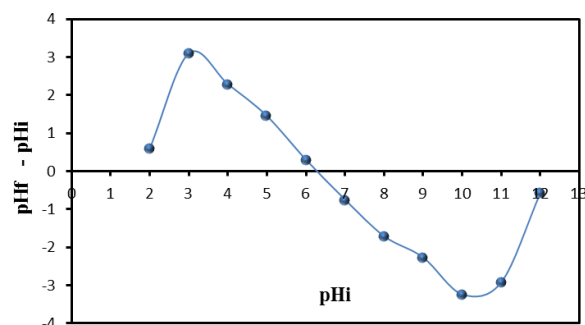


Figure 3. The pH_{PZC} (point zero charge) of the RCS.

3.2. Biosorption studies

Effect of adsorbent dosage

The search for the minimum mass of a material is an essential step in any study on adsorption. Figure 4 represents the Cu (II), Ni (II) and MB removal efficiencies for the study biosorbent. This figure indicates that the percentage removal of Cu (II), Ni (II) and MB increased with increasing biosorbent dose unto mass of 1 g with percentage removal 35, 46 % for Cu (II) and 26, 87 % for Ni (II), and 1.5 g for MB with percentage removal 91.47 %; due to the increase in the number of active sites in surface of adsorbent RCS. The stabilization can be explained by saturation of the active sites in the surface.

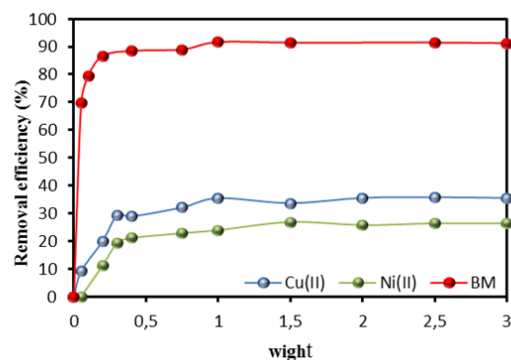


Figure 4. Effect of initial dose of RCS on the biosorption of Cu (II), Ni (II) and MB; (T = 20 °C, contact time: 24 h, C₀ = 100 mg/L).

Effect of pH

It is known that pH value plays an essential role in the removal of organic and inorganic pollutants from aqueous solution, since it indicates the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. Figure 5 shows the effect of pH on biosorption of Cu (II), Ni (II) and MB onto RCS. It can be seen that the percentage removal of Cu (II) and Ni (II) increase with increasing pH value in the pH range of 2-6. At low pH, the cations compete with the H⁺ ions in the solution for the sorption sites and therefore biosorption declines. The optimal pH for Cu (II), Ni (II) removal was 6. For MB it is remarkable that pH doesn't have much influence on the biosorption.

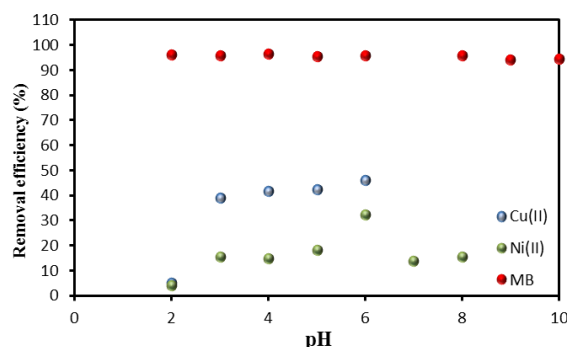


Figure 5. Effect of pH value on the biosorption of Cu (II), Ni (II) and MB by RCS; (T = 20 °C, contact time: 24 h, C₀ = 100 mg/L).

Effect of the initial concentration and the contact time

The influence of the initial concentration of Cu (II), Ni (II) and MB on biosorption by RCS was studied for concentration values of 25, 50, 75 and 100 mg/L shown in figure 6 (a), (b) and (c) respectively. From these figure we observe that the uptake of metal ion and dye occurred in two stages. In the first stage a rapid uptake of solid-liquid contact thanks to the total availability of exposed sites on the adsorbent. Then it becomes slower due to repulsive forces between cations already set and the free ones in solution. For the different concentrations ions, equilibrium is 90 min for Cu (II), 60 min for Ni (II) and 30 min for MB. As well we can observe an increase in the initial concentration leads to an increase in the adsorption.

