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Full Paper

Chemically Modified *Lagenaria vulgaris* as a Biosorbent for the Removal of Cu^{II} from Water

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The ability of a biosorbent based on a chemically modified *Lagenaria vulgaris* shell for Cu^{II} ion removal from aqueous solution was studied in batch conditions. The biosorbent was characterized by Fourier-transform infrared spectroscopy and the effect of relevant parameters such as contact time, pH, biomass dosage, and initial metal ion concentration was evaluated. The sorption process was found to be fast, attaining equilibrium within 40 min, and results were found to be best fitted by a pseudo-second order kinetic model. Experimental data showed that the biosorption is highly pH dependent, and the optimal pH was 5.0. Results were analyzed in terms of the following adsorption isotherms: Langmuir, Freundlich, Temkin, and Flory–Huggins, by a linear regression method. The Cu^{II} biosorption followed the Langmuir isotherm model ($r^2 = 0.998$) with the maximum sorption capacity of 14.95 $mg\,g^{-1}$. The methyl-sulfonated *Lagenaria vulgaris* biomass investigated in this study exhibited a high potential for the removal of Cu^{II} from aqueous solution.

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Introduction

The increasing global population requires new sources of drinking water. On the other hand, the rapid development of industry has led to an increase of the contamination of available water resources. To balance the worlds needs, and with a better awareness about restricted water resources, in the past decades scientists have investigated new technologies for removing toxic contaminants from wastewaters, mainly the heavy metals. The most important technologies include chemical precipitation, electrochemical methods, ion exchange, reverse osmosis, and adsorption onto activated carbon.[1–3] However, these methods have high operational costs or produce sludge so they are not adoptable in developing countries. The potential sources of copper ions in industrial effluents include metal cleaning, plating baths, paper boards, fertilizer, mining, wood pulp, antifouling for paint and pigments, etc.[4] Copper is an essential element for living organisms at trace levels, but acute or chronic exposure to higher concentrations can cause severe kidney and liver disease, even death. The maximum allowed concentration for drinking water which is regulated by the United States Environmental Protection Agency in 2010 is 1.3 $mg\,dm^{-3}$.[5]

Over the years, various materials based on agricultural by-products or waste, in native form or chemically modified, have been studied for their ability to remove heavy metals and pesticides from wastewaters. Besides their low cost, these materials are also widely available and are environmentally friendly.[6] Copper adsorption onto some biomaterials, such as powdered gambir,[4] cone biomass,[7] seed powder,[8] sugar beet pulp,[9] coirpith carbon,[10] wheat shell,[11] grape stalks wastes,[12] rice straw,[13] powdered pine cone,[14] hyacinth roots freshwater weeds,[15] peanut hull,[16] cork biomass,[17] and over 100 more sorbents has already been reported.[18]

The shell of *Lagenaria vulgaris* can be used as a low-cost adsorbent for heavy metals, largely due to its lignocellulosic composition with a capacity for binding metal cations due to hydroxy, carboxylic, phenolic, and ether groups present in their structure. The presented functional groups indicate that the predominant biosorption mechanisms are ion-exchange, complexation, and chelation.[19–21]

Lagenaria vulgaris is the common name in older literature for *Lagenaria siceraria (Molina) Standley*, a species of the Cucurbitaceae family.[22] *Lagenaria* is a large annual, climbing or tailing to a 4–5 m long herb with 20 to 25 bottle fruits, oval or dumbbell shaped fruit giving large yield.[23] It can be grown worldwide, up to 1600 m in altitude, but preferably in hot and humid lowlands on well lit and well drained soils with pH 6–7.[24] It does not require the use of agrochemical assets and specific preparation of soil for cultivation. The shell of the ripe fruit is hard, ligneous, and impermeable to water, and covers a spongy white flesh, which dries out completely on ripening, leaving a thick, hard, hollow shell. For experiments in this study the shell of *Lagenaria vulgaris* was used and grown in the south area of Serbia (near the town of Niš) at ~200 m altitude under controlled conditions with irrigation and without fertilization.

Chemical modification is commonly performed to enhance the metal binding capacity of biosorbent materials by an

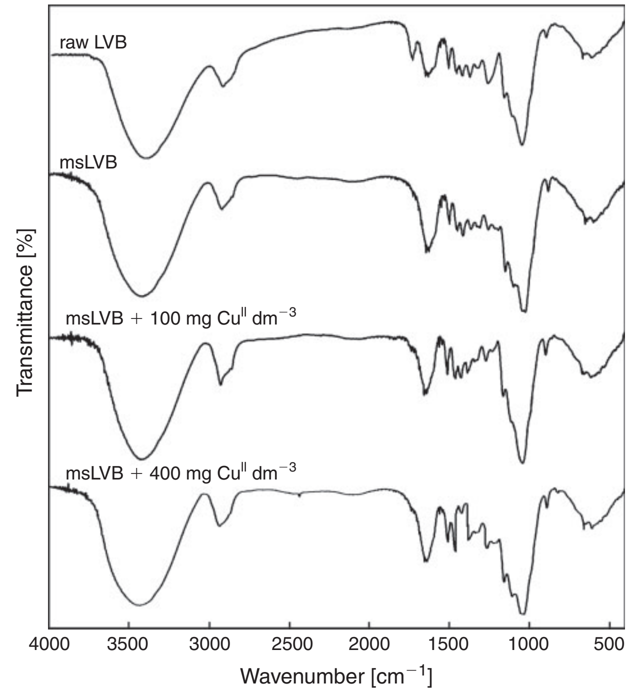

Fig. 1. Fourier-Transform infrared spectra of untreated biosorbent material (LVB) and methyl-sulfonated biosorbent material (msLVB) before and after Cu^{II}-adsorption treatment.

increase of and/or activation of the binding sites on the biomass surface. Such modifications include: pretreatment, binding site enhancement, binding site modification, and polymerization.[25] Methods of exposing the metal-binding sites include introducing the functional groups responsible for hydrogen replacement (carboxy, sulfonate, sulfhydryl, hydroxy, amino, etc.).

In our preliminary investigations, sulfonation of the biomass with Na_2SO_3 did not show significant effects on the biosorption of copper in the case of *Lagenaria vulgaris*. Therefore, methyl-sulfonation was used in order to increase the number of incorporated sulfonic groups in the structure of the lignin component of the biosorbent.

The effect of various experimental parameters such as contact time, solution pH, initial Cu^{II} concentration, and biosorbent dosage has been investigated in order to confirm the improvement due to the applied chemical modification. The equilibrium data were fitted to Langmuir, Freundlich, Temkin, and Flory–Huggins isotherm models, while the kinetics data were correlated according to various kinetics models (pseudo-first order, pseudo-second-order, Elovich, and intraparticle diffusion model).

