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Technological aspects of oxidation processes

PREPARATION AND CHARACTERISATION OF XANTHATED *Lagenaria vulgaris* SHELL BIOSORBENT

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ABSTRACT

Preparation and characterisation of chemically modified, improved biosorbent, xanthated Lagenaria vulgaris shell (xLVB), and its application for Cu(II) ions removal from aqueous solutions, were investigated in the present study. The chemically modified material was characterised by using FTIR, SEM and EDX analysis. Equilibrium isotherms and kinetics were obtained and the effect of various parameters including contact time, initial pH, biosorbent dosage, particle size, temperature, initial Cu(II) concentration was studied under batch conditions. xLVB was applied to test the sorption of Cu(II) ions in batch column system with recirculation of aqueous phase. The experimental data were best fitted by using pseudo-second order kinetics and the Langmuir isotherm model; equilibrium within less than 40 min and sorption capacity of 25.2 mg g^{-1} for Cu(II) ions, at 20°C were achieved. With increasing temperature from 10 to 40°C the free energy change was negative, suggesting that the biosorption was exothermic and spontaneous.

Keywords: copper(II), kinetics, sorption, thermodynamics, xanthated biomaterial.

AIMS AND BACKGROUND

Toxic heavy metals are released into the biosphere via the source of heavy metal include natural sources, mining, smelting, agrochemicals and sewage sludge applications, and livestock manure uses and spread into the environment. Their presence in the environment can be detrimental to people, plants and animals. Rapid industrialisation throughout the world has generated huge volumes of waste containing heavy metals.

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Copper is widely used in various industrial activities including metal plating, mining, electroplating, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries, metalworking and finishing processes[1,2]. Long term exposure of copper can cause irritation of the nose, mouth and eyes as well as headaches, stomach ache, dizziness, vomiting, diarrhea and liver damage[3]. Therefore, it is desirable that heavy metal levels be considerably reduced in industrial and municipal effluents to meet regulatory standards. The conventional methods that are employed to remove heavy metals such as ion exchange, chemical precipitation, reverse osmosis and membrane separation are found to be inefficient or expensive, especially when treating wastewater with low concentration of heavy metals[4–11]. Biosorption is a process that utilises inexpensive biomass to sequester toxic heavy metals and is particularly useful for the removal of trace levels of contaminants from industrial effluents[12].

This study presents the preparation, characterisation and investigation of the ability of xanthated material based on *Lagenaria vulgaris* (xLVB) as a biosorbent for the removal of Cu(II) from water. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and Fourier transform infrared spectroscopy (FTIR) were used to investigate characteristics of xanthated *Lagenaria vulgaris* biosorbent (xLVB) and its interaction with metals. The optimum biosorption conditions were investigated as a function of contact time, initial pH, initial metal ion concentration, biosorbent dose, particle size, temperature, under batch typical conditions. Flow rate and packed-bed height were varied in batch column system with recirculation of aqueous phase.

EXPERIMENTAL

Reagents. All chemicals were of reagent grade and used as received. HNO_3, NaOH, CS_2, $Cu(NO_3)_2$, were purchased from Merck (Germany). All solutions were prepared using deionised water. Standard metal stock solution was prepared by dissolving given amounts of $Cu(NO_3)_2 . 3H_2O$. Standard solutions were stored in a refrigerator at +4°C.

Preparation of xanthated biosorbent. *Lagenaria vulgaris* is a creeping, hardy plant that belongs to the Cucurbitaceae family. It was cultivated and collected from a farm in the south area of Serbia (near the town of Nis)[13,14]. Plant shell was treated with diluted nitric acid and after that by sodium hydroxide, producing a basic *Lagenaria vulgaris* biosorbent (LVB). The dried biomass was fractionised using standard sieves (Endecotts, England).

Xanthation was carried out by employing the following procedure. 10.0 g of the base material was soaked in 100 cm^3 of 5.0 mol dm^{-3} NaOH solution in a 200 cm^3 glass flask, stirred for 90 min and washed with deionised water to remove excess alkali. This material was then esterified with 1.0 cm^3 of CS_2 and 100 cm^3 2.5 mol dm^{-3} NaOH for another 180 min. Xanthated material was allowed to settle and separated by decantation and filtration. Synthesised xanthate was washed with water several times to remove excess alkali until the pH of the water became neutral; this was followed by an acetone wash. As a result, biosorbent with improved ability for the removal of heavy metals from aqueous solutions was prepared.