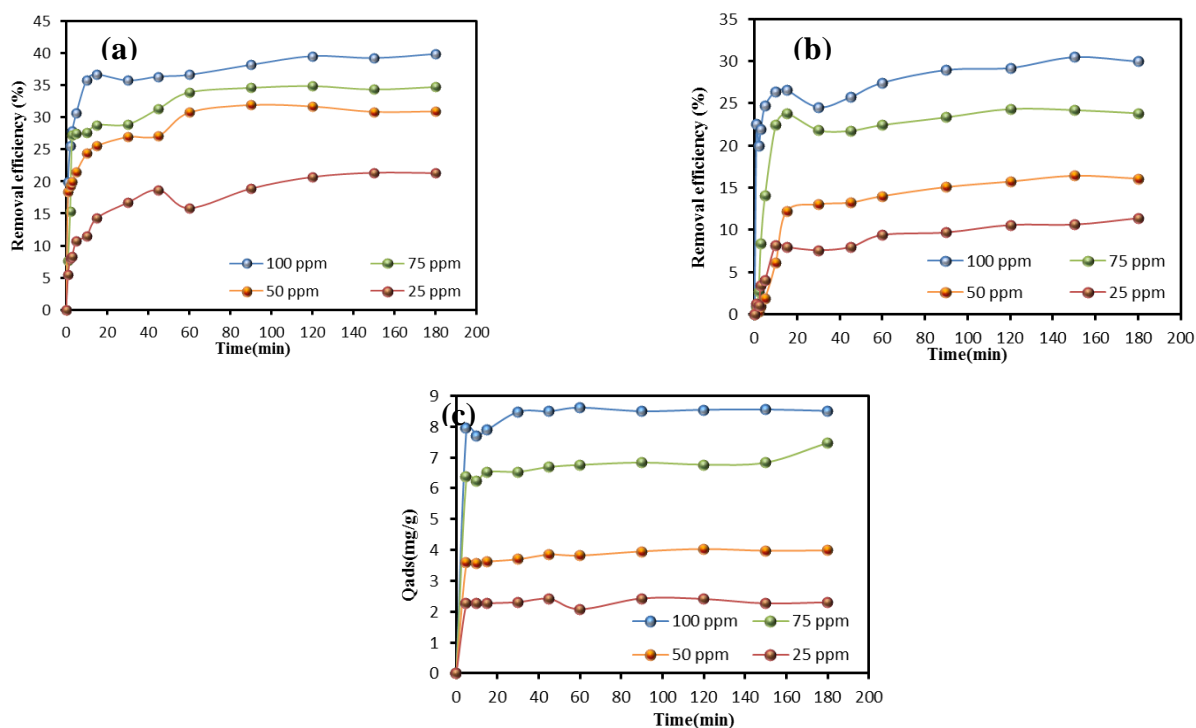


Figure 6. Effect of the initial concentration and the contact time on the biosorption by RCS of (a): Cu (II), (b): Ni (II) and (c): MB.

3.3. Biosorption isotherms

The biosorption isotherms describe how the adsorbate molecules are distributed between the liquid phase and solid phase when the system reaches the equilibrium. In this study the equilibrium data was analyzed by two models: Langmuir and Freundlich. Linearized form of Langmuir isotherm equation is [22]:

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

The Freundlich model is represented by the linearized equation [23]:

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (4)$$

C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorption per unit mass, q_{max} and K_L are Langmuir constants rate of adsorption, K_F (mg/g), is Freundlich constant and $1/n$ is the adsorption intensity values. The estimated adsorption parameters by the different models Langmuir, Freundlich isotherms are shown in

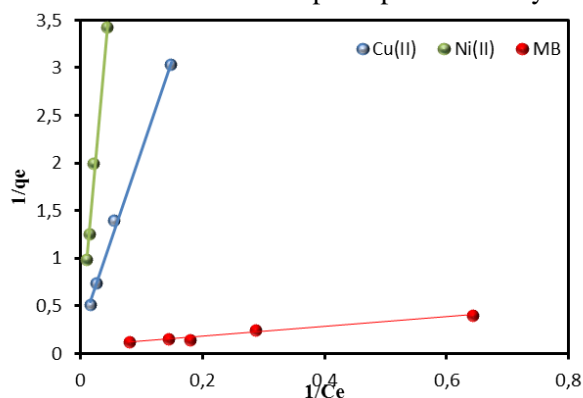


Figure 7. Langmuir Adsorption isotherm for the adsorption of Cu (II), Ni (II) and MB by RCS.

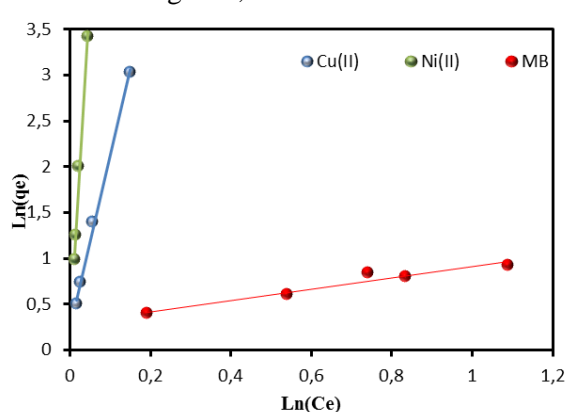


Figure 8. Freundlich Adsorption isotherm for the adsorption of Cu (II), Ni (II) and MB by RCS.

Table 2. From figure 7, figure 8 and table 2 linear Freundlich isotherm showed very good correlation coefficient for Cu (II), Ni (II). Whereas for MB the regression coefficient R^2 show that the Langmuir isotherm fitted quite well with the experimental data, it can be explained that surface monolayer [24]. The values of n are lower than 1 indicating the favorable adsorption of Cu (II), Ni (II) and MB onto RCS. As shown in the Table 1, the maximum adsorption capacities obtained with RCS for were 4.0 mg/g for Cu (II), 3.91 mg/g for Ni (II) and 13.17 for MB.