Results and Discussion

Fourier-Transform Infrared (FTIR) Characterization of Methyl-Sulfonated Lagenaria vulgaris *Bioabsorbent (msLVB)*

FTIR spectra of untreated the biosorbent compared with msLVB before and after adsorption treatment are given in Fig. 1. The spectrum of untreated LVB shows characteristic adsorption bands for a lignocellulose material: a broad band between 3400 and 3500 cm^{-1} attributed to the hydroxy groups in phenolic and aliphatic structures, bands centred around 2925 cm^{-1}, predominantly arising from CH stretching in aromatic methoxy groups and in methyl and methylene groups of side chains, aromatic ring bands at 1507 cm^{-1}, a band at 1420 cm^{-1} due to the stretching characteristic vibration for lignin, a bending vibration of OH at 1328 cm^{-1}, which has been reported for the syringyl ring of hardwood and non-wood lignins,[26] and a C–O stretching band for methoxyl groups at 1269 cm^{-1}. In the spectra of msLVB are characteristic bands of a sulfonic group: at 1112 cm^{-1} for the in-plane deformation of the SOH vibration, and at 1037 cm^{-1} for the symmetrical stretching S–O vibration (Table 1). The latter peak probably suffers overlap with the C–O stretching of carbonyl groups and the bending vibration of hydroxy groups which are usually found at 1040 cm^{-1}. The adsorption band at 1734 cm^{-1} originated from the carbonyl groups of esters.[27,28] The FTIR spectra for the copper loaded biosorbent showed wavenumbers and intensity of some peaks that were shifted or substantially lower than those before biosorption, suggesting the participation of $–SO_3^-$, –OH, and –COOH in the binding of copper by msLVB. The wavenumbers of msLVB shifted from 1112 and 1037 cm^{-1} to 1107 and 1032 cm^{-1}, respectively, after copper (100.0 mg dm^{-3}) uptake. The decrease in the absorption band at 1654 cm^{-1} is probably due to the sulfonation of the aldehyde end groups in the lignin. From the IR results alone is it hard to determine which surface functional groups are responsible for the remarkable decrease of the IR band after sulfonation.[29] In the case of treatment with a solution with an initial copper concentration of 400.0 mg dm^{-3}, the band assigned to O–H stretching vibrations showed a decrease in intensity and shift from 3419 to 3415 cm^{-1} probably indicating that after saturation of sulfonic groups, copper ions interacted with hydroxy groups. Thus, the mechanism of copper binding on msLVB could occur by surface ion-exchange followed by complexation.

Table 1. Band position in the Fourier-transform infrared spectra of characteristic vibrations

v [cm^{-1}]	Band assignment
3415	O–H stretching
2920	C–H stretching
1507	Aromatic rings
1310	SO_2 asymmetric stretching
1435	CH_2 bending
1265	C–O stretching
1112	S–OH bending in-plane
1036	SO_3^- symmetric stretching
635	SO_2 bending in-plane

The elemental analysis of msLVB revealed an increase of S content (14.55 mg g^{-1}) compared with untreated material (0.05 mg S g^{-1}) or even sulfonated LVB which contained 5.43 mg S g^{-1}. This proved that the incorporation of sulfonic groups on the surface of the biomaterial was successful.

Effect of Contact Time

Experiments were performed with model wastewaters containing Cu^{II} ions at an initial concentration of 50.0 mg dm^{-3}, an msLVB dose of 4.0 g dm^{-3}, at 20 ± 0.5°C and pH 5.0. The effect of contact time on the residual concentration of Cu^{II} ions in aqueous solution with msLVB is shown at Fig. 2. Biosorption of metal ions seemed to occur in two phases, similar as reported in the literature.[30] The concentration of copper declined sharply with contact time in the first 10 min and reached equilibrium at ~40 min. The initial fast phase occurs due to a high availability

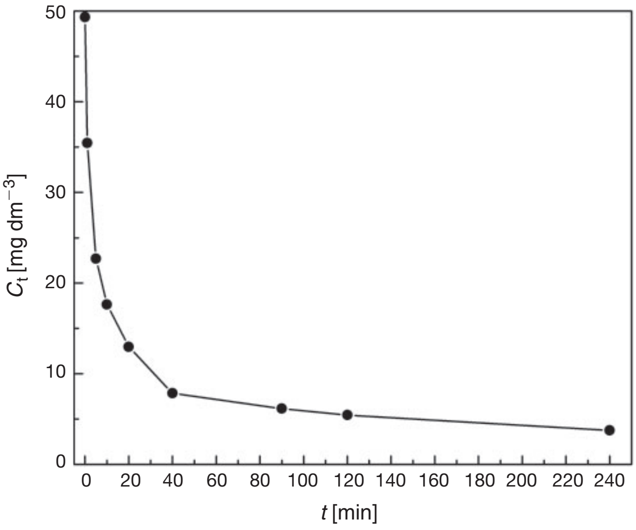

Fig. 2. Effect of contact time on removal of Cu^{II} by methyl-sulfonated *Lagenaria vulgaris* bioabsorbent (msLVB) (initial Cu^{II} concentration 50 mg dm^{-3}, pH 5.0, temp. 20 ± 0.5°C, msLVB dose 4.0 g dm^{-3}).

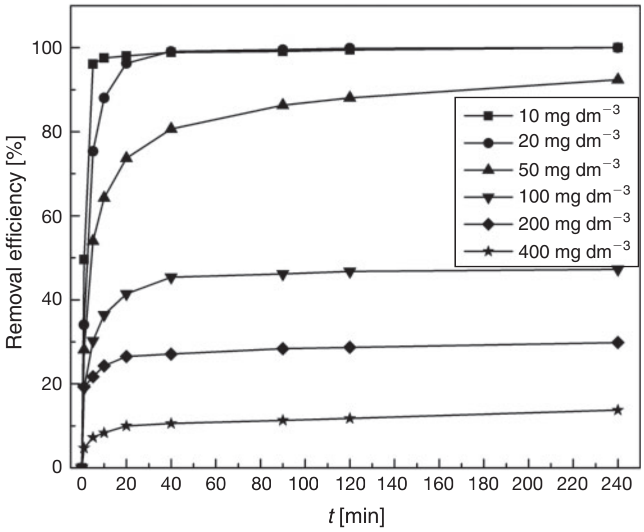

Fig. 3. Effect of initial Cu concentration on the removal efficiency for Cu^{II} ions by 4.0 g dm^{-3} methyl-sulfonated *Lagenaria vulgaris* bioabsorbent (msLVB) at 20 ± 0.5°C and pH 5.0.

