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Biosorption of Zinc(II) and Copper(II) Ions from Aqueous Solution by Pericarps Oak Acorns

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In this study, the biosorption of zinc(II) and copper(II) ions in a binary solution onto pericarps Oak acorns was studied in a batch system as a function of pH of the solution, biosorbent concentration, initial concentration of ions, contact time and temperature. The removal efficiency of Zn(II) and Cu(II) was about 88.76 % at different temperatures. It was determined that the biosorption system obeyed the pseudo-second-order kinetic model by taking into account the correlation coefficient value ($R^2 > 0.99$). The Freundlich isotherm gave a better fit based on the values of the correlation coefficients ($R^2 > 0.99$). The results indicated that, pericarps Oak acorns could be used as an alternative and low-cost biosorbent for removal of zinc(II) and copper(II) ions from aqueous solutions, when suitable conditions are performed.

Keywords: Biosorption, Zinc(II), Copper(II), Oak acorns, Kinetic, Isotherm.

INTRODUCTION

Metallic trace elements (MTE) are chemical elements having a density more than 5 g/cm^3 and, atomic weights between 63.5 and 200.6 [1]. The discharge of waste water loaded with heavy metals in the environment increases with the fast development of various industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, *etc*. Because of their non-biodegradability, heavy metals have a tendency to be accumulating in living organisms. The heavy metals most often considered toxic to humans are lead, mercury, arsenic and cadmium. Others, such as copper, zinc, chromium, yet needed by the body in small amounts, can be toxic in larger doses.

Zinc is a trace element necessary for the metabolism of living beings, essential for many metallo enzymes and transcription factors that are involved in various cellular processes such as gene expression, signal transduction, transcription and replication. On the other hand, an excess of zinc can cause significant health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia [2]. Copper is an essential element in humans and animals (trace element), involved in many metabolic pathways, particularly for hemoglobin formation and maturation of neutrophils. However, the excess copper can cause severe toxicological preoccupations such as vomiting, cramps, convulsions, or even death [3].

To protect the health of humans and animals, it is required to remove maximum amount of metal ions from industrial wastewater before discharging it into the environment. For this purpose several physical and chemical technologies have been used, including precipitation, extraction, ion exchange, oxidation/reduction, filtration and reverse osmosis, But each method has these application limits. Because of their high operating cost and low elimination capacity at small scale industries [4,5].

The main advantages of biosorption compared to conventional technologies are low cost, effectiveness and its easy implement; which allows being the most commonly method used for the removal of heavy metals from industrial wastewater in recent years [4,6,7]. According to previous researches [8,9], biosorption is considered as an interesting technical and economic solution in the field of removal of heavy metals.

In this study, pericarps Oak acorns (POA), which were agricultural waste products, were used as adsorbent for the removal of zinc and copper ions in binary metal solution by using batch technique. The pericarps Oak acorns were characterized by FTIR spectroscopy to identify type of chemical bonds in the molecules present in this biosorbent. Chemical composition and proximate analysis of pericarps Oak acorns were determined using appropriate techniques. The percentage metal removal of Zn(II) and Cu(II) ions by the pericarps Oak acorns was investigated under different experi-

mental conditions, including pH, temperature, biosrobent dose, biosorption time and initial concentration of Zn(II) and Cu(II) ions.

The experimental data were analyzed using Langmuir and Freundlich models. In addition, kinetic parameters and maximum sorption capability were calculated and compared with those of some traditional sorbents.

EXPERIMENTAL

Preparation of biosorbent and solutions: Pericarps Oak acorns provided from a region of Sidi Yahia in Algeria were used in this study. The sample was dried at room temperature (about 20 °C) under atmospheric conditions and then dried in an oven at 100 °C prior to using the pericarps Oak acorns The sample was sieved and the fraction between 1 mm and 0.5 mm (0.5 mm < Ø < 1 mm) was maintained and used like biosorbent in this study. Finally the pericarps Oak acorns were stored in plastic bottles for further use.

Experimental solutions of mélange Zn(II) and Cu(II) ions with specified concentrations were prepared using analytical reagent grade $ZnCl_2$ and $CuCl_2{\cdot}2H_2O$ that was supplied by Merck during the study. The pH values of the solutions were adjusted to the desired values by using 0.1 N solutions of NaOH and 1 N of HCl. Preparation of all working solutions and dilutions were carried out using distilled water.

Analysis of pericarps Oak acorns

Proximate analysis of the pericarps Oak acorns: Samples were conducted using conventional AFNOR standard methods. For this purpose, AFNOR T90-102 use to determine ash content of the samples. Also, the moisture content of pericarps Oak acorns samples was determined using a DAIHAN LABTSCHCO, LTD moisture measurement device at 105 °C to constant weight.

BET analysis: This was performed by the adsorption of N_2 at 77 K using Quantachrome Nova Win2 apparatus. Before measuring the adsorption of N_2, the sample was subjected to degassing for 6 h at a final pressure of 133.32×10^{-4} Pa. The surface area or pore size/volume was estimated from the volume of N_2 (as liquid) held at a relative pressure (P/P_0) of 0.99.

FTIR analysis: The chemical properties of the pericarps Oak acorns were characterized using Fourier-transform infrared (FTIR) spectroscopy. FTIR spectra were acquired using a FTIR spectrometer (BRUKER ALPHA-T) by averaging 15 scans in the range of 4000–400 cm^{-1}. For FTIR analysis the 5 mg pericarps Oak acorns samples were homogenized with 150 mg KBr to obtain mass ratio of 1:30. This mixture was pressed for 2 min using a hydraulic press to prepare pellets with1 mm thickness. The pellets were dried at 80 °C for 120 min and then stored in desiccators. Pure KBr pellet of 155 mg was used as a reference.

