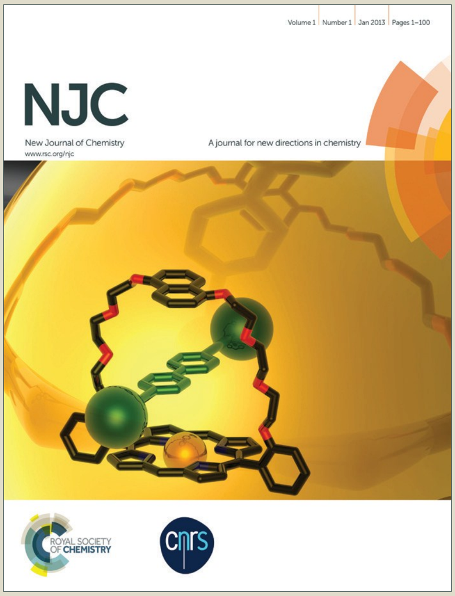

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ARTICLE

Biosorption of copper(II) ions by methyl-sulfonated *Lagenaria vulgaris* shell: Kinetic, thermodynamic and desorption studies

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The biosorption of Cu(II) ion on chemically modified *Lagenaria vulgaris* shell was investigated as a function of temperature at different initial metal ion concentrations. Also, the effects of particles size and agitation rate on the adsorption yield were studied. Efficiency of biosorbent based on chemically modified *Lagenaria vulgaris* shell for Cu(II) ion removal from aqueous solution was studied in batch conditions. The thermodynamic parameters of copper biosorption indicated the process was spontaneous and exothermic. Kinetic models applied to the sorption data at various particle size showed that Cu(II) ion uptake process followed the pseudo-second order rate model and the adsorption rate constants decreased with increasing dimension of particles. Desorption studies revealed that the studied biosorbent can be regenerated using 0.1M HNO_3 and reused. The results indicate that the chemically modified *Lagenaria vulgaris* shell can be use as a promising alternative for the adsorption of Cu(II) ions from aqueous solution.

Keywords: methyl-sulfonated *Lagenaria vulgaris,* Biosorption, Cu(II) ions, Thermodinamics, Kinetics

Introduction

One of the consequences of industrialization is excessive release of heavy metals into the environment, which is a serious environmental problem, because these elements are toxic, non-biodegradable, cumulative, and their ions are mobile and easily transportable through the food chain.[1] Potential sources of copper in the environment is a metal cleaning and planting baths, mood pulp production, fertilizer industry, food packaging, etc. In addition to being an essential metal for living world at trace levels, copper can be toxic to the same if it is present in concentrations greater than allowed.[2] Excessive intake of copper in the body can lead to hemolytic anemia, kidney, gastrointestinal and cardiovascular systems disorders.[3] According to the Environmental Protection Agency maximum allowable concentration of this metal in drinking water is 1.3 mg dm^{-3}.[4] Copper could be released into water by natural weathering of soil (average concentration of copper: 50 ppm, ATSDR, 2002) [5] or discharges from industrial and sewage treatment plants. Also, copper compounds are usually applied to water to destroy algae. Copper released into water is primarily in particulate form and tends to settle out, precipitate out, or be adsorbed by organic matter, hydrous iron, manganese oxides, or clay in sediments. The Cu(I) ion is unstable in aqueous solution and tends to disproportionate to Cu(II) form and copper metal unless a stabilizing ligand is present.[6]

Along with industrial development, researches are motivated to develop new technologies for removal of heavy metals from waste water, such as chemical precipitation, ion exchange, membrane separation, adsorption, solvent extraction.[7, 8] During the process of developing new technologies, the main aspiration is to get a cheaper, reusable, more efficient material which is easily accessible in the environment or it is a by-product of an industrial processes.[2, 7] According to the literature a number of studies were done on the untreated and/or the chemically modified biomasses, such as papaya wood [9], *Coriandrum sativum* [10], peanut hull pellets [11], sago waste [12], rice husk ash and neem bark [13], grape stalk wastes [14], *Lagenaria vulgarias* shell [15], etc.

Low-cost, widespread plant *Lagenaria vulgaris* which belongs to Cucurbitaceae family [16] we used in this study. It is a large annual, climbing or tailing herb, oval or dumbbell shaped fruit giving large yield [17]. Its shell represents a lignocellulosic material with ability for binding metal cations due to presence of hydroxyl, carboxylic, lactonic and phenolic groups in its structure. The main objectives of study were the characterization of the biosorbents surface morphology, structure and active centres. Also, evaluation of the effects of experimental conditions on copper removal as well as particle sizes, stirring speed and temperature were performed. For obtaining the information about reusability of methyl-sulfonated *Lagenaria vulgaris* biosorbent (hereinafter msLVB), desorption experiments were carried out using various acids as eluents.

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Experimental

Preparation of biosorbent

Harvested fruit was washed from dirt and dust, dried at room temperature, and crashed into pieces (2-3 cm), ground in a crusher mill (Waring 8010 ES, Germany) and dried in hot air oven at 55 °C for 24 hours to a constant weight, and then sieved to fractonize particles different sizes (<0.40 mm, 0.40-0.80 mm, 0.80-1.25 mm and 1.25-2.50 mm) using successive sieving. Methyl-sulfonation was performed by procedure described in Stanković et al., 2013.[18]

Characterization of biosorbent

A scanning electron microscopy (SEM Joel JSM-6460 LV) was used to examine the surface morphology of the biosorbent. An energy dispersive X-ray spectrometry with the scanning electronic microscope (SEM-EDX) was used to determine the elemental composition of the biomass before and after metal uptake.