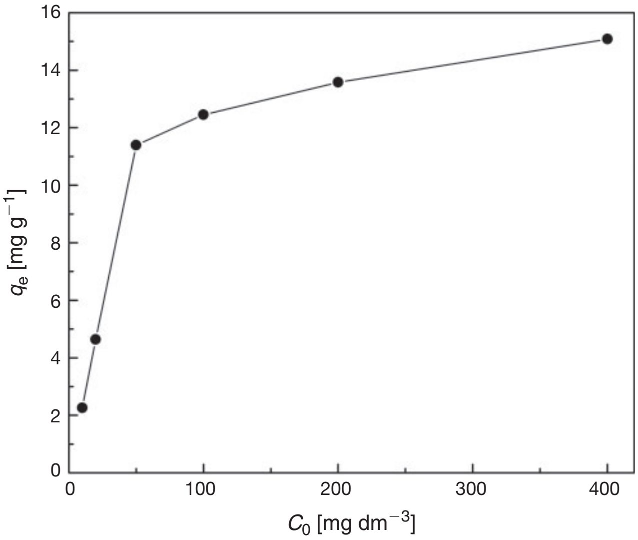

Fig. 4. Effect of the initial solute concentration on the adsorption of Cu^{II} onto methyl-sulfonated *Lagenaria vulgaris* bioabsorbent (msLVB) (pH 5.0, msLVB dose 4.0 g dm^{-3}, temp. 20 ± 0.5°C).

of the number of active binding sites (sulfonic groups) on the adsorbent surface and it is typically controlled by the diffusion process from the solution to the surface. A further increase in contact time did not show a significant decrease of Cu^{II} concentration, which occurs due to diffusion of the copper ions into the inner part of the biomass. This result is important because it indicates a significant removal ability of msLVB for copper in a short time interval making this biosorbent very efficient for wastewater treatments.

Effect of Initial Cu^{II} Concentration

The initial concentration of metal ions in the solution has a key role as a driving force to exceed the mass transfer resistance between the aqueous and solid phases. Batch experiments were conducted at different initial Cu^{II} concentrations ranging from 10.0 to 400.0 mg dm^{-3} in contact with 4.0 g dm^{-3} of msLVB at 20 ± 0.5°C and pH 5.0. The influence of initial Cu^{II} concentration on removal efficiency is shown in Fig. 3. In the case of low initial Cu^{II} concentrations of 10.0 and 20.0 mg dm^{-3}, the removal efficiency reached 100 %. For an initial Cu^{II} concentration of 50.0 mg dm^{-3} it reaches ~92 %, and decreases to nearly 14 % for an initial Cu^{II} concentration of 400.0 mg dm^{-3}. At low metal concentrations, abundant availability of the active sites on the surface area made the interaction with all copper ions present in the solution more rapid allowing the binding of a greater number of ions and thus facilitated 100 % adsorption. At higher concentrations, more Cu^{II} ions are left unadsorbed in solution due to saturation of the limited available binding sites in the biomass.[31] However, comparing q_e values (Fig. 4), a gradual increase in binding with increasing initial concentration to reach an adsorption capacity of 15.08 mg Cu^{II} per g of msLVB for the highest initial Cu^{II} concentration is observed.

This implies that the absolute adsorbed amount of copper onto the biomass is enhanced upon increasing the initial concentration which provides an important initial impulse to overcome all mass transfer resistances of Cu^{II} ions between the aqueous and solid phase, hence a higher initial concentration of Cu^{II} ions will develop the adsorption process.[32] As shown in Fig. 3, the uptake of Cu^{II} ions depends on the initial solute concentration, increasing with the increase in C_0 from 10.0 to 50.0 mg dm^{-3} and then reaching a plateau in the range 100.0–400.0 mg dm^{-3} which could indicate that the saturation is already achieved at 100.0 mg dm^{-3}. It could also be noted that the contact time required to reach the maximum removal of Cu^{II} ions increases with increasing initial metal concentration within the time interval up to 20 min (Fig. 3).

Sorption Kinetics

Kinetics studies offering information on the rate of the metal uptake by sorption, which is very important for biosorption process design, have been performed.[21] Kinetic studies of metal adsorption by the msLVB were developed in order to determine the minimum time to achieve the sorption equilibrium. Pseudo-first order and pseudo-second order, as the most frequently used models, as well as the Elovich and the intra-particle diffusion models were used in this study.

Pseudo-First-Order Model

The pseudo-first-order rate equation of Lagergren[33] is represented in logarithmic form as:

$$\ln(q_e - q_t) = \ln q_e - kt \tag{1}$$

where q_e (mg g^{-1}) is the mass of metal ions adsorbed at equilibrium, q_t (mg g^{-1}) is the mass of metal adsorbed at time t, and k (min^{-1}) is the pseudo-first-order reaction rate equilibrium constant. A straight line of $\ln(q_e - q_t)$ versus t indicates application of the pseudo-first-order kinetics model, where, in a true pseudo-first-order process, $\ln q_e$ should be equal to the intercept and k equal to the slope of a plot of $\ln(q_e - q_t)$ against t, respectively.

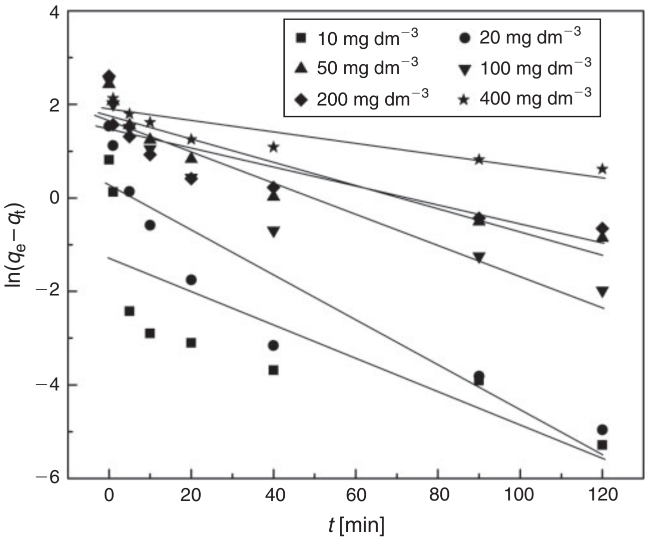

Fig. 5. Pseudo-first-order kinetics for adsorption of Cu^{II} ions on methyl-sulfonated *Lagenaria vulgaris* bioabsorbent (msLVB) (pH 5.0, msLVB dose 4.0 g dm^{-3}, temp. 20 ± 0.5°C).

The plot of $\ln(q_e - q_t)$ as a function of time and for the series of initial concentration of copper ranging from 10.0 to 400.0 mg dm^{-3} is given by Fig. 5. The pseudo-first-order model shows the low correlation coefficient values ($0.6920 < r^2 < 0.8430$, Table 2) indicating that the pseudo-first-order model did not fit well to the experimental data (Table 2). The kinetic constants vary in a random way and independently of the initial concentration. By comparing the experimentally obtained values of q_e to those calculated using Eqn 1 it could be noted that sorption of Cu^{II} ions did not follow the pseudo-first-order reaction. However, similarly to other sorption processes,[34] looking at the initial period of the biosorption process independently, the pseudo-first-order model could fit the experimental data well.