SEM analysis: The particle morphology of pericarps Oak acorns was examined by using a scanning electron microscope (ESEM XL30 filament) with an accelerating voltage of 20 kV.

Equipment and procedure: The experiments were performed in 6 parallel beakers using a magnetic shaker, at an agitation speed of 350 rpm. The content of all beakers were prepared in the same conditions. At the end of the certain contact time, the biosorbent was separated from the aqueous phase by filtration. The residual concentration of Zn(II) and Cu(II) in the filtrate was analyzed by anatomic adsorption spectrophotometer (SOLAAR AASPECTROMETER Thermo Elemental)

Each experiment was conducted by mixing 100 mL of mélange Zn(II) and Cu(II) solutions with a certain amount of the pericarps Oak acorns sample in 250 mL beaker. The pH of the solution was adjusted with 1 N NaOH and 0.1 N HCl. the experiments, in which the effect of temperature, pH, contact time, biosorbent concentration and initial concentration of mélange Zn(II) and Cu(II) ions were examined. The ranges of these considered parameters were 20–40 °C, 2.0–9.0, 5–140 min, 0.2–2 g/100 mL and 100–500 mg/L, respectively.

The amount of Zn(II) and Cu(II) ions removed by the biosorbent phase q_e (mg/g) was calculated from the expression (eqn. 1):

$$q_e = V \times (C_0 - C_e)/m \quad (1)$$

The biosorption percentage of Zn(II) and Cu(II) ions was calculated using the equation expressed as follows (eqn. 2):

$$\text{Biosorption yield } (\%) = (C_0 - C_e) \times 100/C_0 \quad (2)$$

where, C_0 and C_e, are the initial and final (equilibrium) concentrations of the Zn(II) and Cu(II) ions in solution (mg/L), respectively, m is the mass of the biosorbent (g) and V is the volume of the solution (L).

Equilibrium and kinetic studies: Interaction of adsorbate with the adsorbent materials is indicated by the adsorption isotherm. It is important to establish the most appropriate correlations for the equilibrium data of the system for optimizing the design of adsorption process to remove Zn(II) and Cu(II) ions. The Langmuir and the Freundlich isotherms were used to correlate the equilibrium data for zinc(II) and copper(II) removal. Linear regression is generally used to find the best fitted isotherm and also the correlation coefficients R^2 are evaluated to compare the practicality of isotherm equation.

The Langmuir isotherm model is applicable to monolayer adsorptions and can be defined as [10] (eqn. 3):

$$C_e/q_e = [1/(K_L\, q_m)] + (C_e/q_m) \quad (3)$$

where q_e (mg/g) is the equilibrium zinc(II) and copper(II) biosorption capacity of the pericarps Oak acorns, C_e (mg/L) is the metal ion concentration in the solution at equilibrium. Also, q_m (mg/g) and K_L (L/mg) are Langmuir constants related to maximum adsorption capacity and rate of adsorption which are obtained from the slope and intercept of the linear plot of C_e/q_e *versus* C_e.

The empirical Freundlich isotherm proposes a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules and can be expressed as [11] (eqn. 4):

$$\log (q_e) = \log (K_F) + (1/n) \log (C_e) \quad (4)$$

where, K_F (mg/g) and n (g/L) are the Freundlich adsorption constant and heterogeneity factor, respectively. K_F is related to the bonding energy and 1/n value is related to intensity of the adsorption. Values of n > 1 represent favourable adsorption condition [12].

Kinetic studies are required to determine the equilibration time for biosorption, thus the pseudo-first, pseudo-second order, Elovich and diffusion kinetic models were used to investigate the kinetics of Zn(II) and Cu(II) biosorption on pericarps Oak acorns. A model which fits better was determined according to the regression coefficient (R^2) and degree of similarity of the experimental and the calculated q_e values to each other. The pseudo-first order rate expression is defined as [13] (eqn. 5):

$$\log (q_e - q_t) = \log (q_e) - [(K_1)/2.203] \quad (5)$$

where q_e and q_t (mg/g) are biosorption capacities at equilibrium at time t (min), respectively and K_1 (min^{-1}) is the rate constant of pseudo-first order adsorption. The values of K_1 and q_e were calculated from the slopes and intercepts of the linear plots of $\log (q_e - q_t)$ *versus* t.

The pseudo-second order model is more suitable for the description of the kinetic behaviour of adsorption in which chemical sorption is the rate controlling step. The pseudo-second order kinetic model is presented as [14] (eqn. 6):

$$t/q_t = [1/(K_2 q_e^2)] + t/q_e \quad (6)$$

where K_2 (g/(mg min)) is the rate constant of pseudo-second order adsorption [11]. If pseudo-second order kinetic equation is suitable, q_e and K_2 can be determined experimentally from the slope and intercept of plot t/q_t *versus* t.

Elovich order rate expression is defined as [15] (eqn. 7):

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \quad (7)$$

where q_t (mg/g) is the biosorption capacity of zinc(II) and copper(II) on the pericarps Oak acorns at time t (min), α is the constant of initial velocity (mg g^{-1} min^{-1}), β is the constant of adsorption (g mg^{-1}).

The values of α and β were calculated from the slopes and intercepts of the linear plots of q_t *versus* ln t.