The product obtained is similar in performance to expensive commercial ion exchange resins. Other advantages are that the biosorbent can be easily separated from the water phase by decanting and filtration and, unlike other natural materials (orange peel, rice straw, sugarcane bagasse, etc.[11]) does not change in consistency and particle size due to the usage and manipulation.

Methods. The morphology of the xLVB surface was analysed by scanning electron microscopy (SEM). EDX analysis (Thermo Scientific NORAN System 7, USA) provides elemental information via analysis of X-ray emissions from the adsorbent surface. Fourier transform infrared spectroscopy (FTIR) was used in order to characterise the xanthated *Lagenaria vulgaris* biosorbent (xLVB) and its interaction with metals (Bomem Hartmann & Braun MB-100 spectrometer).

Batch biosorption experiments. A stock solution of 1.00 g dm^{-3} Cu(II) was prepared using $Cu(NO_3)_2$ and working standard solutions were prepared just before use by appropriate dilution of the stock solutions. Batch sorption experiments were performed with known quantities of dried biosorbent suspended in 250 cm^3 of Cu(II) solutions, at a concentration range of between 10 and 400 mg dm^{-3}. The biosorption experiments were conducted at temperatures of 10, 20, 30 and 40°C. The effect of pH on the sorption capacity of xanthated *Lagenaria vulgaris* (xLVB) for Cu(II) was evaluated in the pH range from 2 to 6. The pH of each solution was adjusted to the required value with 0.1/0.01 mol dm^{-3} NaOH/HNO_3 solutions using a pH-meter (SensIon5, HACH, USA). The pH was maintained during treatment and kept to within ± 0.2 units by adding 0.01 or 0.1 mol dm^{-3} HNO_3 in small portions. Samples (4 cm^3) were taken before mixing the biosorbent solution and Cu(II) ion bearing solution and at pre-determined time intervals (0, 1, 5, 10, 20, 40, 90, 120 and 180 min) for the residual Cu(II) ion concentrations in the solutions. All experiments were conducted in triplicate. Average values ± SD (error bars) are presented in all data outputs. The concentration of residual Cu(II) ions in the solutions were determined by using an atomic absorption spectrophotometer (AAnalyst 300; Perkin Elmer, USA). The amount of metal adsorbed q_t (mg g^{-1}) was determined by using the following equation:

$$q_t = \frac{(c_0 - c_t) \times V}{m}, \tag{1}$$

where c_0 and c_t are the initial and final concentrations of the metal ion in solution (mg dm^{-3}); V – the solution volume (dm^3), and m – the mass of the biosorbent (g).

The removal efficiency (RE) of metal ions by biosorbent was calculated using the following equation:

$$\text{RE (\%)} = \frac{c_0 - c_t}{c_0} \times 100 \tag{2}$$

where c_0 and c_t are the initial and final concentrations of the metal ion in the solution (mg dm^{-3}), respectively.

Biosorption experiment of batch column system with recirculation of aqueous phase. Chemically modified xanthated material was applied to test the sorption of Cu(II) ions in a packed-bed column and recirculation of the aqueous phase, with a variation of the packed-bed height and flow rate.

Adsorption experiments, using a column, were conducted in a transparent cylindrical polypropylene column. Appropriate amount of xLVB (4.0 g dm^{-3}) was packed between two discs of sintered alumina into a 200 mm length column. Cu(II) ions solution were pumped from the bottom of the column to the top at a desired flow rate using a peristaltic pump model SP 311 (VELP Scientifica, Italy). The effect of packed-bed height on the biosorption process was investigated by using different columns (9–19 mm internal diameter). By changing the inner diameter of the column 9, 11, 13 and 19 mm, at constant amount of the biosorbent, packed-bed height was changed and had the following values: 190, 165, 141 and 85 mm, respectively. The flow rate was changed from 0.5 to 5.0 cm^3 min^{-1}. All of the experiments were performed at 20 ± 0.2°C and pH 5.0 ± 0.2. Samples were collected from the exit of the column after 120 min and analysed for the residual Cu(II) ions concentration, as described above. Biosorption experiments were conducted using a reference solution containing 50.0 mg dm^{-3} of Cu(II) ions.