Pseudo-Second-Order Model

The pseudo-second-order equation[34] based on equilibrium adsorption can be expressed in a linearized form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order reaction rate equilibrium constant. A plot of t/q_t against t should give a linear relationship for the applicability of the pseudo-second-order kinetics model (Fig. 6).

The initial sorption rate is calculated according the following equation:

$$h = k_2 q_e^2 \tag{3}$$

The experimental data fit very well to the pseudo-second-order equation, where the r^2 values were observed to be close to

Table 2. A comparison of pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion kinetic models rate constants and calculated equilibrium from experimental data

Please see main text for definitions of the parameters listed

Parameter	Concentration of initial Cu^{II} solution [mg dm^{-3}]					
	10	20	50	100	200	400
q_e^{exp}	2.2613	4.6425	11.3975	12.4525	13.5800	15.0823
Pseudo-first order						
k_1	0.0358	0.0482	0.0221	0.0332	0.0206	0.0125
q_e^{cal}	0.2814	1.3312	5.7001	5.1248	4.3956	6.9137
r^2	0.8293	0.8150	0.8259	0.8430	0.6959	0.6920
Pseudo-second order						
k_2	0.8068	0.1654	0.0176	0.0306	0.0266	0.0089
q_e^{cal}	2.2655	4.6751	11.5220	12.5786	13.6240	15.1008
h	4.1408	3.6140	2.3339	4.8473	4.9430	1.4641
r^2	1.0000	1.0000	0.9997	0.9999	0.9995	0.9902
Elovich model						
α	2767.4	53.9297	27.027	91.8473	15202.8600	32.4082
β	6.1843	1.9482	0.6980	0.7144	1.1014	0.6920
r^2	0.4927	0.7403	0.9581	0.9085	0.9672	0.9803
Intraparticle diffusion model						
K_{id1}	0.9668	1.5637	2.9629	3.5197	3.7802	4.4053
C_1	0.0549	0.0066	0.1814	0.5217	0.0123	0.0083
r^2	0.9874	0.9991	0.9854	0.9173	0.9981	0.9989
K_{id2}	0.0096	0.1566	0.6286	0.7327	0.9688	1.1386
C_2	2.1750	3.6565	6.0644	7.4124	7.8096	10.1056
r^2	0.9833	0.7305	0.9309	0.9469	0.9883	0.9989

unity. The theoretical q_e values for the Cu^{II} ions were also very close to the experimental q_e values suggesting that metal sorption by msLVB followed a pseudo-second-order reaction (Table 2). The good fit to the pseudo-second-order kinetics indicates that the adsorption mechanism depends on the nature of adsorbate and adsorbent, and the rate-limiting step may be chemisorption involving a sharing or exchanging of electrons between the adsorbate and the surface of the adsorbent.[35] Also, the mechanism of ion exchange is probably involved which is favoured by the presence of sulfonic groups with strong ion-exchange potential. The rate constant obtained through the pseudo-second-order kinetic model varies inversely with an increase in initial concentration which could be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained.[36]

Elovich Model

The Elovich model describes several reaction mechanisms including bulk and surface diffusion and the activation and deactivation of catalytic surfaces. It is represented as:

$$q_t = \frac{1}{\beta}(\ln \alpha\beta) + \frac{1}{\beta}\ln t \tag{4}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}).[37]

A plot of q_t versus $\ln t$ should give a linear relationship if the Elovich equation is applicable with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The correlation coefficients r^2 generally increased with an increase of initial Cu^{II} ion concentrations (Table 2), which also indicates that more chemisorption phenomena occur. This may be explained by, as the amount of copper ions increases, the ion exchange of sulfonic groups reaches saturation and other functional groups (hydroxy, carboxy, phenolic, etc.) on the surface take a part in adsorption.

Intraparticle Diffusion Model

The adsorption process can be described by consecutive steps starting with liquid film diffusion, internal diffusion, and adsorption of solute on the interior surfaces of the pores of the sorbent. The intraparticle diffusion equation[38] can be written as follows:

$$q_t = K_{id}t^{\frac{1}{2}} + C \tag{5}$$

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 $t^{1/2}$.

The plots for the intraparticle diffusion presented in Fig. 7 can be divided into a multilinearity correlation indicating that three independent stages occur during the adsorption process of Cu^{II} ions. During the first shape portion (from 0 to 5 min) Cu^{II} ions were transported to the external surface of the biosorbent through the solution and it represents a rapid external mass transfer (external diffusion) and surface adsorption (film diffusion).[39] The second portion is the gradual adsorption stage where the intraparticle diffusion can be the rate-limiting step. The third portion (after 60 min) corresponds to the final equilibrium stage where the intraparticle diffusion starts to slow down due to the low solute concentration in solution.[40] If the intraparticle diffusion is the only rate-limiting step, the q_t versus $t^{1/2}$ plots should pass through the origin,[41] which is not the case in the present study, but it is very close (Fig. 7). Therefore, it could be considered that both surface chemisorptions and intraparticle diffusion are operating in parallel during the msLVB adsorption process. The first and second steps are more valuable than the final step for the adsorption of Cu^{II} ions onto msLVB. In Fig. 7 it can be observed that the slope and intercepts increase with an increase of initial concentration in the case of both first and second portions. This implies that the rate parameters for chemisorptions and intraparticle diffusion increase with increasing Cu^{II} concentration, probably due to a greater driving force with increasing C_0. Comparing the values of K_{id1} and K_{id2} it can be noted that film diffusion is more efficient than intraparticle diffusion. Also, the thickness of the boundary layer was steadily augmented with the initial concentration increasing the contribution of the film diffusion in the rate-limiting step. After all, it can be considered that both film diffusion and

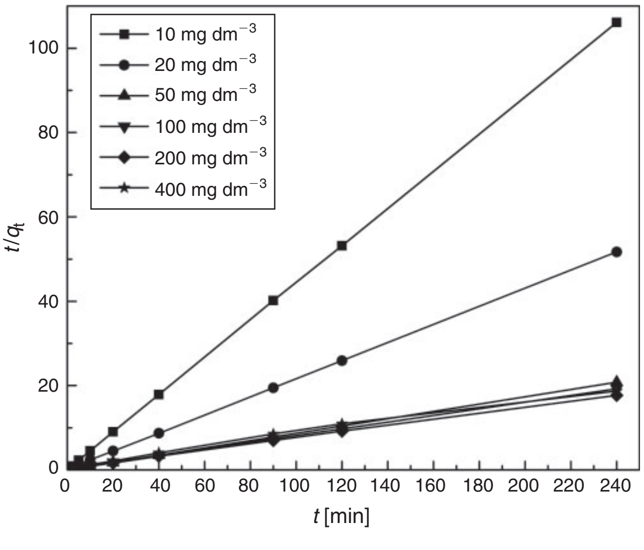

Fig. 6. Pseudo-second-order kinetics for adsorption of Cu^{II} ions on 4.0 g dm^{-3} methyl-sulfonated *Lagenaria vulgaris* bioabsorbent at 20 ± 0.5°C, and pH 5.0.