Modeling the transfer of a solute from a liquid phase to a solid phase, to express the outreach is often given by diffusion expression [16] (eqn. 8):

$$-\log\left(1-\left(\frac{q_t}{q_e}\right)^2\right) = \left(4\pi^2 \times \frac{D}{2.3d^2}\right) \times t \quad (8)$$

where q_e and q_t (mg/g) are biosorption capacities at equilibrium at time t (min), respectively, d is the particles diameter, D is the diffusivity material (cm^2 s^{-1}). The value of D can be determined experimentally from the slope and intercept of plot $-\log (1-(q_t/q_e)^2)$ *versus* t.

The criterion for measuring the accuracy of theoretical and experimental values of "q_e" is the according to partial hybrid error (eqn. 9) and standard deviation of percentage Marquart MPSD (eqn. 10):

$$\text{HYBRID} = \frac{100}{n-p} \sum_{i=1}^{n} \frac{(q_{e\,exp} - q_{e\,cal})^2}{q_{e\,exp}} \quad (9)$$

$$\text{MSPD} = 100 \sqrt{\sum_{n-p}^{n} \frac{1}{n-p} \left(\frac{q_{e\,exp} - q_{e\,cal}}{q_{e\,exp}}\right)^2} \quad (10)$$

RESULTS AND DISCUSSION

Characterization of pericarps Oak acorns: The physical characterization of pericarps Oak acorns showed that moisture content was 34.027 %, since they require drying before the use. The average bulk density of pericarps Oak acorns was found to be 389 kg/m^3 and it is characterized with a very small percentage of ash (0.375 %), this is advantageous for the biosorbent proprieties of our material, because a low percentage of ash indicates an important organic matrix [17].

BET analysis: Multi point BET surface area of the pericarps Oak acorns was determined by the nitrogen adsorption method as 1.087 m^2/g using a Quantachrome Nova Win2 apparatus.

FTIR analysis: In order to provide qualitative information of the characteristic functional groups which exist in the pericarps Oak acorns structure, the FTIR spectra of the samples were taken and the results were shown in Fig. 1. The –OH stretching vibrations, strong and broad intensity at 3423.24 cm^{-1} indicated the presence of phenols and alcohols, which confirms the presence of cellulose and lignin in the pericarps Oak acorns samples. Cellulose and lignin molecules contain –OH groups. The band observed at about 2919.24 cm^{-1} could be assigned to the O–H stretch, correspond to the –COOH group of the carboxylic acid.

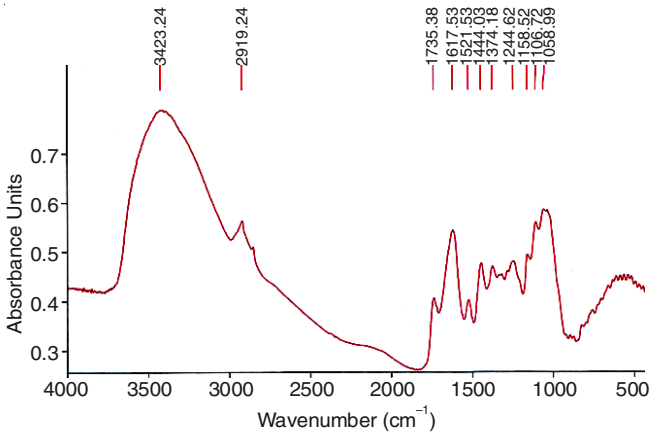

Fig. 1. FTIR spectra of pericarps Oak acorns sample

The peak at1735.38 cm^{-1}, correspond to the C=O stretching vibrations, indicated the presence of esters. The peaks observed at 1617.53 cm^{-1} correspond to the primary amine group. The bands at 1521.53 cm^{-1} representing bonded –NH groups of secondary amine, not always visible. At 1444.03 cm^{-1}, the O-H stretching vibrations occurred within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded O–H bands of carboxylic acids.

A peak at 1374.18 cm^{-1} corresponds to the O-H stretching, indicated the presence of aromatic alcohols or tertiary alcohols. 1058 cm^{-1}: C–OH stretching vibration of cellulose and hemicelluloses.

SEM analysis: Scanning electron microscopy (SEM) technique was used to examine the physical morphologies and surface properties of pericarps Oak acorns. The textural structure examination of pericarps Oak acorns particles could be observed from the SEM images at 250; 500 and 1000 times