The surface functional groups of the loaded and unloaded biosorbent were analysed by Fourier Transform Infrared (FTIR) spectroscope. The spectra were recorded from 4000-400 cm^{-1}. FTIR spectra of the samples were taken with Bomem Hartman & Braun MB-100 spectrometer under ambient condition. Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr with a sample/KBr ratio 1:100 in an agate mortar.

Boehm titration has been applied to characterize and quantify oxygen functional groups on msLVB surface. Although the Boehm titration is a valuable technique, it is limited to special functional groups: carboxylic, phenolic and lactonic groups.[19] This method is based on acid-base titration of carbon acidic or basic centers. Surface acid groups are selective neutralized with a series of bases with increasing strength as follows: $NaHCO_3$ neutralizes carboxylic groups; Na_2CO_3 neutralizes carboxylic groups and allows lactonic groups to open and form carboxylic groups, which are then neutralized; NaOH neutralizes carboxylic, lactonic, and phenolic groups.[20] Similarly, the basic sites were determined by neutralization with HCl.

The surface chemistry characterization of the msLVB was performed with pH drift method, which was conducted to determine the pH of the point of zero charge. This value is determined by the change in pH of the appropriate electrolyte solution under the influence of biosorbent. As the electrolyte was used 0.1 M $NaNO_3$ solutions in the initial pH range between 2 and 10, which are adjusted adding HNO_3 or NaOH (0.01/0.1 M). For this purpose, 50 mL of prepared solutions with 0.2 g biosorbent were stirred in a polyethylene bottles during 24 hours. The pH was measured after stirring and the plot $pH_{final} = f(pH_{initial})$ was formed, and pHpzc determined as the point when $pH_{initial} = pH_{final}$. Suspension pH ($pH_{sus}$) is related to the overall presence of acidic or basic functional groups on the adsorbent surface.[21] In the present study, 0.2 g of msLVB was suspended into 30 mL of deionized water and stirred in closed polyethylene bottles for 24 h. The resulting pH was denoted as pH_{sus}.

Potentiometric titration is also used to study the acid-base properties of surfaces properties of msLVB.[22, 23] The msLVB was added to beaker with 0.1 mol L^{-1} HNO_3 under N_2 atmosphere and ionic force adjusted to 0.10 mol L^{-1} with $NaNO_3$ making a total volume of 100 mL. The suspension was shaken until pH equilibrium was reached; and then titrated with NaOH concentration of 0.1 mol L^{-1} by digital burette. pKa value was determined from graphical functionality of volume NaOH added versus the pH value.

Chemical Solutions

Stock solution of copper (1000 mg L^{-1}) was prepared dissolving $CuSO_4 \cdot 5H_2O$ (Merck) in deionized water. The solution was diluted to appropriated concentrations as needed. NaOH and acids HNO_3, H_2SO_4 and HCl were, also, obtained from Merck and used for pH value adjustment and desorption reactions.

The batch adsorption experiments

The adsorption equilibrium experiments were conducted in 250.0 mL Erlenmeyer flasks, containing 125.0 mL different concentrations (from 10.0 to 400.0 mg L^{-1}) of the metal model solution during 240 min. Aliquots of solutions (4.0 mL) were withdrawn at preset time intervals, filtrated and the filtrates were analyzed for Cu(II) using AAS. All experiments were conducted at ambient temperature (20.0±0.5°C), at initial pH 5.0±0.1 and carried out in duplicates.

Sorption kinetics was investigated in batch conditions, using 125.0 mL of the solution with 50.0 mg L^{-1} of Cu(II) ions, 4.0 g L^{-1} of msLVB following particle sizes (<0.40 mm, 0.40-0.80 mm, 0.80-1.25 mm and 1.25-2.50 mm), at pH 5.0±0.1 and 20.0±0.5°C. The experiments were performed using magnetic stirrer on 200 rpm.

The influence of stirring rate on copper adsorption was studied under abovementioned conditions with particles sized 0.80-1.25 mm using magnetic stirrer at speeds of 100, 200, 400, 600 and 800 rpm. Stirring speed was measured using a laser tachometer, model DT6234C (Sinometer, China).

The effect of temperature on the adsorption characteristics was studied to determine the thermodynamic parameters. The results of adsorption isotherms were presented in Stanković et al. (2013).[18]

The amount of adsorption at time t, q_t (mg/g), was obtained as follows:

$$q_t=(C_0-C_t)V/m \tag{1}$$

where C_0 and C_t (mg L^{-1}) are the liquid-phase concentrations of solutes at initial and any time t, respectively, V is the volume of solution (L) and m is the dosage of adsorbent (g).