RESULTS AND DISCUSSION

FTIR, SEM and EDX characterisation of the xLVB. FTIR analysis of xLVB biomass before and after sorption of Cu(II) ions is represented in Fig. 1. The broad and intense absorption vibrational bands at around 3401.77 cm^{-1} from xLVB, corresponds to the O–H stretching vibration due to inter- and intra-molecular hydrogen bonding of polymeric compounds such as phenols, alcohols, and carboxylic acids, as in cellulose and lignin, thus showing the presence of hydroxyl groups on the biomass surface[15]. The band at 2921.58 cm^{-1} is attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids. The bands at 1625.44 and 1458.86 cm^{-1} are due to asymmetric and symmetric stretching vibration of C=O in ionic carboxylic groups (–COO–). The intense band at 1061.61 cm^{-1} is related to the C–OH stretching vibration of alcoholic groups and carboxylic acids[16]. The presence of sulphur groups in the xLVB has been identified by the appearance of bands at 1226.49, 1158.99, 1025.93 and 534 cm^{-1} corresponding to O=C=O, S–C–S, C=S and C–S (Ref. 17). Some distinct changes are noted in the spectrum of xLVB Cu100 and xLVB Cu400, the solutions with initial copper concentration of 100.0 and 400.0 mg dm^{-3}, respectively. The FTIR spectrum of Cu(II) loaded xLVB showed some shift in wavenumber or reduction in intensity. The band at 3401.77 cm^{-1} shifted to 3428.76 and 3431.66 cm^{-1} after Cu(II) ion adsorption 100 and 400 mg dm^{-3}, respectively, which could indicate the involvement of –OH (hydroxyl) groups in the sorption of Cu(II) ions. The FTIR spectra of xLVB and Cu(II)-sorbed xLVB showed that the band expected at 1226.49 cm^{-1} correspond to the O=C=O had shifted to 1230.24 cm^{-1} for xLVB Cu100 and 1228.42 cm^{-1} for xLVB Cu400. In the xLVB spectrum, the band centered at 1025.93 cm^{-1} corresponding to the C=S stretching vibrations shifts to 1033.64 cm^{-1} for xLVB Cu100 and 1031.71 cm^{-1} for xLVB Cu400. From the foregoing results, it is hypothesised that the mechanism of copper binding on xLVB, could occur by surface ion-exchange followed by complexation.

The morphology of the xLVB was analysed by scanning electron microscopy (SEM) at nominal magnifications of ×150 (Fig. 1*B*) and ×500 (Fig. 1*C*). The presence of voids on the surface of xLVB biomass revealed the possibility of Cu(II) ion accumulation. The surface was of a rough texture and porosity could be distinctly noticed.

The EDX spectra obtained for the native as well as copper-loaded biosorbent (Fig. 2) indicates the presence of C, O, Na, Al and S. The presence of S Kα and Na Kα peaks (Fig. 2), recorded in the xLVB spectra indicate the anchoring of xanthate groups on the biomass surface with regard to basic *Lagenaria vulgaris* biosorbent (results not shown). After adsorption of Cu(II) ions, a new peak was observed at 0.93 keV (Cu Lα) which represents Cu(II) ions (Fig. 2). The presence of sodium, which is capable of ion exchange with Cu(II) ions, was noted at high concentration before the sorption of Cu(II) ions. Furthermore, before the adsorption of the Cu(II) ions, the concentration of sodium was high (3.0%); however, in the EDX spectrum of Cu(II) ions loaded xLVB concentration of sodium decreased, thus suggesting an ion exchange process.