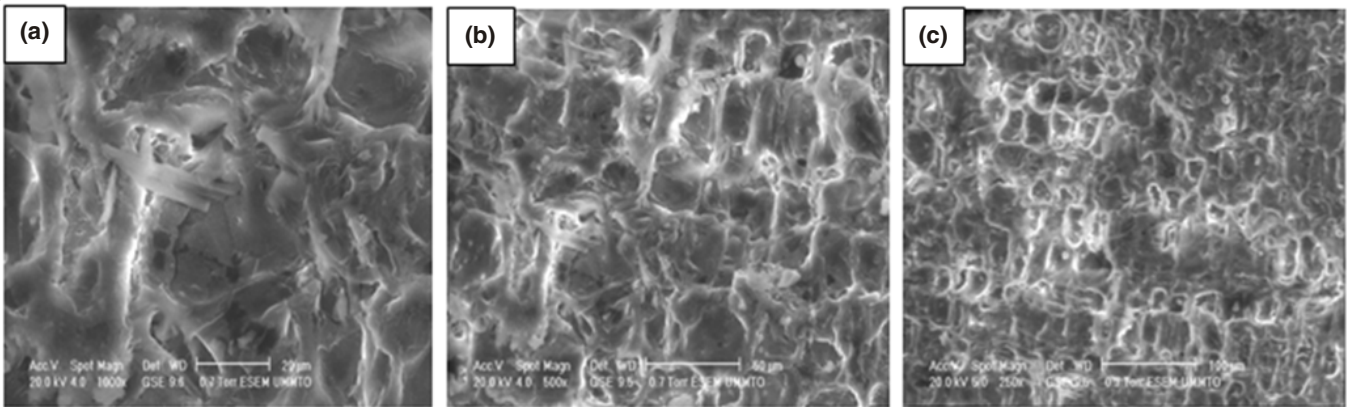

Fig. 2. SEM images of pericarps Oak acorns at (a): 250×, (b): 500× and (c): 1000× magnification

magnication (Fig. 2). It was seen that pericarps Oak acorns had sponge-like morphology and macropores with different pore sizes and pore shapes.

Effect of pH: It is well known that the pH of the solution is one of the most important parameters in the removal of heavy metals from aqueous solution. The pH of the solution has an ability to affect the surface charges of the biosorbent, the concentration of the counter ions on the functional groups of the biosorbent, the degree of ionization of the biosorbent during biosorption and the forms of the metal ions in aqueous solutions [18,19].

In this study the effect of pH on the biosorption of Zn(II) and Cu(II) ions on the pericarps Oak acorns was investigated. These experiments were carried out by changing the initial pH of the solutions from 2 to 9, while the other operational parameters were kept constant.

Biosorption of Zn(II) and Cu(II) were measured at given contact times for six different experimental values of pH (2, 3, 5.5, 7, 8 and 9) at 100 mg/L as a total initial metals ion concentration and 2 g/100 mL as a biosorbent dosage. The effect of the pH on the biosorption percentage over the given time is shown in Fig. 3. In acidic conditions (2-3), the adsorption of Zn(II) and Cu(II) ions onto pericarps Oak acorns was quite low. Because large hydrogen ions compete with metal ions at sorption sites and restrict the approach of metal cations as a result of the repulsive force [20-22]. At high acidic pH, the concentration of protons is high, so metal binding sites become positively charged and metal cations and protons compete for binding sites, resulting in lower uptake capacity of metal. The removal capacity increased rapidly when pH increased from 2 to 5.5. When the pH of the solution was raised from 2 to 5.5, the removal efficiency was increased from 30.546 to 50.304 % for Zn(II), 44.191 to 86.782 % for Cu(II) ion. The maximum removal was found to be 88, 93 % for Zn(II) at pH 8 and 86.782 % for Cu(II) ions at pH 5.5, while the optimal pH for the total [Zn(II) + Cu(II)] is 7 which corresponds to a removal efficiency of 86.759 %. This could be explained by the increase in density of the negative charge on the cell surface, causing proton removal on the cell bonding sites, thereby increasing its biosorption capacity. Comparison between those results and the results from this study is difficult because of the different parameters that play a role in the adsorption mechanism such as inherent characteristics of the

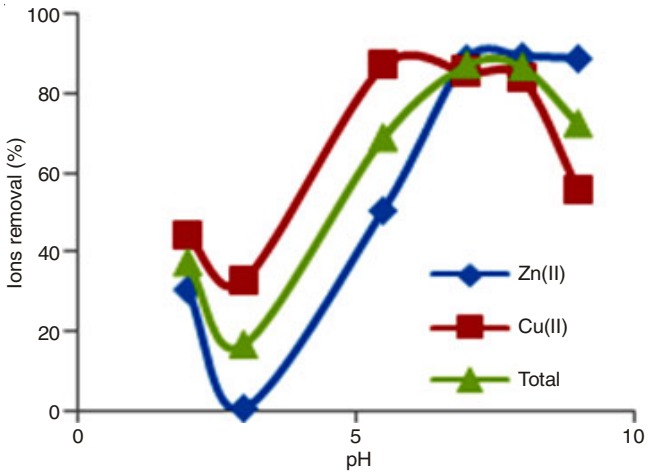

Fig. 3. Effect of pH on Cu(II) and Zn(II) biosorption by pericarps Oak acorns. [Cu(II) and Zn(II) concentration: 100 mg/L, biosorbent dosage: 2 g/100 mL, temperature: 20 °C, contact time: 140 min]

adsorbent (surface area, composition and surface charge capacity), metal affinity and experimental conditions (pH, temperature, *etc*) [23].

Effect of bisorbent dosage on metals biosorption: The biosrobent dosage is an important parameter as it determines the capacity of a biosorbent for a given initial concentration [24]. The removal of Zn(II) and Cu(II) ions on pericarps Oak acorns was studied using different biosorbent dosages of 0.2, 0.5 1, 1.5 and 2 g/100 mL in 100 mg/L total initial metal ions concentration and at pH 7 is shown in Fig. 4.

There was an increase in sorption capacity whenever there was an increase in biosorbent dosage from 0.1 to 2 g/100 mL. Moreover, the maximum removals were 88.368 % and 85.150 % for Zn(II) and Cu(II) respectively, which is 86.759 % for the total at 2 g/100 mL of biosorbent dosage.