Desorption study

Desorption of copper from msLVB sorbent was studied in a batch system using three eluents including 0.05 M H_2SO_4, 0.1 M HCl, and 0.1 M HNO_3. Pre-adsorbed msLVB (0.5 g) was added to 125 mL of above mentioned eluent and stirred at 200 rpm for 3 h. The eluents were filtered and tested for desorbed copper. After acid desorption, the biosorbent was washed with de-ionized water to remove any residual desorbing solution, regenerated with 0.1 M NaOH and used for the next adsorption cycle. The neutralization of biomass was necessary because pH values of the acid-washed biosorbent are so low (pH 1-2) so metal uptake would be significantly reduced. The percentage of elution was calculated from the amount of metal in solution with respect to the initial amount of metal in the biomass before each experiment. Consecutive biosorption–desorption cycles were repeated four times by using the same biosorbents and 0.1 M HNO_3 as eluent.

Results and discussion

The biosorbent surface characterization

The SEM microphotographs were recorded using SEM Joel JSM-6460 LV microscope under 2 kV accelerating voltage at a work distance of 10 mm and magnification of 100× to 5000×. The SEM images of the surface morphology of biosorbent prepared from msLVB are shown in Fig. 1. It can be observed that material is of fibrous structure characteristic for lignocellulosic material. Methyl-sulfonated shell of *Lagenaria vulgaris* consist parallel stripes (20-35 µm in diameter) with uneven and rough, macroporous, surface. The presence of macropores (pores with diameter > 50 nm) and stripes increases the msLVB surface area. Therefore, the diffusion of solution through the biosorbent increases improving possibility for copper ions penetration into the biosorbent through pores and tubes and their adsorption onto numerous interior active centres.[15, 24] There are no such obvious differences in structure before and after adsorption of copper, except the pores of the fibrous materials were slightly expanded, which shows the physical integrity of the biomatrix. The presence of copper ions on the biosorbent surface is not possibly to be verified using SEM, since the scale of the micrograph is micrometers and the dimension of the Cu(II) ions are in nanometer scale.

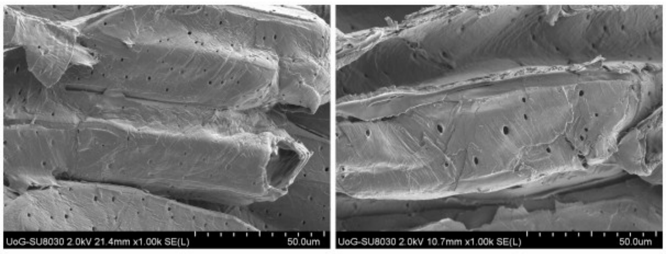

Fig. 1. SEM micrographs of unloaded and loaded msLVB material

This assumption is confirmed by FTIR analyses (Fig. 2). The FTIR spectra of the samples were taken with Bomem Hartman & Braun MB-100 spectrometer in the region 4000-400 cm^{-1} using KBr pellet method. Beside the functional groups characteristic for lignocellulose material, as broad band between 3400-3500 cm^{-1} attributed to the hydroxyl groups in phenolic and aliphatic structures, the bands centered around 2925 cm^{-1}, attributed to CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains, the band at 1420 cm^{-1} of the stretching vibration for lignin, the FTIR spectrum of msLVB shows also the characteristic bands of sulfonic group at 1112 cm^{-1} for in-plane deformation SOH vibration, and at 1037 cm^{-1} for symmetrical stretching S-O vibration. The sulfonate S=O bands appear usually in the fingerprint region where the assignments are difficult to attribute as the superimposed vibration bands take place within this region. After copper adsorption, the FTIR spectrum shows the decrease in the absorption band at 1654 cm^{-1}due to the sulfonation of the aldehyde end groups in the lignin, and also the decreasing in intensity and shift from 3419 to 3415 cm^{-1} for band assigned to O–H stretching vibrations indicating that after saturation of sulfonic groups, copper ions interacted with presented hydroxyl groups. Thus, the mechanism of copper binding on msLVB could occur by surface ion-exchanging followed with complexation.[18]

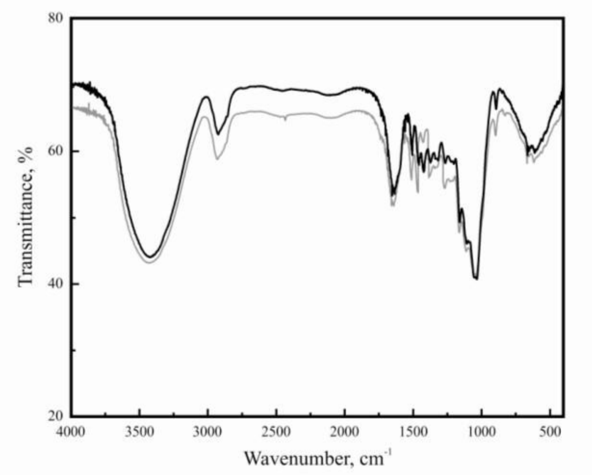

Fig. 2. FTIR spectra of unloaded and copper loaded msLVB material

EDX analysis provides information about elemental content through analysis of X-ray emissions caused by a high-energy electron beam. Energy Dispersive X-ray microanalysis was performed using Thermo-Noran NSS System 7 with ultra-dry detector under 10 kV accelerating voltage at working distance of 15 mm.