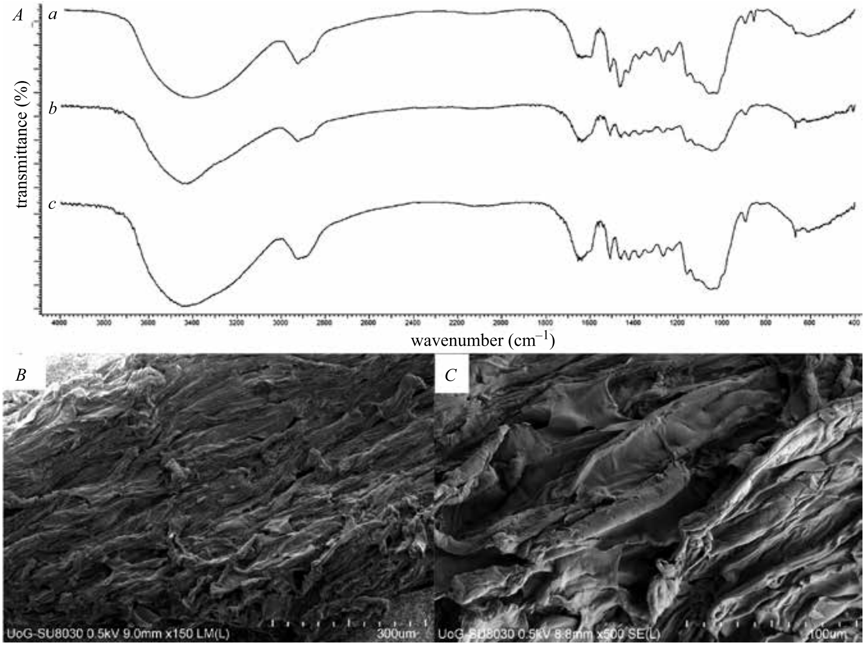
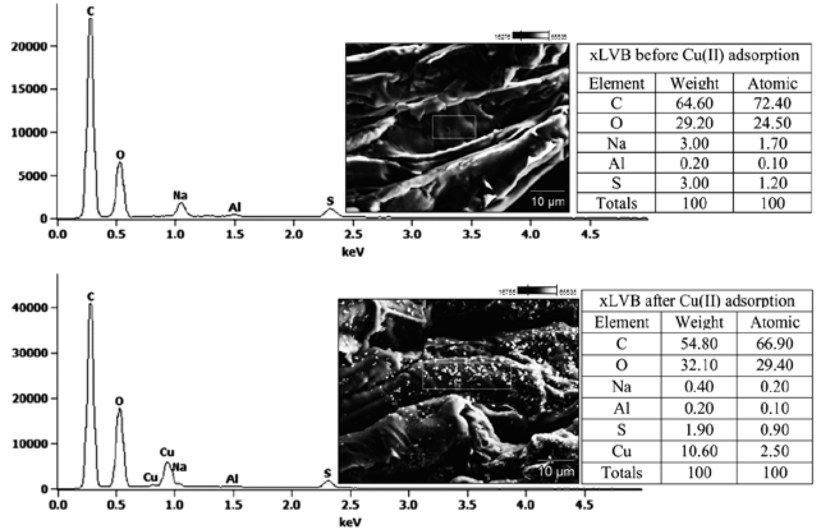


Fig. 1. FTIR spectra (*A*) of: xLVB – *a*; xLVB Cu100 – *b*, and xLVB Cu400 – *c*
Scanning electron micrographs (*B*) of: xLVB 150 × magnification – *B* and 500 × magnification – *C*



xLVB before Cu(II) adsorption		
Element	Weight	Atomic
C	64.60	72.40
O	29.20	24.50
Na	3.00	1.70
Al	0.20	0.10
S	3.00	1.20
Totals	100	100

xLVB after Cu(II) adsorption		
Element	Weight	Atomic
C	54.80	66.90
O	32.10	29.40
Na	0.40	0.20
Al	0.20	0.10
S	1.90	0.90
Cu	10.60	2.50
Totals	100	100

Fig. 2. EDX analysis of xLVB before and after adsorption of Cu(II) ions

The elemental analysis of sulphur in xLVB provided important evidence of increased S content (17.4 mg g^{-1}) compared to the untreated material (0.2 mg S g^{-1}). This elemental analysis of sulphur together with new bands in the FTIR spectra and the results of EDX analysis proved that incorporation of sulphur groups occurred on the surface of the biomaterial and that xanthation was successful.