It is well known that the removal efficiency of metals depend on the type and quantity of the biosorbent. An increase in biosorbent concentration generally increases the adsorbed metals concentration because of large adsorption surface area. The same trend has also been reported in the removal of Zn(II) and Cu(II) ions by some other materials [25,26]. The results indicated that a dose of 2 g/100 mL of biosorbent could be sufficient for the optimum removal of Zn(II) and Cu(II) ions.

Effect of initial concentration on metals biosorption: In order to investigate the effect of the initial concentration of

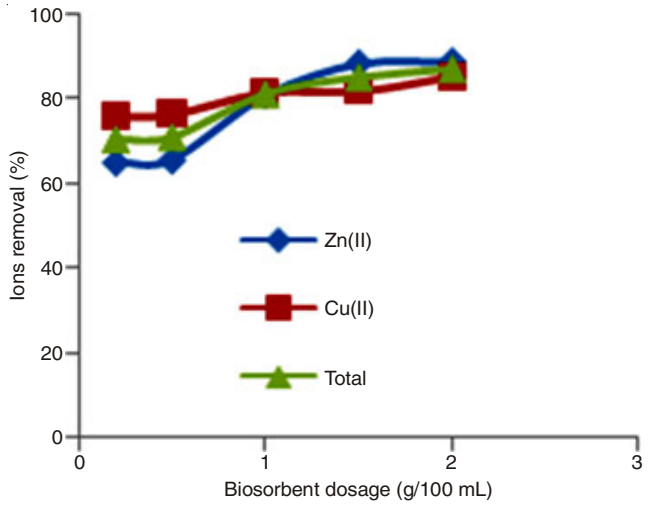

Fig. 4. Effect of pericarps Oak acorns dosage on Zn(II) and Cu(II) biosorption [pH: 7, Zn(II) and Cu(II) concentration: 100 mg/L temperature: 20 °C, contact time: 140 min]

Zn(II) and Cu(II) on biosorption behaviour, experiments were carried out according to the optimum conditions obtained in previous tests, that is, pH value of 7 and adsorbent dosage of 2 g/100 mL, initial concentration of metal ions varied from 100 to 500 mg/L. Results (Fig. 5) revealed as the removal efficiency of biosorption of Zn(II) and Cu(II), on pericarps Oak acorns decreased with increasing of initial concentration of metal ions in the aqueous solution. The maximum removal of the total [Zn(II) + Cu(II)] was obtained, with a total initial concentration 100 mg/L.

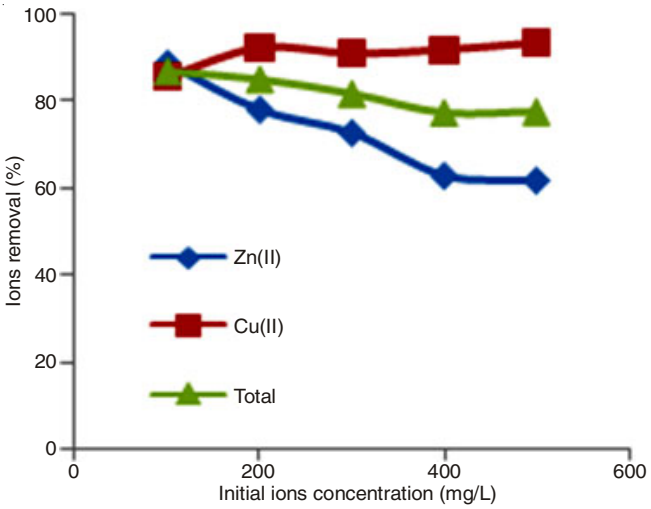

Fig. 5. Effect of initial ions concentration on Zn(II) and Cu(II) biosorption (pericarps Oak acorns concentration: 2 g/100 mL; pH: 7; temperature: 20 °C; contact time 140 min)

The reason for this trend might be due to limited number of active sites on the biosorbent, which would have become saturated above a certain concentration. Increase of the total initial concentrations of Zn(II) and Cu(II) results in a decrease in the initial rate of external diffusion and increase in the intraparticle diffusion rate [27].

Effect of contact time-temperature on Zn(II) and Cu(II) biosorption: The effect of contact time (5-140 min) on the biosorption of Zn(II) and Cu(II) by pericarps Oak acorns was studied by using 2 g of biosorbent with 100 mL of 100 mg/L zinc and copper solution at three different temperatures (20, 30 and 40 °C).

Kinetics studies provide important information about the possible mechanism of adsorption that involves the diffusion (bulk, external and intraparticle) and chemical reactions. In general, it is assumed that the metal ion transport occurs in the following steps: (1) external diffusion (from the bulk solution to the external surface of the sorbent); (2) the transport across the boundary layer; (3) the transfer in the pores to the internal parts of the adsorbent and uptake by the active sites; (4) sorption and desorption [28].

The kinetic curves in Fig. 6, show that in the initial stages of the sorption process the amounts of mixture Zn(II) and Cu(II) retained on pericarps Oak acorns increased sharply with increasing contact time of the phases. Reaching values that remained then almost constant.

A similar trend was observed for the case of removal of Zn(II) by rapeseed waste [29] and the removal of Cu(II) by chemically treated tomato waste [26]. In this context, it can be considered that the retention of Zn(II) and Cu(II) ions on pericarps Oak acorns takes place in two distinct steps, a relatively fast phase followed by a slower one. This two phases of biosorption may be explained by taken into account the fact that the number of active sites in a system is fixed and each active site can adsorbed only one ion. The metal uptake by the biosorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensies by the metal ions remaining in solution [30].