The spectra (Fig. 3a) indicate the presence of C and O as major elements of biosorbent surface which is in accordance with the chemical composition of lignocellulose. Also, a clear signal of the presence of sulphur due to the formation of sulfonic functional groups can be observed. The observed Na signal is the result of treatment the native material with Na_2SO_3 used in sulfonation process leading to the conversion of the acid groups into their sodic form, as described by Aziz et al, 2009.[25] EDX spectra presented in Fig. 3b described the additional copper signal confirming the adsorption of the metal ion to the surface of the biosorbent.

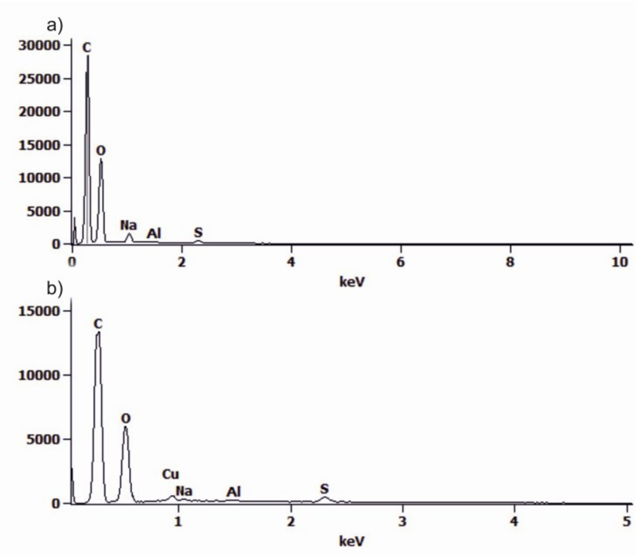

Fig. 3. EDX analyses of unloaded (a) and copper loaded (b) msLVB material

The point of zero charge represents the state of the surface material when the sum of negative charge is equal to the sum of the positive charge. The result of the point of zero charge of the biosorbent is presented in Fig. 4. From the Fig. 4 it was observed that the pHpzc of msLVB is 7.28. This means that below this pH value the surface of the msLVB is predominated by positive charges while at pH greater than 7.28 the surface charge will be negative. High value of pHpzc confirms that surface acid functional groups are probably in form of Na-salts. Although, pHpzc is quite high, msLVB shows significant adsorption activity toward metal cations even at lower pH where the expected overall charge is negative.[15] It is assumed that ion exchange has a significant contribution in the mechanism of adsorption of metal ions, whereas at pH values below 7.28 the functional groups of msLVB are deprotonated. The suspension pH is 7.14.

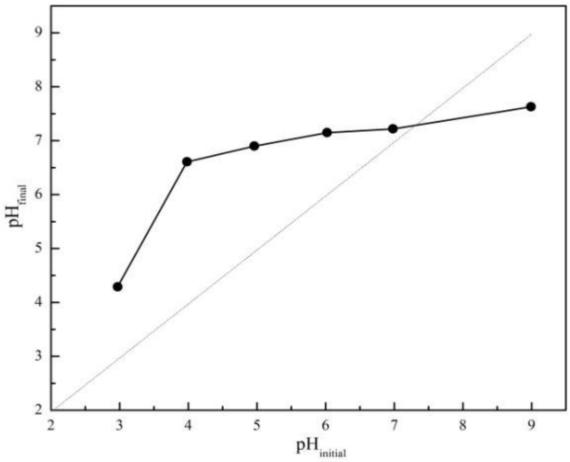

Fig. 4. pH_{pzc} determination curve

Table 1 summarizes some of important properties of methyl-sulfonated *Lagenaria vulgaris* shell as biosorbent.

Table 1. Characteristics of msLVB

Characteristics	
Total acid groups (meqg^{-1})	0.934
Carboxylic group (meq g^{-1})	0.302
Phenolic group(meq g^{-1})	0.570
Lactone group (meq g^{-1})	0.062
Basic group (meq g^{-1})	3.225
pHpzc	7.28
pHsus	7.14
pH potentiometric	6.94
Cation exchange capacity (meq g^{-1})	0.1359

Effect of temperature

Adsorption of Cu(II) ions onto msLVB as a function of metal ion concentration was studied at three different temperatures (10, 20 and 30°C) at various initial concentration of copper (10 mg L^{-1}, 20 mg L^{-1}, 50 mg L^{-1}, 100 mg L^{-1}, 200 mg L^{-1}), while keeping all other parameters constant. The effect of temperature on copper adsorption on msLVB is shown in Fig. 5.

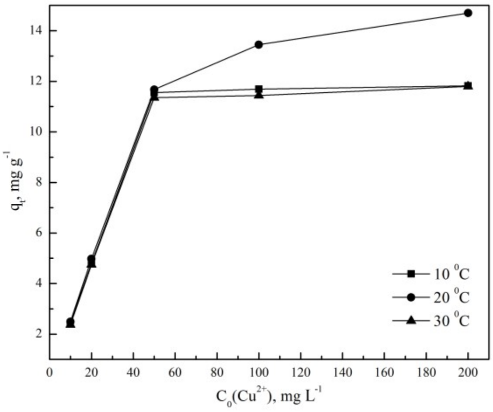

Fig. 5. Effect of different temperature on adsorption of copper onto msLVB

The maximal adsorption capacity was found at 20 °C. Despite the fact that an increasing trend of adsorption was observed with increasing temperatures to 20 °C, adsorption capacity of msLVB decreased with temperatures higher than 20 °C.