Effect of initial pH. The influence of initial pH on the removal of Cu(II) ions from aqueous solution was investigated at five different initial pH values: 2.0, 3.0, 4.0, 5.0 and 6.0. The results are shown in Fig. 3. The removal efficiency of Cu(II) ions increased from 25.1 to 98.0% when the solution pH was increased from 2.0 to 5.0, followed by a slight decrease to 95.2% at pH 6.0.

A maximum sorption capacity was achieved at pH 5.0 for Cu(II) ions. At low pH, there is a high concentration of H^+ ions that have high mobility as compared to metal ions and competition between H^+ with metal ions decreases their adsorption. As the pH is increased, the overall surface on the xLVB became more negative and adsorption increases. On the other hand, as the pH value of the solution increases, adsorption also increases due to a decrease in H^+ ions and a greater number of surface ligands with negative charges[18]. Insoluble copper hydroxide starts precipitating from the solution at pH > 6 leading to the decision to carry out experimental work only at pH values below 6.0.

Basic material LVB, from which xLVB was obtained has an RE value of 6.8% at pH 2.0, which indicates that the initial pH has a much smaller influence on xLVB, because of the presence of the strong acid xanthate groups, which are in the form of the sodium salt under the conditions applied. These negative groups have a high affinity for binding of positive charged metal ions, probably by an ion exchange mechanism.

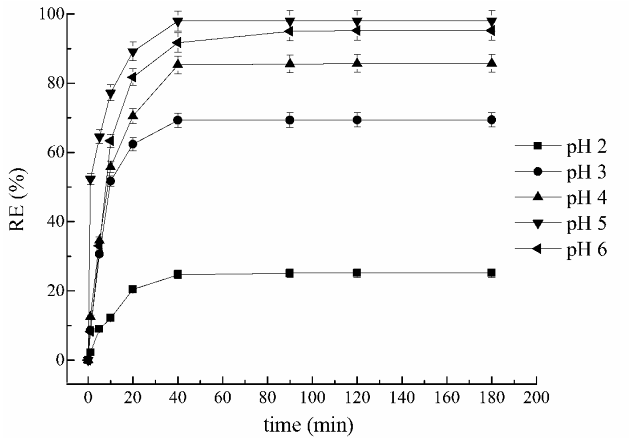


Fig. 3. Effect of initial pH on the removal of Cu(II) ions from aqueous solutions by xLVB $[Cu(II)]_0$ = 50.0 mg dm^{-3}, biosorbent dose – 4.0 g dm^{-3} and temperature 20.0 ± 0.2°C

Effect of biosorbent dosage. The effects of biosorbent concentration on the removal of Cu(II) ions was studied by varying the dose of biosorbent from 0.5 to 8.0 g dm^{-3} at fixed amount of sorbate concentration, pH and temperature. The results are presented in Fig. 4*a*. The removal efficiency of Cu(II) ions increased from 16.8 to 98.1% by increasing the biosorbent concentration from 0.5 to 4.0 g dm^{-3}. A further increase in biosorbent dosage (>4.0 g dm^{-3}) did not cause a significant improvement in adsorption. This can be explained by the fact that the greater mass available, results in a more effective contact surface area for adsorption[18]. Thus, the optimum dosage of xLVB for adsorption of Cu(II) ions is found to be 4.0 g dm^{-3} and all sorption experiments were conducted at this concentration of biosorbent.