The biosorption capacities at 20, 30 and 40 °C were not signicantly different (Fig. 6), suggesting that the Zn(II) and Cu(II) biosorptions by pericarps Oak acorns were stable over a wide range of temperatures.

Kinetic studies: The kinetic of the adsorption explains the variation in uptake of an adsorbate in terms of time and its parameters give important information about modeling and designing the process of biosorption [31]. To this end, the biosorption data were analyzed with four kinetic models:

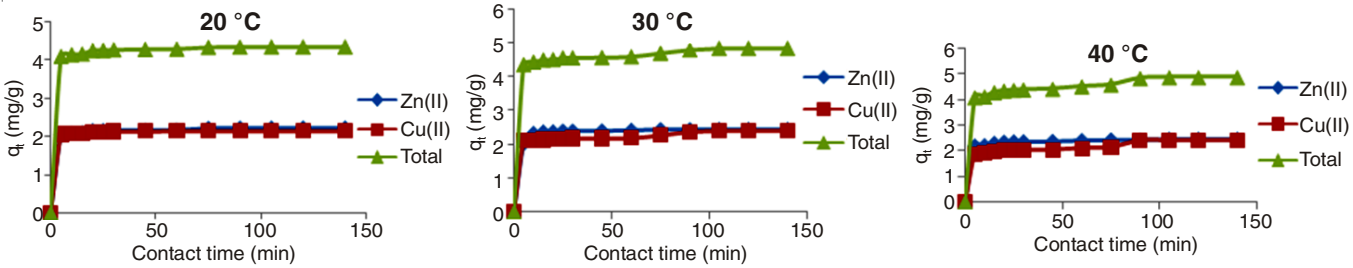

Fig. 6. Effect of contact time on Zn(II) and Cu(II) biosorption (pericarps Oak acorns concentration: 2 g/100 mL; pH 7; metals concentration 100 mg/L, contact time 140 min at different temperatures)

pseudo-first order, pseudo second-order, Elovich and diffusion model.

The parameters K_2 and q_e can be obtained directly from the intercept and slope of the plot of (t/q_t) *versus* t (Fig. 7). According to Table-1, the pseudo-second-order kinetics model achieved a larger correlation coefficient ($R^2 > 0.99$) and between q_e cal and q_e differences achieved less. As a result shows, the pseudo second-order kinetic model was more representative than other kinetic models for simulating the kinetic data at different temperatures.

High regression coefficients and low errors for two metal ions and for the total metal ions were observed. This result implicates that the pseudo second-order equation is applicable to all the sorption data and also shows that chemisorptions is the dominant process. The advantages of pseudo second-order equation include the biosorption capacity, rate constant of pseudo second-order and the initial biosorption rate, all of which can be determined from the equation without knowing any parameter [22].

The adequacy of pseudo-second order model with experimental results, is confirmed by the perfect superimposition of the curves plotted using experimental data and those predicted by the model at different temperatures (Fig. 8).

Isotherm studies: Modeling is important for prediction and comparison of biosorption capacity, for which two, three and four parameter isotherm models are available. However, two-parameter models are usually preferred because of their simplicity and easy linearization. The equilibrium sorption

TABLE-1
KINETIC PARAMETERS FOR THE REMOVAL OF Zn(II) AND Cu(II) BY PERICARPS OAK ACORNS

Metal	Temperature (°C)	Pseudo first- order kinetic model				
		R^2	K1 (min^{-1})	q_e cal (mg/g)	HYBRID	MPSD
Zn(II)	20	0.839	0.044	0.301	187.223	93.342
	30	0.826	0.041	0.239	222.783	96.511
	40	0.834	0.029	0.342	209.362	94.289
Cu(II)	20	0.887	0.076	0.671	122.610	76.374
	30	0.703	0.021	0.473	185.597	91.769
	40	0.613	0.029	0.897	122.639	74.307
Total	20	0.896	0.048	0.417	394.999	96.339
	30	0.821	0.023	0.618	422.943	95.896
	40	0.751	0.025	1.021	360.739	86.888
Metal	Temperature (°C)	Pseudo second- order kinetic model				
		R^2	K2 (g/(mg.min))	q_e cal (mg/g)	HYBRID	MPSD
Zn(II)	20	0.999	0.583	2.222	0.078	1.942
	30	1	0.729	2.457	0.013	0.741
	40	0.999	0.369	2.469	0.118	2.316
Cu(II)	20	1	1.888	2.137	0.008	0.621
	30	0.998	0.165	2.404	1.293	7.836
	40	0.994	0.091	2.463	2.259	1.799
Total	20	1	0.448	4.367	0.058	1.180
	30	0.999	0.139	4.854	0.883	4.488
	40	0.998	0.077	4.926	1.931	6.827
Metal	Temperature (°C)	Elovich kinetic model				
		R^2	a*	b*	HYBRID	MPSD
Zn(II)	20	0.950	0.051	1.966	0.007	0.567
	30	0.918	0.051	2.206	0.011	0.699
	40	0.954	0.084	2.054	0.016	0.844
Cu(II)	20	0.863	0.026	2.010	0.006	0.536
	30	0.779	0.098	1.856	0.134	2.465
	40	0.820	0.176	1.495	0.339	3.977
Total	20	0.942	0.077	3.976	0.010	0.478
	30	0.914	0.150	4.062	0.049	1.029
	40	0.912	0.260	3.550	0.155	1.185
Metal	Temperature (°C)	Diffusion kinetic model				
		R^2	$D \times 10^{-3}$ ($mm^{-2}.min^{-1}$)	HYBRID	MPSD	
Zn(II)	20	0.828	0.292	0.081	1.969	
	30	0.801	0.262	0.034	1.206	
	40	0.797	0.204	0.058	1.588	
Cu(II)	20	0.881	0.481	0.018	0.937	
	30	0.671	0.131	0.338	3.649	
	40	0.616	0.204	1.363	8.333	
Total	20	0.846	0.321	0.099	1.546	
	30	0.708	0.160	0.313	2.649	
	40	0.737	0.175	0.738	4.179	