Thermodynamic study

Thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process.[26] Thermodynamic parameters such as Gibbs free energy change ($\Delta G°$), entalphy change ($\Delta H°$) and entrophy change ($\Delta S°$) of Cu(II) adsorption onto msLVB can be estimated from the variation of the equilibrium constant at different temperature. The Gibbs free energy change (ΔG^o) of the sorption reaction is given by the following equation:

$$\Delta G^o = -RT \ln K \qquad (2)$$

where K is the equilibrium constant, which can be obtain from Langmuir isotherm at different temperature, T is absolute temperature and R is the gas constant.

It is known that $\Delta G°$ is the function of ΔH^{o} and change in standard entrophy ($\Delta S°$):

$$\Delta G° = \Delta H° - T\Delta S° \tag{3}$$

If Eq. (3) is inserted into Eq. (2), it becomes

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{4}$$

$\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of plot ln$K$ against $1/T$. Fig. 6 illustrates Van't Hoff plot of effect of temperature on biosorption of Cu(II) on msLVB. Previous study showed that the adsorption equilibrium data for the adsorption of copper ions on msLVB fitted the best by the Langmuir model.[18]

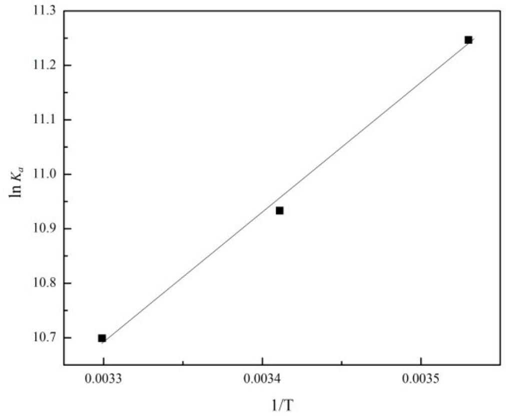

Fig. 6. Thermodynamic plot of $\ln K_a$ versus $1/T$ of Cu(II)-sorption onto msLVB

Here, the thermodynamic parameters have been calculated using the Langmuir isotherm model constant K_a, which replaced the equilibrium constant, K from Eq (2). The observed thermodynamic values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ were given in Table 2, where that is clearly K_a values decrease by increasing temperature suggesting that the adsorption process is exothermic.

Table 2. The thermodynamic parameters for the adsorption of Cu(II) ions onto msLVB

Temperature	283 K	293 K	303 K
q_{max}	11.885	14.708	11.8892
K_L	1.2065	0.882	0.6978
K_a	76612.75	56007.00	44310.30
R^2	0.99994	0.99881	0.99981
$\Delta G°$ [KJ mol^{-1}]	-26.475	-26.647	-26.966
$\Delta H°$ [KJ mol^{-1}]	-19.730		
$\Delta S°$ [J mol^{-1} K^{-1}]	23.774		

The negative values of $\Delta G°$ at various temperature indicated the adsorption process is favourable and spontaneous at all temperatures studied and inversely proportional to the temperature. The decrease in the value of $\Delta G°$ with increasing temperature indicated that the adsorption of Cu(II) ions on msLVB become more favorable at higher temperature.[27] The negative value of $\Delta H°$ confirms the exothermic nature of biosorption process, which suggests that may involve mainly physical sorption.[28] The positive value of $\Delta S°$ suggested the increase randomness at the solid/solution interface during the biosorption of copper ions on msLVB.[29]

Physical adsorption phenomenon is associated with the presence of weak van der Waal's forces, and the heat evolved during the physical adsorption process is ranged between 2.1–20.9 kJ mol^{-1}. Other side, the heats of chemisorption generally change from 80 to 200 kJ mol^{-1}.[30, 31] Adsorption of copper ions on msLVB had boundary values of the heat energy of biosorption between the physical and chemical adsorption.[32]

Mostly, biosorption of copper was found to have negative values of $\Delta H°$, but however not all the copper biosorption systems are exothermic (Table 3). The thermodynamic parameters indicated that the biosorption process can be used for the removal of Cu(II) ions by msLVB due to the process of adsorption of copper onto msLVB is favored by both enthalpy and entropy.

Table 3. A comparison of thermodynamic parameters for the biosorption of copper by different biosorbents.

Biosorbent	Reference	q_{max} (mg g^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1}mol^{-1})
Sugar beet pulp	[28]	28.50	−0.74	−66.30	−220.0
Tomato waste	[28]	34.48	2.66	−79.30	−270.4
T. grandis L.f.	[34]	15.43	−12.67	−9.89	418×10^{2}
P. putida	[35]	107.72	−16.50	23.12	128.0
Chestnut shell	[36]	12.56	−0.88	−17.42	−54.667
Modified orange peel	[37]	72.73	−3.30	−8.55	−17.00
Pine cone powder	[38]	26.32	73.08	17.73	-198.4×10^{3}
R.oligosporus biomass	[39]	79.37	−24.67	−240.35	−0.71
Banana peel	[40]	27.78	−6.94	0.06	-244×10^{2}
Spent tea leaves	[41]	90.00	−1.13	−117.91	−0.389
Uncaria gambir	[42]	9.95	−20.00	6.28	86.0
Neem leaf powder	[43]	146.30	−4.66	26.70	70.0
Olive leaves	[44]	71.43	−2.07	18.14	68.95
Teak leaves	[45]	166.78	−1.75	−62.42	−219.0
ms LVB	*This study*	*12.15*	*−26.65*	*−19.73*	*23.77*