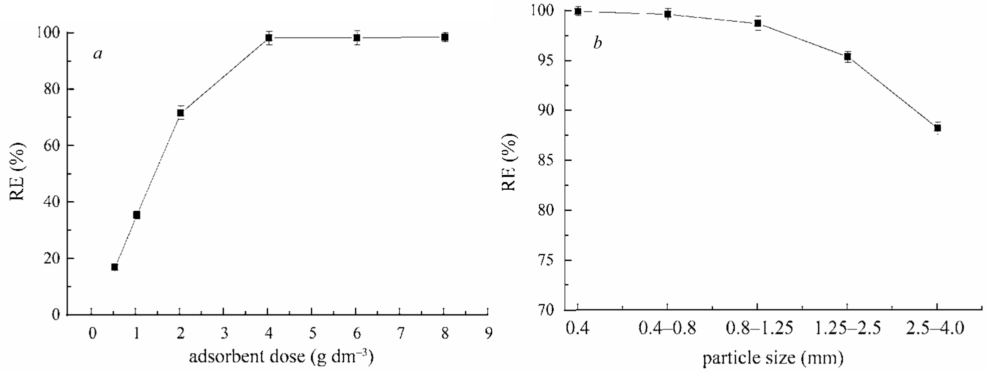


Fig. 4. Effect of adsorbent dose (*a*) and of biosorbent particle size (*b*) on removal of Cu(II) ions from aqueous solutions by xLVB
Experimental conditions: pH 5.0 ± 0.2; initial metal concentration 50.0 mg dm^{-3}; contact time 180 min, and temperature 20 ± 0.2°C

Effect of particle size. The effect of varying biosorbent particle size is presented in the data in Fig. 4*b*. Xanthated *Lagenaria vulgaris* shell was graded to five particles sizes, i.e. 0.4–0.8, 0.8–1.25, 1.25–2.5 and 2.5–4.0 mm with standard sieves. The data in Fig. 4*b* shows that the removal efficiency of Cu(II) ions increased from 95.4 to 99.9% by decreasing the particle sizes from 2.5–4.0 to 0.4–0.8 mm. This was most probably due to the increase in the effective surface area as the particle size decreased, which provided more sorption sites for the metal ions[19,20]. The aforesaid particle size of 0.8–1.25 was selected for further study because particles of 0.4–0.8 mm size were too small (not suitable for handling) and the difference in removal efficiency was also very small; on the other hand, 1.25–2.5 and 2.5–4.0 mm size fractions show lower efficiency due to the smaller surface area compared to the 0.8–1.25 mm fraction.

Kinetic studies. In order to further investigate the adsorption mechanism, the minimum time to achieve the sorption equilibrium of Cu(II) ions onto xLVB and the rate-controlling steps in the diffusion process, a kinetic investigation was conducted. The kinetics of the xLVB and Cu(II) ion interactions was tested by using different kinetic models including pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models. Used equations of these models are available in paper by Binti et al.[21], Rehman et al.[22], Khan and Wahab[23], Hossain et al.[24] and Weber and Morris[25].

The effect of contact time on the removal efficiency of Cu(II) ions by xLVB and basic *Lagenaria vulgaris* biosorbent (LVB), was investigated at time intervals from 0 to 180 min. The concentration of Cu(II) ions declined sharply with contact time in the first 10 min and reached equilibrium at about 40 min for xLVB. After this equilibrium period the amount of adsorbed metal ions did not change significantly with an increase in contact time. The initial fast phase occurs due to high availability in the number of active binding sites on the biosorbent surface. A further increase in contact time did not show a significant decrease of Cu(II) concentration, that occurs due to diffusion of the copper ions into the inner part of the biomass. It can be seen that xLVB gave significantly better results than LVB (Fig. 5), after 180 min of contact time, 98.0 and 70.3%, respectively. xLVB show a higher affinity for binding Cu(II) ions than basic *Lagenaria vulgaris* biosorbent (LVB), which has different surface functional groups.

The results on the determination of the kinetics parameters for the adsorption of Cu(II) ions are presented in Table 1.

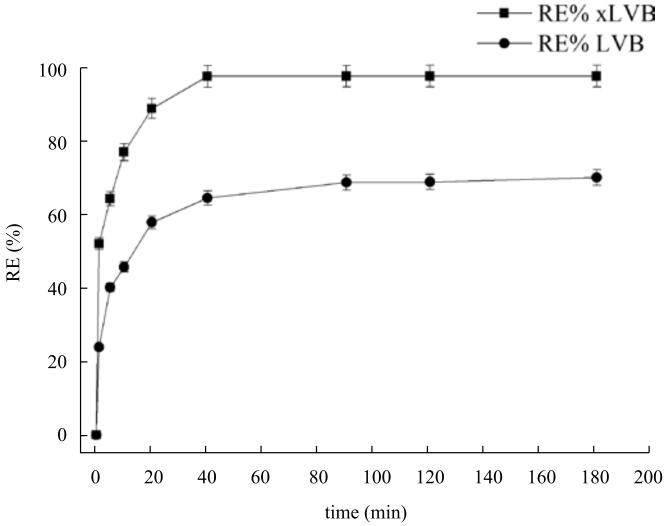


Fig. 5. Removal efficiency of Cu(II) ions from aqueous solutions by xLVB and LVB
Experimental conditions: pH 5.0 ± 0.2; biosorbent dose 4.0 g dm^{-3}; initial metal concentration 50.0 mg dm^{-3}, and temperature 20 ± 0.2°C