Table 2. Isotherm model analysis for the adsorption of Cu (II), Ni (II) and MB onto RCS.

Adsorbate	Langmuir			Freundlich		
	q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
Cu(II)	4.00	0.013	0.995	0.02	1.17	0.999
Ni(II)	3.91	0.003	0.989	0.01	1.12	0.991
MB	13.17	0.14	0.976	1.98	1.62	0.941

Table 3. The comparison between the adsorption potential of Cu (II), Ni (II) and MB removal from aqueous solution by RCS and by other biosorbents.

Adsorbate	Bioorbent	q_{\max}	References
MB	Luffa cylindrica fibers	19.319	[24]
	Caulerpa racemosavar.cylindracea	5.23	[25]
	Raw carob shells	13.17	This study
Ni	Palm fibers powder	4.42	[26]
	Sugarcane bagasse	2	[27]
	Raw carob shells	3.91	This study
Cu	Rice	2.95	[28]
	Oil palm shell	1.75	[29]
	Raw carob shells	4	This study

3.4. Biosorption Kinetics

Parameters from two kinetic models, pseudo first-order and pseudo second-order were fit to experimental data to examine the biosorption kinetics of Cu (II), Ni (II) and MB uptake onto RCS. The pseudo-first-order rate expression is given by the linearized equation as follows [30]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

The pseudo-second-order equation is given by the following linearized form [31]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e} t \quad (6)$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg/g), k_1 (1/min) is the rate constant and K_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg.min). The calculated kinetic parameters are given in Table 4. The correlation coefficients obtained from pseudo second-order model was very reliable ($R^2 = 0.99$), compared with R^2 obtained from pseudo first-order model. The experimental values of q_e and the

calculated values, indicate the applicability of pseudo-second order approach on the adsorption process of Cu (II), Ni (II) and MB at various concentrations.

Table 4. Kinetic model analysis for the biosorption of Cu (II), Ni (II) and MB onto RCS at various concentrations.

Concentration	Pseudo-first-order	Cu(II)	Ni(II)	MB	Pseudo-second-order	Cu(II)	Ni(II)	MB
50 mg/L	$q_{e,exp}$ (mg/g)	1.14	0.54	3.99	$q_{e,exp}$ (mg/g)	1.14	0.54	3.99
	$q_{e,cal}$ (mg/g)	0.52	0.44	0.54	$q_{e,cal}$ (mg/g)	1.13	0.56	4.02
	k_1 (1/min)	0.035	0.031	0.049	K_2 (g/mg min)	0.39	0.20	0.17
	R^2	0.93	0.86	0.81	R^2	0.99	0.99	0.99
75mg/L	$q_{e,exp}$ (mg/g)	2.60	1.53	6.83	$q_{e,exp}$ (mg/g)	2.60	1.53	6.83
	$q_{e,cal}$ (mg/g)	1.15	0.61	0.63	$q_{e,cal}$ (mg/g)	2.32	1.56	6.85
	k_1 (1/min)	0.03	0.036	0.055	K_2 (g/mg min)	0.20	0.12	0.15
	R^2	0.78	0.43	0.86	R^2	0.99	0.99	0.99
100mg/L	$q_{e,exp}$ (mg/g)	3.51	2.74	8.51	$q_{e,exp}$ (mg/g)	3.51	2.74	8.51
	$q_{e,cal}$ (mg/g)	1.24	0.84	1.59	$q_{e,cal}$ (mg/g)	3.50	2.80	8.56
	k_1 (1/min)	0.013	0.019	0.126	K_2 (g/mg min)	0.15	0.05	0.20
	R^2	0.65	0.59	0.64	R^2	0.99	0.99	0.99

4. Conclusion

During this study, raw carob shells was used as low-cost natural biosorbents for the removal of Cu(II), Ni (II) and MB from aqueous solutions, giving higher adsorption capacity for MB than Cu (II) and Ni (II).

The biosorption efficiency was tested by using different biosorption conditions. It was found that the biosorption increases with the increase of biosorbent dosage with an optimum at 1g/L for Cu (II), Ni (II) and 1.5 g/L for BM. The equilibrium time was obtained at 90 min for Cu (II), 60 min for Ni (II) and 30 min for MB. The rate biosorption was increased with an increase in the initial ions concentration in solution. The adsorption kinetics will best follow the pseudo-second-order kinetic model. The results of batch adsorption experiments were best fitted to the Langmuir model for BM and Freundlich model for Cu (II) and Ni (II) with the maximum capacity of 4.0, 3.91 and 13.17 mg/g for Cu (II), Ni (II) and MB, respectively. The result shows that MB may exhibit higher affinity and selectivity to raw carob shells.

Acknowledgements- The authors would like to thank the chemist members of the Laboratory of Mathematics and Applied Sciences, Ghardaia University, Algeria, and the chemist members of the Laboratory of Process Engineering, Laghouat University ,Algeria.also the members of the doctoral project team entitled management and development of natural resources in the Saharan regions,for their assistance during the development of the work.

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