Effect of particle size

The influence of particle size on copper adsorption onto msLVB was investigated using the solution with 50.0 mg L^{-1} of Cu(II) ions, 4.0 g L^{-1} of msLVB following particle sizes (<0.40 mm, 0.40-0.80 mm, 0.80-1.25 mm and 1.25-2.50 mm), at pH 5.0±0.1 and 20.0±0.5°C. The results of variation of particle sizes on copper adsorption are shown in Figure 7. It can be observed that the adsorption of Cu(II) increases as the particle size decreases and hence the percentage removal of copper also increases.

The removal efficiency of msLVB decreased from 90.5% to 84.6% as the particle size increased from <0.40 mm to 1.25-2.50 mm. This behaviour is probably the result of larger effective surface area that is associated with smaller particles, as well as the fact that the smaller particles of biosorbent have shortened diffusion path. This leads to the increasing ability of solution penetrating to all internal pore structure of the biosorbent.[46] This behaviour could be also explained by

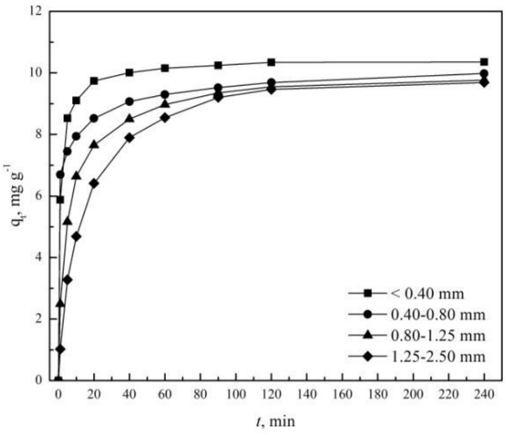

Fig. 7. Effect of particle size on adsorption of copper onto msLVB

increasing in number of binding sites with decreasing of biosorbent size.[47] Optimal particle size chosen for further experiments was 0.80-1.25 mm due to their very high adsorption capacity, while smaller particles (<0.40 mm) beside better capacity were not suitable because it was more difficult to remove from dispersion.

It can be observed that there is no significant difference among q_e values with varying particle sizes of msLVB, which means that dimensions of particles have small influence at adsorption capacity of msLVB to Cu(II) ions. At other side, the equilibrium time for <0.4 mm particles is about 20 minutes, while for the largest particles (1.25-2.5 mm) it is needed about 90 minutes for reaching the equilibrium state. This behaviour can be explained also by decreasing of effective surface area with increasing of particle sizes which leads to prolonged eqilibrium time.[48] Other authors [49-51] claimed that for larger particles, the diffusion resistance to mass transfer is higher and most of the internal surface of the particle may not be utilized for adsorption.

Pseudo-second order kinetic model could be applied for explanation of copper adsorption process onto msLVB. The plot of *t/qt* against *t* gives a linear relationship with a slope of ($1/q_e$) and an intercept of ($1/k_2q_e^2$). The values of pseudo-second order kinetic model parameters are given in Table 4. The pseudo-second order reaction rate equilibrium constant k_2 decreases with increasing the particle sizes which is in correlation with results presented at Fig. 7 and equilibrium times.

Table 4. Pseudo-second order kinetic models rate parameters for Cu(II) ions adsorption onto msLVB of different particle sizes

	q_e (mg g^{-1}), exp	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1}), cal	R^2
< 0.4 mm	10.36	0.07625	10.41	0.99998
0.4-0.8 mm	9.69	0.04768	9.76	0.99987
0.8-1.25 mm	9.77	0.01906	9.95	0.99973
1.25-2.5 mm	9.69	0.00934	10.51	0.99971

Sorption mechanism

The kinetic results were analyzed by the Chrastil's model [52-54] proposed for diffusion limited systems, to investigate sorption mechanism, i.e. to get answer if the sorption process is under the influence of diffusion control:

$$q_t = q_e[1 - e^{-k_c A_0 t}]^n \qquad (5)$$

where q_t and q_e are as abovementioned, k_c is a rate constant (L g^{-1} min^{-1}), A_0 is the concentration of msLVB (g L^{-1}) and n is a structural diffusion resistance constant which ranges from 0 to 1. This constant is independent of the metal ions concentration, sorbent concentration, A_0, and temperature, but dependent on sterical structure of the system.[54, 55] When n value is low ($n \leq 0.6$) the system is strongly limited by diffusion resistance, otherwise, when n tends to 1, the diffusion resistance is small and the reaction is of the first order kinetics.[56]