Table 1. Comparison of experimental and calculated values for pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models rate constants

	Concentration (mg dm^{-3})					
	10	20	50	100	200	400
q_e^{exp}	2.25	4.74	12.23	17.48	22.45	24.78
			Pseudo-first order			
k_1	0.071	0.044	0.035	0.028	0.017	0.019
q_e^{cal}	1.59	2.36	6.31	12.34	14.92	15.58
r^2	0.973	0.938	0.908	0.975	0.873	0.874
			Pseudo-second order			
k_2	0.128	0.067	0.020	0.006	0.004	0.005
q_e^{cal}	2.30	4.83	12.49	18.18	22.77	25.06
r^2	0.999	0.999	0.999	0.998	0.993	0.996
			Elovich model			
α	4.85	12.66	19.39	9.48	10.20	15.00
β	3.27	1.60	0.58	0.36	0.28	0.26
r^2	0.933	0.918	0.938	0.989	0.992	0.994
			Intraparticle diffusion model			
K_{id1}	0.586	1.211	2.831	3.322	3.864	5.273
C_1	0.037	0.159	0.306	0.214	0.128	–0.192
r^2	0.984	0.935	0.955	0.984	0.996	0.995
K_{id2}	0.174	0.439	1.206	1.628	2.100	1.991
C_2	1.042	1.935	4.310	4.020	4.506	7.450
r^2	0.773	0.819	0.863	0.982	0.971	0.989

The results show that when the initial metal ion concentration was increased from 10.0 to 400.0 mg dm^{-3}, the loading capacity of the biosorbent increased from 2.2 to 24.8 mg of Cu(II) ions per gram of xLVB. Generally, at lower concentrations, all Cu(II) ions present in solution could interact with the binding sites on xLVB and thus the percentage adsorption is higher than that at higher initial Cu(II) ion concentrations. With increasing metal ion concentration, the percentage of metal removal decreases due to the diminishing loading capacity of the biomass.

The correlation coefficients (r^2) values obtained using the Lagergren model at all the initial concentrations examined were not acceptable, ranging from 0.873 to 0.975. Furthermore, the calculated q_e values for the first-order model did not give reasonable values, i.e. they were too low compared with experimental q_e values. The analysis of the results shows that the r^2 values obtained for the pseudo-second order kinetic model were very good. In addition to the high r^2 values of coefficient of correlation, a close agreement between experimental and estimated q_e values suggests that the sorption process followed a second-order mechanism. The theoretical q_e values for Cu(II) ions were also very close to the experimental q_e values. These observations suggest that metal sorption by xLVB follows second-order kinetics, and implies that the rate-limiting step is the chemical adsorption process between Cu(II) ions and xLVB. The pseudo-second order kinetic analysis reveals that the values of the rate constant decreases with an increase in the initial Cu(II) ion concentration. This indicates decreased competition for the sorption surface sites at lower concentrations while at higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. The experimental data fit very well to the Elovich kinetic model where the r^2 values (Table 1) were found to be closer to unity (0.918 to 0.994). The high value of the constant α implies that a chemisorption reaction takes place; increasing the initial metal ion concentration results in a reduction of the β-values (3.27 to 0.26 g mg^{-1}). Thus, $1/\beta$ (which is indicative of the number of sites available for adsorption) showed a distinct increase with an increase in metal ion concentration; again reinforcing the chemisorption hypothesis[24].