*a = 1/β; *b = 1/β·ln(α.β)

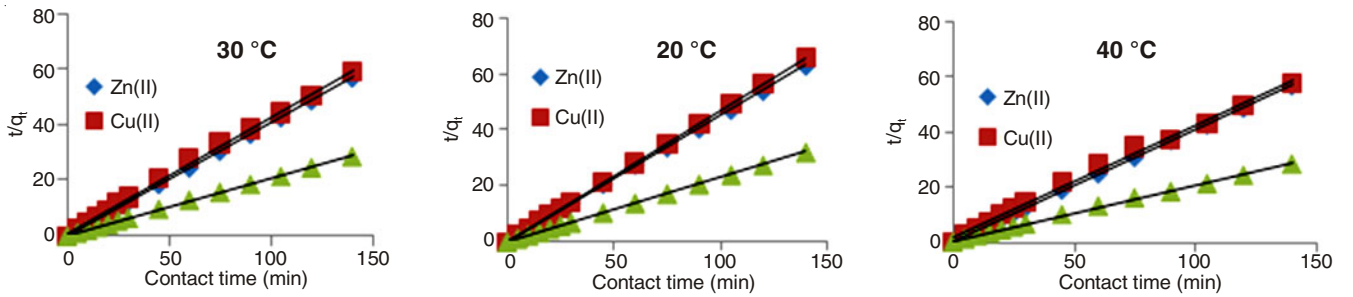

Fig. 7. Pseudo-second-order kinetic plots, for the removal of Zn(II) and Cu(II) at different temperatures

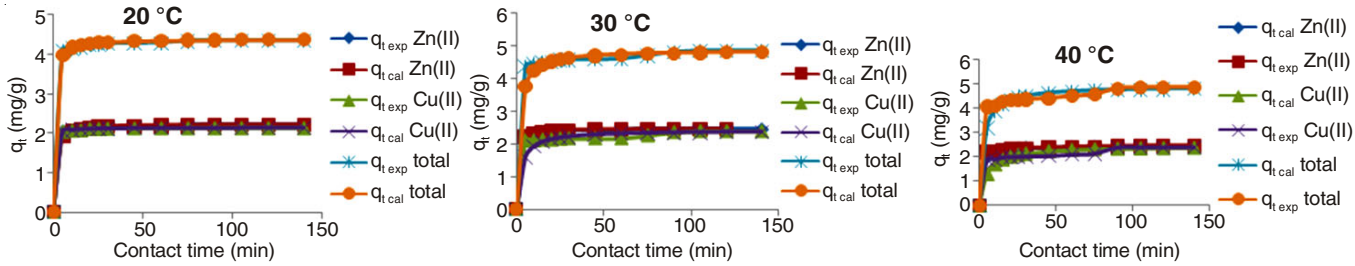

Fig. 8. Comparison of experimental data of the kinetic of adsorption of Zn(II) and Cu(II) by pericarps Oak acorns with that obtained by the pseudo-second order model at different temperatures

isotherm, which indicates the capacity of the sorbent, is important in the design of biosorption systems; it is a description (by a sorption isotherm) characterized by certain constant values that express the surface properties and affinity of the sorbent. The equilibrium relationships between sorbent and sorbate are described by sorption isotherms, as they are usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. In the present work, two isotherm models, Langmuir and Freundlich were used to describe the equilibrium between the metals Zn(II) and Cu(II) sorbed onto the pericarps Oak acorns and the metal ions in the solution.

The biosorption capacities q_e as a function of C_e was shown in Fig. 9. The equilibrium adsorption amount was increasing while the initial concentration increased, which is consistent with literature data: copper adsorption by hazelnut shell [32], copper adsorption by almond shell [33] and adsorption of methylene blue by bentonite [34].

The Langmuir isotherm [35] describes the ion adsorption to ligand sites in a single layer on the biosorbent surface and no interaction with the adsorbed species.

The Freundlich isotherm is applied for heterogeneous surfaces adsorption accompanied by interaction between biosorbed molecules.

The isotherm constants and the correlation coefficients (R^2) with the experimental data are given in Table-2, which shows that the R^2 value is greater ($R^2 > 0.99$) in the Freundlich isotherm than the Langmuir isotherm. It was determined that