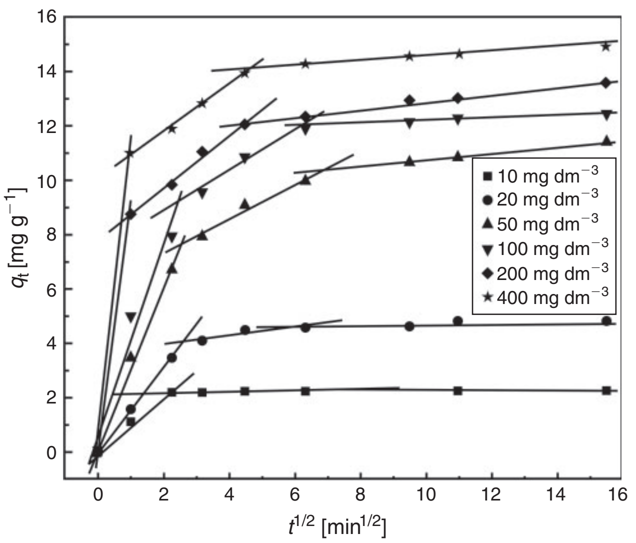

Fig. 7. Intraparticle diffusion kinetic model for adsorption of Cu^{II} ions on methyl-sulfonated *Lagenaria vulgaris* bioabsorbent.

intraparticle diffusion were concurrently operating during the process of the adsorption of Cu^{II} onto msLVB and were enhanced with the increase of initial concentration. The correlation coefficients for the intraparticle diffusion model are slightly lower than those of the pseudo-second-order kinetic model, except for initial concentrations of Cu^{II} ions of 400.0 mg dm^{-3}, indicating that the adsorption of Cu^{II} ions onto msLVB could follow the intraparticle diffusion model. The q_e values are closer to the experimental values; nevertheless in comparison the pseudo-second-order kinetic equation had the better fit.

The results of the kinetics parameters for Cu^{II} ions, calculated from the linear plots of pseudo-first-order and pseudo-second-order kinetic models, as well as for Elovich and intraparticle diffusion models are presented in Table 2.

The methyl-sulfonated material shows much better sorption characteristics than the basic material we used in previous research (aLVB),[42] which has a significantly lower value of q_e^{exp}, 7.97 mg g^{-1}, according to the pseudo-second-order model for an initial concentration of Cu^{II} of 50.0 mg dm^{-3}. Also, it has slightly better performances compared with the 'cold carbonated' material (ccLVB).

Adsorption Isotherms

The adsorption isotherm data have been obtained by varying the initial Cu^{II} concentration (10.0–400.0 mg dm^{-3}), while the other parameters are kept constant. Besides the Langmuir and Freundlich isotherm models, which are commonly used in describing adsorption, the experimental data were fitted to the Temkin and Flory–Huggins isotherm models in order to examine the relationship between sorbed (q_e) and the solution concentration (C_e) at equilibrium.

Langmuir Isotherm Model

The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.[43]

The Langmuir parameters can be determined from a linearized form, by plotting C_e/q_e versus C_e:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \qquad (6)$$

where C_e is the equilibrium metal ion concentration in solution (mg dm^{-3}), q_e is the amount of metal ions adsorbed onto the unit mass of the adsorbent (to form a complete monolayer on the surface) (mg g^{-1}), q_{max} is the Langmuir equilibrium constant related to maximum adsorption capacity (to the affinity of binding sites) (mg g^{-1}), and K_L is the Langmuir constant which is related to the enthalpy of adsorption (dm^{-3} mg^{-1}). The plot of C_e/q_e versus C_e for the Langmuir adsorption gives a straight line of slope equal to $1/(K_L q_{max})$ and intercept corresponding to $1/q_{max}$ (Fig. 8). Although this is the most often used isotherm applied for explaining the adsorption equilibrium, the Langmuir isotherm offers no insights into the mechanistic aspects of biosorption.[44]

The Langmuir isotherm model gives us the possibility to predict if an adsorption system is favourable or unfavourable by calculating R_L, a dimensionless constant referred to as the equilibrium parameter using the following equation:[45]

$$R_L = \frac{1}{1 + K_L C_0} \qquad (7)$$

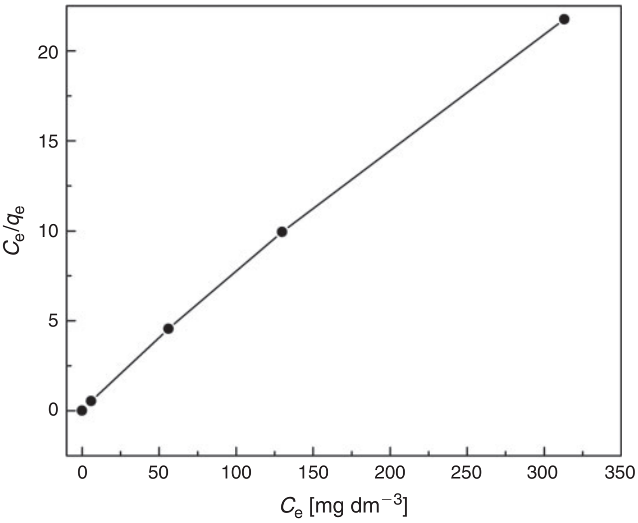

Fig. 8. Langmuir isotherm model plot for the adsorption of copper on methyl-sulfonated *Lagenaria vulgaris* bioabsorbent (msLVB) (initial Cu^{II} concentration 10.0–400.0 mg dm^{-3}, pH 5.0, msLVB dose 4.0 g dm^{-3}, temp. 20 ± 0.5°C).

where K_L is the Langmuir constant (dm^3 mg^{-1}) and C_0 is the initial Cu^{II} concentration (mg dm^{-3}). If the R_L value is between 0 and 1, the adsorption process is favourable. However, if $R_L > 1$ the process is unfavourable. When the value of R_L is equal to 0 the adsorption process is irreversible. If R_L is equal to 1 the process is linear. The value of R_L determined using Eqn (7) is 0.003 indicating that the adsorption of Cu^{II} ions onto msLVB is a favourable process, which points to the good adsorption characteristics of msLVB for removal of Cu^{II} from solutions.