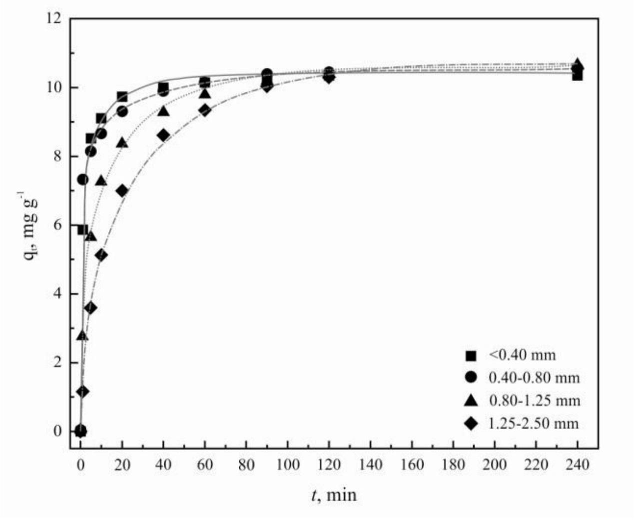

Fig. 8. Chrastil's diffusion sorption kinetics of Cu(II) onto msLVB

Parameters of the model were determined by non-linear regression analysis of the experimental data using OriginPro 8.0 software (OriginLab Corporation, USA). The values obtained are shown in Table 5. As it can be seen, the coefficients of multiple determinations obtained for Chrastil's diffusion kinetic model in all cases were very high (R^2>0.99), as it is shown by the regression curves in Fig. 8. The results obtained for the diffusion resistance constant were between 0.1053 and 0.4684 (Table 5), indicating that the sorption process of Cu onto msLVB is considerably limited by diffusion resistance. Also, a significant decrease on the diffusion coefficient, from n = 0.4684 (particle size of 1.25-2.5 mm) to 0.1053 (particle size of 0.4-0.8 mm) was observed, implying that in the biomass with the smaller particle size exists higher resistance to the diffusion of copper(II) ions. However, the decrease of the particle size of the msLVB leads to the significant increase on the rate constant. These results are in accordance with those for biosorption Pb(II), Cd(II) and Cd(II) onto cork [57] and LVB [54].

Table 5. Chrastil's diffusion kinetic parameters for sorption Cu onto msLVB of various particle sizes

	q_e (mg g^{-1}), exp	k$_c$ (dm^3 g^{-1} min^{-1})	q_e (mg g^{-1}), cal	n	R^2
< 0.4 mm	10.36	0.01225	10.42	0.1510	0.9976
0.4-0.8 mm	9.69	0.00848	9.67	0.1053	0.9996
0.8-1.25 mm	9.77	0.00700	9.74	0.3000	0.9970
1.25-2.5 mm	9.69	0.00555	9.83	0.4684	0.9970

In order to get insight into the diffusion mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber-Morris (1963) [58] intraparticle diffusion model, which equation is expressed as:

$$q_t = K_{id}t^{1/2} + C \qquad (6)$$

where C is the intercept, providing information about the thickness of the boundary layer, and K_{id} is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$) determined from a plot q_t versus $t^{1/2}$.

It is obvious from Fig. 9 that the mechanism of adsorption of Cu(II) onto msLVB involves three steps: rapid external mass transfer (external diffusion) and surface adsorption, intraparticle diffusion and finally, adsorption of the metal ions on the interior sites of the sorbent. The last one is very rapid and the adsorption rate parameter which controls the batch process for most of the contact time is intraparticle diffusion.[59, 60] The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater is thickness of boundary layer leading to the significant role of the surface sorption in the rate controlling step.

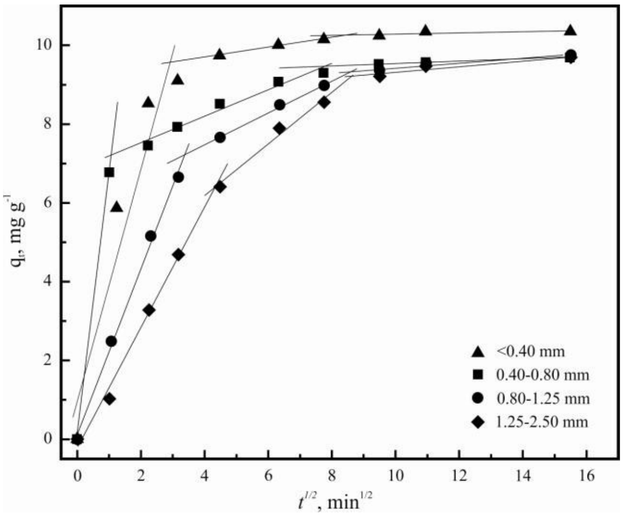

Fig. 9. Intra-particle diffusion sorption kinetics of Cu(II) onto msLVB

The calculated intraparticle diffusion coefficient K_{id} values are listed in Table 6. If the intraparticle diffusion is the only rate-limiting step, the q_t versus $t^{1/2}$ plots should pass through the origin.[61] However, the linear plots of each particle size did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step and that surface chemisorptions (such as complexation or ion-exchange) probably have considerable role during adsorption onto msLVB. However, relatively high determination coefficients indicate that intraparticle diffusion might play a significant role at the beginning of the sorption process. The value of intercept give an information about the thickness of boundary layer i.e., larger the intercept greater is the boundary layer.