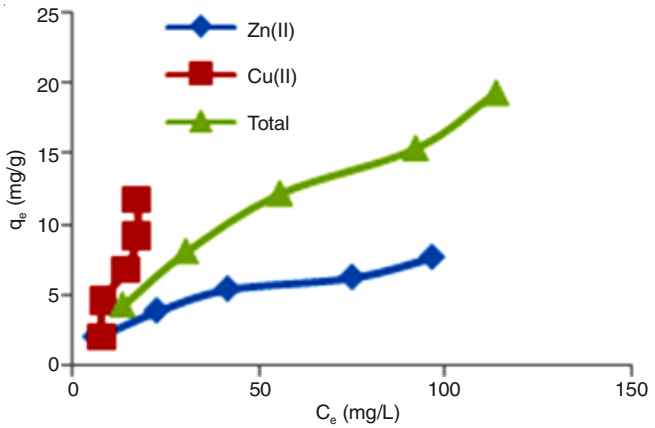

Fig. 9. Adsorption isotherm of pericarps Oak acorns for zinc and copper(II) at pH 7; Temperature: 20 °C; amount of biosorbent: 2 g/100 mL; initial metals concentration: 100-500 mg/L

the Freundlich isotherm better represented the equilibrium biosorption of Zn(II) and Cu(II) on pericarps Oak acorns evidenced by the HYBRID and MPSD values were (1.252; 24.805; 3.890) and (4.297, 16.572, 6.752) for Zn(II), Cu(II) and the total [Zn(II) + Cu(II)], respectively. This is confirmed by the significant correlation between $q_{e\,exp}$ and $q_{e\,cal}$, shown in Fig. 12. 'n' values were 2.283; 1.248 and 1.605 for Zn(II), Cu(II) and the total, respectively, in the range $1 < n < 10$, which indicated an effective or favourable biosorption by pericarps Oak acorns. The high values of K_f show high feasibility of Zn(II) and Cu(II) adsorption.

TABLE-2
ISOTHERM CONSTANT AND VALUES OF R^2 FOR ZINC AND COPPER ADSORPTION ON PERICARPS OAK ACORNS

Metals	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
Zn(II)	8	0.073	0.941	1.007	2.283	0.997
Cu(II)	10.869	0.240	0.659	0.966	1.248	0.976
Total	22.727	0.027	0.803	0.962	1.605	0.996

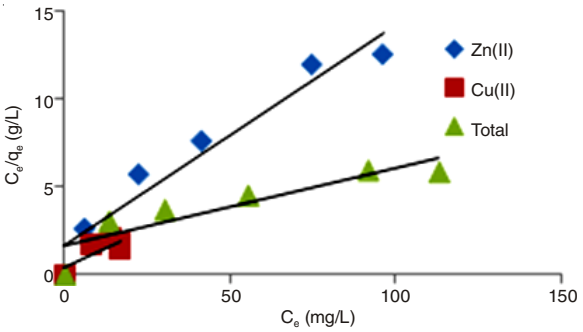

Fig. 10. Langmuir isotherm

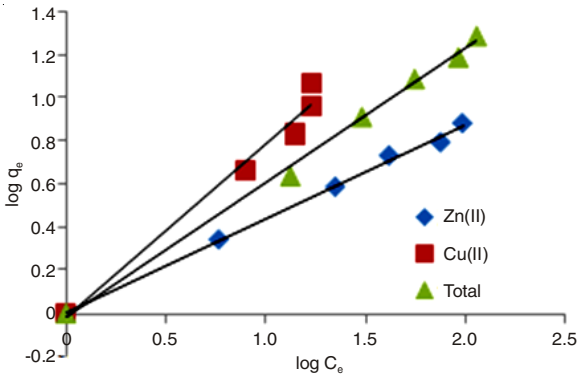

Fig. 11. Freundlich isotherm

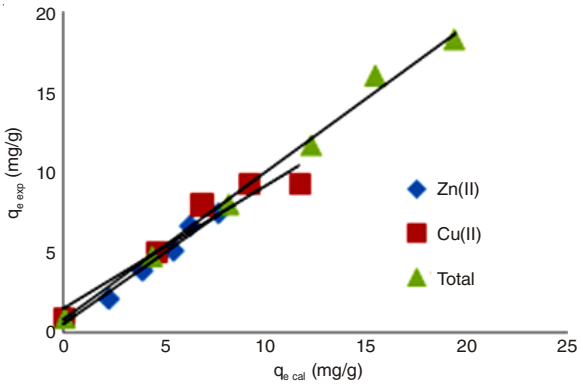

Fig. 12. Correlation between the experimental data and those calculated by the model of Freundlich

Conclusion

In this study, the biosorption of Zn(II) and Cu(II) ions from a binary solution by using pericarps Oak acorns, agricultural waste as a sorbing agent was implemented. The biosorption capacity has been examined at various pH, biosorbent dosages, initial concentrations of mixture, temperature and contact time.

• Maximum metal ion uptake was found at pH 7 with a biosorption capacities about 85.15 % for zinc(II), copper(II) and the mixture at different temperatures.

• The Langmuir and Freundlich isotherm models were utilized for the mathematical description of the biosorption equilibrium of zinc(II), copper(II) and mixture onto pericarps Oak acorns. The Freundlich model was determined as the best for the biosorption data.

• Pseudo-first order, pseudo-second order, Elovich and diffusion kinetic models were used to test the biosorption kinetics. It was shown that the biosorption of zinc(II) and copper(II) onto pericarps Oak acorns could provide the best results by the pseudo-second order model, showing that chemical sorption can control the biosorption.

• Various biosorbents were used to uptake zinc(II) and copper(II) ions from aqueous solutions. However, no report on the utilization of natural pericarps Oak acorns agricultural waste, for biosorption of zinc(II) and copper(II) in a binary solution has been found in literature. Obtained results of zinc(II) and copper(II) bio-sorption onto pericarps Oak acorns agricultural waste are in a good agreement with the literature.

Based on these results, when suitable conditions are performed, pericarps Oak acorns natural agricultural waste can be used as an effective and economically feasible biosorbent to remove zinc(II) and copper(II) from binary aqueous solutions.

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