The Langmuir isotherm represents the best fitting model having the highest correlation regression coefficient compared with the other models (Table 3) indicating that the uptake of copper ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. This implies that all the adsorption active sites are energetically equivalent and the surface is uniform, where the adsorbed Cu^{II} ions do not interact with each other and the equilibrium is established where a monolayer is formed at the adsorbent. The absence of interactions between adsorbed ions indicates that the chemical mechanism of sorption probably prevails.

Freundlich Isotherm Model

On the other hand, the Freundlich empirical adsorption isotherm equation is based on adsorption on a heterogeneous surface and can be expressed in the logarithmic, linear form as:[46]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

where q_e is the amount of adsorbed metal ions per unit mass of the adsorbent (mg adsorbate per 1 g adsorbent), C_e is the equilibrium concentration of the adsorbate in solution (mg dm^{-3}), and K_F and n are Freundlich empirical constants related to adsorption capacity (of the bonding energy) and adsorption intensity (capacity and heterogeneity of the adsorption surface sites), respectively. This model assumes that the uptake of metal

Table 3. Langmuir, Freundlich, Temkin, and Flory–Huggins parameters for the adsorption isotherms of Cu^{II} by methyl-sulfonated *Lagenaria vulgaris* bioabsorbent

Please see main text for definitions of the parameters listed

Isotherms	Constants	Value	r^2
Langmuir			
$C_e/q_e = 1/K_L q_{max} + C_e/q_{max}$	q_{max} [mg g^{-1}]	14.9531	0.9988
	K_L [L mg^{-1}]	0.8390	
Freundlich			
$\log q_e = \log K_F + (1/n)\log C_e$	n	6.4185	0.8206
	K_F [L mg^{-1}]	6.1598	
Temkin			
$q_e = (RT/b)\ln K_T + (RT/b)\ln C_e$	b [kJ mol^{-1}]	2.3742	0.9166
	K_T [L mg^{-1}]	1627.8201	
Flory–Huggins			
$\log(\theta/C_0) = \log K_{FH} + n\log(1-\theta)$	n	−0.6730	0.7614
	K_{FH} [L mg^{-1}]	0.0013	

ions occurs on a heterogeneous surface by multilayer adsorption where the stronger binding sites are occupied first and the binding strength decreases with increasing degree of site occupation,[46,47] therefore, it is more indicative of the physical mechanism of adsorption.

A plot of $\log q_e$ versus $\log C_e$ for the Freundlich adsorption isotherm should give a straight line where K_F could be calculated from the intercept and n from the slope. The factor n indicates a favourable adsorption condition if its value is between 1 and 10. The plot of $\log q_e$ versus $\log C_e$ for the Freundlich isotherm is not shown as the calculated correlation coefficient is low (0.8206, Table 3) which indicates that the adsorption of Cu^{II} ions onto msLVB does not follow this isotherm model and physical sorption.

Temkin Isotherm Model

The Temkin adsorption isotherm model takes into account adsorbing species–adsorbate interactions.[48] The derivation of the Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions rather than logarithmic, as implied in the Freundlich equation.[49] This equation implies that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.[50] The isotherm is applied in the linearized form:

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \tag{9}$$

where b is the Temkin constant related to heat of sorption (J mol^{-1}), A is the Temkin isotherm equilibrium binding constant (L g^{-1}) which corresponds to the maximum binding energy, R the universal gas constant (8.314 J mol^{-1} K^{-1}), and T the absolute temperature (K). Although the correlation coefficient for the Temkin isotherm model (0.9166, Table 3) indicates that it does not satisfactorily fit the experimental data, it is still significantly better than the Freundlich and Flory–Huggins models, which also confirms that adsorption of copper onto msLVB is primarily a chemisorption process. However, the Temkin equation is more applicable for predicting the gas phase equilibrium, but it is not usually appropriate for complex adsorption systems including liquid phase adsorption.[50]

Table 4. Comparison of maximum uptake capacities for Cu^{II} ions onto various adsorbents as reported in literature

Adsorbents	q_{max}^{A} [mg g^{-1}]	Ref.
Seed powder	68.36	[7]
Dehydrated wheat bran	51.50	[51]
Coirpith carbon	39.70	[9]
Water hyacinth roots	22.70	[14]
Peanut hull	21.25	[52]
Cinnamomum Camphora leaves powder	16.76	[34]
Methyl-sulfonated *Lagenaria vulgaris*	14.95	This study
Chestnut shell	12.56	[53]
Cotton boll	11.40	[31]
Wheat shell	10.80	[10]
Grape stalks wastes	10.10	[11]
Uncaria gambir	9.95	[4]
Pine bark	9.53	[54]

[A] q_{max} is the Langmuir equilibrium constant related to maximum adsorption capacity.

Flory–Huggins Isotherm Model

The Flory–Huggins model takes into account the degree of surface coverage characteristics of the adsorbate on the adsorbent.

$$\log\frac{\theta}{C_0} = \log K_{FH} + n_{FH}\log(1-\theta) \tag{10}$$

where $\theta = (1 - C_e/C_0)$ is the degree of surface coverage, K_{FH} is the Flory–Huggins model equilibrium constant, and n_{FH} is the Flory–Huggins model exponent. The correlation coefficient for the Flory–Huggins model is very low (0.7614, Table 3), so this model could not be applied for describing the adsorption of Cu^{II} onto msLVB.

The fitting of the data to the Langmuir, Freundlich, Temkin, and Flory–Huggins isotherms shows that the biosorption of Cu^{II} ions onto msLVB follows the Langmuir model better than the other models on the basis of the correlation factor r^2 (Table 3). The Langmuir isotherm model indicates a chemically equilibrated and saturated mechanism of sorption. The maximum biosorption capacity was found to be 14.95 mg g^{-1}. A comparison of the ability of the biosorbent in the present study with other adsorbents to remove Cu^{II} ions from wastewaters is presented in

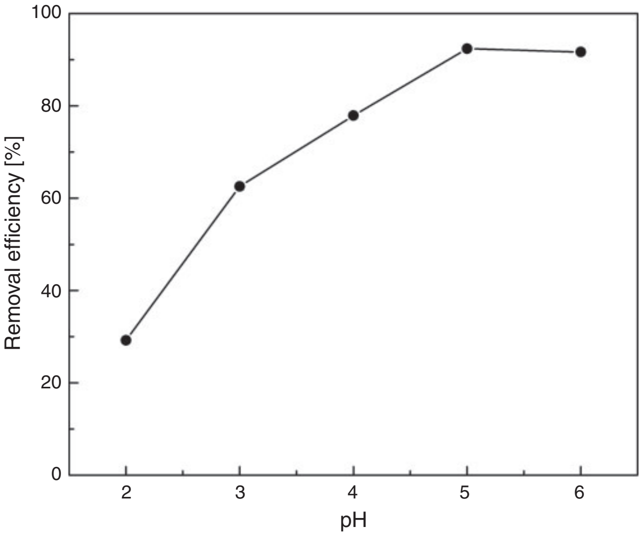

Fig. 9. Effect of initial pH on the removal efficiency for Cu^{II} ions from 50.0 mg dm^{-3} solutions by 4.0 g dm^{-3} methyl-sulfonated *Lagenaria vulgaris* bioabsorbent at 20 ± 0.5°C and at equilibrium.