Table 6. Intra-particle diffusion kinetic parameters for sorption Cu(II) ions onto msLVB of various particle sizes

	K$_{id2}$	C$_2$	R^2
<0.40 mm	0.2775	8.3271	0.7882
0.40-0.80 mm	0.3353	6.8504	0.9525
0.80-1.25 mm	0.0340	5.8741	0.9924
1.25-2.50 mm	0.4113	5.3192	0.9937

Effect of Stirring Rate on Cu(II) Adsorption

Stirring ensures good contact between the phases in a heterogeneous system. Biosorbent based on shell of *Lagenaria vulgaris*, like most other biosorbents, has a relatively low specific gravity, so msLVB partially floating at the solution surface, and mixing achieves optimal contact between the sorbent and the solution phase. Besides, stirring rate plays an important role in the adsorption process. The effect of stirring speed on adsorption capacity of copper has been studied by varying the stirring speed from 100–800 rpm using msLVB particles sized 0.80-1.25 mm and keeping all other conditions constant.

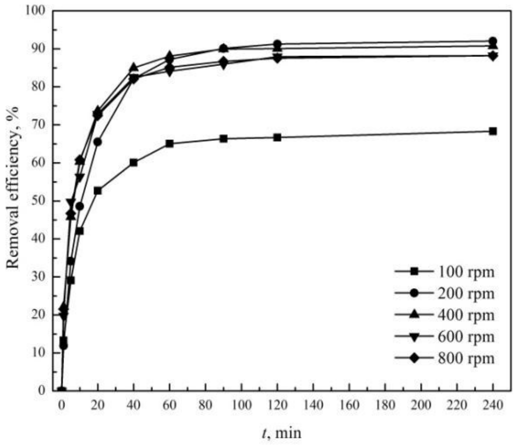

Fig. 10. Effect of stirring speed on adsorption of copper onto msLVB

The removal efficiency of msLVB at different stirring speeds is shown in Fig. 10. It can be observed that enhancement of stirring speed leads to negligible decrease of the removal efficiency from 92.02% at 200 rpm to 88.19% at 800 rpm, while at 100 rpm is just about 68.35%. This is because with low stirring speed the greater contact time is required to attend the equilibrium. It is assumed that the decreasing of copper removal efficiency with increasing of speed from 200 rpm to 800 rpm is probably due to the appearance of "twister effect" in the flask, which reduces the area of contact between the liquid-solid phases.[62, 63] Also, with the increasing of stirring speed, increases the efficiency of diffusion of copper ions through a boundary surface of the diffusion layer of the biosorbent, due to reducing of its thickness. As the removal efficiency in the range of 200 to 800 rpm is more or less the same, the 200 rpm stirring speed was selected as optimal for all experiments.

Desorption Study

For successful applications of any biosorbent, its regeneration and subsequent reuse is of the crucial importance in industrial practice. The desorption process should regenerate the biosorbent close to the starting conditions for effective reuse without any physical change or damage and with undiminished pollutant uptake.[64]

Desorption of copper from msLVB sorbent was investigated using per 125 mL of three eluents (0.05 M H_2SO_4, 0.1 M HCl, and 0.1 M HNO_3) on copper-loaded msLVB (4.0 g L^{-1}) at 20.0±0.5°C and stirred on 200 rpm during 3 h.

Table 7. The copper desorption efficiency of different desorbents (copper concentration: 50.00 mg L^{-1}, msLVB dose 4.0 g L^{-1}, biosorption time 240 min, desorption time 180 min)

Desorbent	**0.1 M HCl**	**0.1 M HNO_3**	**0.05 M H_2SO_4**
Desorption efficiency, %	95.16	95.41	91.47

As seen from Table 7, 0.1 M HNO_3 and 0.1 M HCl were found to be the most efficient desorbent agent with desorption efficiencies of 95.41% and 95.16%, respectively. Solvents act in two ways: change the chemical form of the adsorbed species and/or destroy the bonding between the adsorbate and the adsorbent. H^+ ions released from the acids-desorbent successfully replaced Cu(II) ions from sulfonic and carboxyl sites on the surface of msLVB.[65] The recovery and reuse processes for chemically modified msLVB can be continued up to 4 times using 0.1 M HNO_3 with negligible decreasing in removal efficiency.

Conclusions

The adsorbent was well characterized by various techniques. SEM results indicate that surface of msLVB consists of parallel fibers with macroporeous which presents an suitable morphological profile to bind Cu(II) ions. The spectroscopic data (EDX, FTIR) together with data about pH of suspension and zero point charge pH suggest the presence of the sodium salt form of acid functional groups on the biosorbent surface. The negative values of ΔG° and ΔH° indicated the spontaneity and exothermic nature, while positive value of ΔS° showed increase randomness at the solid/solution interface during the biosorption. Heat energy of biosorption indicates that adsorption of copper ions on msLVB is mainly physical with contribution of chemical adsorption. The biosorption rate decreased with an increase in particle size. The sorption order kinetics followed the pseudo-second order rate equation. The good correlation with Chrastil's diffusion model suggests the adsorption process of Cu onto msLVB is considerably limited by diffusion resistance, implying the adsorption is under both kinetic and diffusion control. Desorption studies showed that the copper(II) ions sorbed on to methyl-sulfonated *Lagenaria vulgaris* shell could be desorbed effectively using 0.1 N HNO_3 and the biosorbent could be reused four times after regeneration, without appreciable decrease in the sorption capacity.

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Table of contents

Chemically modified *Lagenaria Vulgaris* shell was found to be an efficient, regenerative biosorbent to remove copper ions from wastewater models.