Table 4. The comparison shows that msLVB has a similar adsorption capacity for copper as many other reported biosorbents, reflecting a promising effectiveness for msLVB utilization in copper removal from wastewaters.

Effect of Initial pH

pH is one of the most important factors controlling the adsorption of Cu^{II} ions onto adsorbent particles and affects the surface charge of the adsorbents, the solubility of the metal ions, and the degree of ionization of the adsorbate during the adsorbing process. The influence of the initial pH was examined at different pH values ranging from 2.0 to 6.0, with a msLVB dose of 4.0 g dm^{-3} and a temperature of 20 ± 0.5°C. Fig. 9 shows the effect of pH on the removal of Cu^{II} ions by msLVB.

The Cu^{II} removal by msLVB increased with increasing pH and attained values of 92.40 % at an initial pH of 5.0. The Cu^{II} uptakes increased significantly from 29.20 to 92.40 % at a pH ranging from 2.0 to 5.0, and then slightly decrease to 91.68 % at pH 6.0. The pH of the solution is one of the most significant parameters in the adsorption of metal ions from aqueous solutions. This parameter is straightforwardly related to the ability of H$^+$ ions to compete with copper ions for the active surface sites containing –SO_3^- groups on the msLVB surface. The removal efficiently (RE) shows minimum values at pH 2.0. At this pH value, the overall surface charge on the active sites become positive and metal cations and H$^+$ ions compete for surface active sites, which results in a lower uptake of metal. As the solution pH was increased, the ability of Cu^{II} ions to compete with H$^+$ ions was also increased, but at pH 6.0 enhanced metal removal from solution could be, partly, a result of metal hydroxide precipitation. The results suggest that the biosorption of Cu^{II} ions to the msLVB is mainly due to electrostatic attraction.[55] Thus, all studies were performed at an initial pH of 5.0 in order to correlate metal removal with the adsorption process. The adsorption capacity of msLVB at pH 5.0 was 11.40 mg g^{-1}. The adsorption capacities of msLVB as a function of the initial pH are presented in Fig. 10.

At lower pH values, msLVB features a much better RE compared with untreated biomaterial obtained from the *Lagenaria vulgaris* shell which removes ~5 and 35 % of dissolved Cu^{II} ions at pH 2.0 and 3.0, respectively (results not shown). This trend is also maintained at higher pH values, whereas aLVB uptakes up to 70 % of Cu^{II} ions contrary to the ~92 % removed by msLVB at pH 5.0.

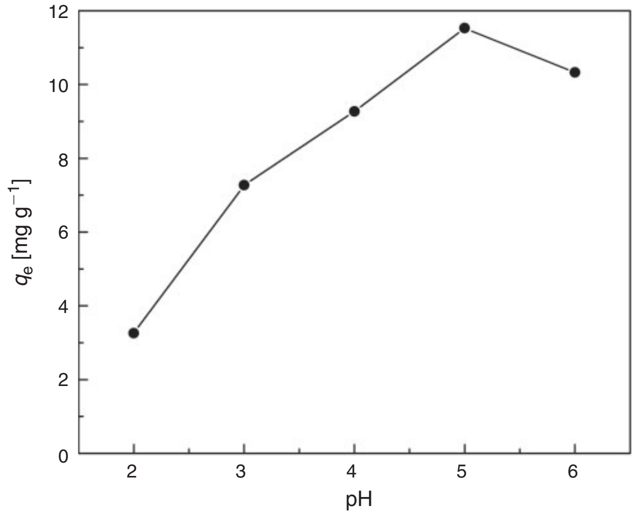

Fig. 10. Effect of different pH values on the adsorption of Cu^{II} onto methyl-sulfonated *Lagenaria vulgaris* bioabsorbent (msLVB) (initial Cu^{II} concentration 50.0 mg dm^{-3}, msLVB dose 4.0 g dm^{-3}, temp. 20 ± 0.5°C).

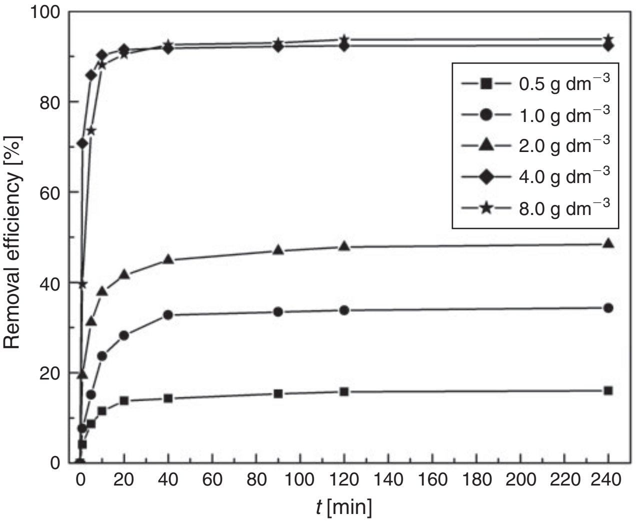

Fig. 11. Effect of adsorbent dose on the removal of Cu^{II} from the 50 mg dm^{-3} solution, at pH 5.0, temp. 20 ± 0.5°C.

Effect of Adsorbent Dose on Cu^{II} Removal

The adsorbent dosage represents an important parameter because it strongly affects the efficiency of an adsorbent on removal of the adsorbate from solution. The effect of adsorbent dose was determined at a different msLVB dose ranging from 0.5 to 8.0 g dm^{-3}, an initial Cu^{II} concentration of 50.0 mg dm^{-3}, at pH 5.0 and 20 ± 0.5°C.

The dependence of the RE of msLVB upon adsorption of Cu^{II} on adsorbent concentration is depicted in Fig. 11. The increase in adsorbent dose from 0.5 to 8.0 g dm^{-3} resulted in an increase of Cu^{II} ion removal efficiency from 16.0 to 93.9 %. This is due to the higher availability of active sites on msLVB for ion exchange with Cu^{II} ions. It is noteworthy that an adsorbent dose of 4.0 g dm^{-3} shows a removal efficiency of 92.4 %. As a reason for this behaviour, some authors suggest that high biomass concentrations favour the electrostatic interaction between cells and therefore the aggregation and/or agglomeration of sorbent particles, which would lead to a decrease of the number of available active sites for metal sorption on the surface area.[51,56,57] Other authors explained this trend as binding of almost all ions to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining unadsorbed in the solution.[51]

With increasing the adsorbent dose from 0.5 to 8.0 g dm^{-3}, the adsorption capacity of msLVB for Cu^{II} decreased from 13.54 to 5.30 mg g^{-1}. These results imply that adsorption sites remain unsaturated during the adsorption reaction with application of a higher adsorbent dose.

Conclusions

In this study, the shell of *Lagenaria vulgaris* was chemically modified with formaldehyde and Na_2SO_3 in order to improve the adsorption of Cu^{II} from aqueous medium. Modification of the biosorbent was confirmed by the presence of characteristic absorption bands for a sulfonic group using FTIR spectroscopy. Research proved that the biosorption of Cu^{II} onto msLVB was rapid, with equilibrium achieved after less than 40 min. The kinetics studies showed that the investigated adsorption system followed pseudo-second-order kinetics and that chemisorption might be the rate-limiting step that controls the adsorption process. The adsorption process could also be well described by the three-stage intraparticle diffusion model, which indicated that both a chemical and diffusion process was involved in the biosorption of Cu^{II} ions onto msLVB. The initial pH strongly affects the sorption of Cu^{II} onto msLVB. The sorption capacity of msLVB is negligible at low pH, and increased with the increase of initial pH, with an optimal value of 5.0. Above pH 6.0 copper was precipitated as a hydroxide. The extent of the removal of the Cu^{II} ions is directly related to the concentration of msLVB in the suspension, with an optimal biosorbent dose of 4.0 g dm^{-3}. The Langmuir isotherm model showed the best fit to experimental data in describing the adsorption of copper on biosorbent. The maximum adsorption capacity was determined as 14.95 mg g^{-1}. The methyl-sulfonated biosorbent showed sorption improvement, reaching equilibrium in a shorter period and an increased sorption capacity compared with untreated material and it has the potential to be used as an efficient and cost-effective biosorbent for the removal of Cu^{II} ions from aqueous solutions.

Experimental

Reagents and Chemicals

All chemicals were of analytical grade and used without further purification. Deionized water ($<5\ \mu S\ cm^{-1}$) was used to prepare all aqueous solutions. A standard stock solution of Cu^{II} (1000 mg dm^{-3}, $CuSO_4{\cdot}5H_2O$, Merck) was used to prepare appropriate concentrations for the sorption studies. The pH of the solutions was adjusted pH-metrically to the required value with nitric acid or sodium hydroxide (0.1/0.01 M), without buffering. The pH of solutions was determined by a SensION3 (HACH, USA) pH meter.

Preparation of Biosorbent

Harvested fruit was washed to remove dirt and dust, dried at room temperature, and smashed into larger pieces (5–7 cm). The seeds and dried pulp were removed and the inner surfaces of pieces were scraped. These pieces were crushed into smaller pieces (2–3 cm), ground in a crusher mill (Waring 8010 ES, Germany), dried in hot air oven at 55°C for 24 h to a constant weight, and then sieved to particles with sizes ranging from 0.8 to 1.25 mm using successive sieving.

Methyl-sulfonated-LVB was prepared by adding 200 mL of a 1.5 % solution of formaldehyde to 10 g of raw material with a particle size from 0.8 to 1.25 mm. After heating in a flask under reflux at 80°C for 2 h, 25 g of Na_2SO_3 (Merck) was added and the reaction mixture was heated for 3 h at 100°C again under reflux. After cooling, the material was washed thoroughly with de-ionized water until the flushing water had no reaction to the presence of sulfate. The biosorbent was oven-dried at 55°C for 1 day to a constant weight. The obtained material was used for metal sorption studies. The prepared adsorbent was denoted as msLVB for convenience.

FTIR Characterization of msLVB

The functional groups available on the surface of msLVB before and after adsorption of Cu^{II} ions were detected by KBr technique using FTIR spectroscopy (Bomem Hartman & Braun MB-100 spectrometer). The spectra were recorded at room temperature in a range from 4000 to 400 cm^{-1}. The KBr pellets were prepared from 1.5 mg of finely powdered msLVB dispersed in 150 mg of anhydrous KBr. The obtained FTIR spectra were analyzed using Win Bomem Easy software.

Elemental Analyses of msLVB

For analysis the prepared biomass was acid digested ($HNO_3 + H_2O_2$) in a microwave oven (MWD) (ETHOS, Milestone, Italy). The concentrations of sulfur in the biomaterial were determined using inductively coupled plasma–optical emission spectroscopy (ICP-OES) model iCAP 6500 Duo (Thermo Scientific, UK) equipped with a CID86 chip detector, in order to measure the amount of sulfur incorporated into the biomaterial.

The Batch Adsorption Experiments

The adsorption equilibrium experiments were conducted in 250 mL Erlenmeyer flasks, containing 125 mL of the metal model solution at different concentrations (from 10.0 to 400.0 mg dm^{-3}). Aliquots of solutions (4.0 mL) were withdrawn at preset time intervals, the biomaterial was removed by filtration through a 0.45 μm membrane filter, and the filtrates were analyzed for Cu^{II}. All experiments were conducted at ambient temperature (20 ± 0.5°C). Kinetic experiments were performed by taking samples at defined intervals up to 240 min. In order to evaluate the effect of solution pH on the biosorption process, experiments were carried out at different initial pH values, from 2.0 to 6.0, with all other parameters kept constant. The adsorption pH was chosen in this range in the aim to avoid the precipitation of the studied metal ion as a hydroxide which occurs above pH 6.3.[21] All the experiments were carried out in triplicate and the average values were used for further calculations.

The concentrations of residual Cu^{II} ions in the solution before and after adsorption were determined by using an atomic absorption spectrophotometer (AAS Analyst 300, Perkin–Elmer, USA) at a wavelength of 324.8 nm. The spectrophotometer was calibrated by a series of standard solutions. The adsorption capacity of the biosorbent at equilibrium was calculated as:

$$q_e\ (\mathrm{mg\,g^{-1}}) = \frac{(C_0 - C_e)V}{m} \tag{11}$$

where q_e is the amount of Cu^{II} ion adsorbed per unit weight of the adsorbent, V is the volume of solution, C_0 is the initial concentration of metal ion ($\mathrm{mg\,dm^{-3}}$), C_e is the equilibrium metal ion concentration ($\mathrm{mg\,dm^{-3}}$), and m is the mass of the adsorbent (g).

The copper RE of the adsorbent was estimated according to the following equation:

$$\mathrm{RE}\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (12)$$

where C_0 and C_e are the initial and equilibrium concentrations ($\mathrm{mg\,dm^{-3}}$) of $\mathrm{Cu^{II}}$ in solution, respectively.

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