The intra-particle diffusion plots show multi-linearity indicating that the biosorption involves three processes. If the plot of q_t versus $t^{1/2}$ passes through the origin, the rate-limiting step is exclusively due to intra-particle diffusion[14,26]. If that is not the case, but it is very close, film diffusion as well as intra-particle diffusion needs to be taken into account. The first and second steps are more important than the final step for the adsorption of Cu(II) ions onto xLVB because the final stage is attributed to the final equilibrium for which the intra-particle diffusion starts to slow down due to extremely low biosorbate concentration left in solution. In the data in Table 1 it can be observed that the K_{id1} and K_{id2} increase with increasing initial concentration in the case of both first and second portions. This implies that the rate parameters for chemisorption and intra-particle diffusion increase with increasing Cu(II) ion concentration, probably due to a greater driving force with increasing C_0. Therefore, film diffusion and intra-particle diffusion are concurrently operating during the process of the adsorption of

Cu(II) ions onto xLVB and are enhanced by the increase in initial concentration. The correlation coefficient values for the intraparticle diffusion model are slightly lower than those of the pseudo-second order kinetic model.

Sorption isotherms. Adsorption isotherm studies provide information on the capacity of the adsorbent which is the most important parameter for an adsorption system. In order to determine an isotherm that best describes the experimental data, the Langmuir, Freundlich and Temkin models were analysed. The original equations are presented in detail in paper by Langmuir[27], Freundlich[28], Dash and Murthy[29] and Horsfall and Spiff[30].

Isotherm models for xLVB at different temperatures are shown in Table 2. The adsorption characteristic of Cu(II) ions on the functionalised xLVB follows the Langmuir isotherm model most closely. Values for K_L and q_{max} increase with increasing temperature from 10 to 40°C. The increase in the values of K_L with increasing temperature indicates that the Cu(II) ions are favourably adsorbed by xLVB at higher temperatures, which shows that the adsorption process is endothermic. High values of K_L indicate that there is a chemical interaction between the sorbent and the sorbate. The monolayer adsorption capacity q_{max} was 25.2 mg g^{-1} at the optimum pH of 5.0 and temperature of 20 ± 0.2°C. Correlation coefficients for the Langmuir model were determined in the range of 0.995–0.998 for all temperatures studied. Furthermore, the values of the dimensionless factor, $R_{L,}$ were between 0 and 1. This also suggests a favourable adsorption between xLVB and Cu(II) ions[21].

Values for the Freundlich constant, K_F, which is a measure of adsorption capacity and n, increase with increasing temperature from 10 to 40°C. The values of n obtained were between 1 and 10, which represent a favourable adsorption[31]. Correlation coefficients for the Freundlich model were in the range 0.599–0.682 for all temperatures studied and these values are much less analogous than for the Langmuir model.

Correlation coefficients for the Temkin model were in the range of 0.846–0.890 for all temperatures studied (Table 2). The Temkin adsorption potential, K_t, of xLVB biomass for Cu(II) ions is about 5.3 to 10.0, indicating a high biomass metal ion potential for Cu(II) ions; probably due to its large ionic radius. The Temkin constant, B, related to the heat of sorption for the Cu(II) ions was 0.7 kJ mol^{-1} indicating that interactions between the sorbate and sorbent are neither purely through ion-exchange, nor purely through physisorption.

Table 2. Equilibrium model parameters for the adsorption of Cu(II) ions onto xLVB at different temperatures

Sorption model	Parameter	Temperature (°C)			
		10	20	30	40
	r^2	0.998	0.998	0.997	0.995
Langmuir	K_L (dm^3 mg^{-1})	0.1224	0.1239	0.1265	0.1285
	q_{max} (mg g^{-1})	22.92	25.23	26.12	26.78
	r^2	0.682	0.599	0.621	0.671
Freundlich	K_F (dm^3 g^{-1})	4.5235	5.1448	5.5192	5.8127
	n	3.1702	3.2953	3.3854	3.4377
	r^2	0.884	0.846	0.862	0.890
Temkin	K_t	5.2838	6.6527	8.2705	10.004
	B (J mol^{-1})	750.44	734.53	762.99	794.74

Biosorption thermodynamics. Thermodynamic parameters such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$) can be estimated using equilibrium constant values as a function of temperature. The original equations are presented in details in papers by Ozer et al.[18] and Yao et al.[32].

The standards enthalpy and entropy changes are determined from the slope and intercept of the plot of ln K against $1/T$, respectively (Fig. 6).

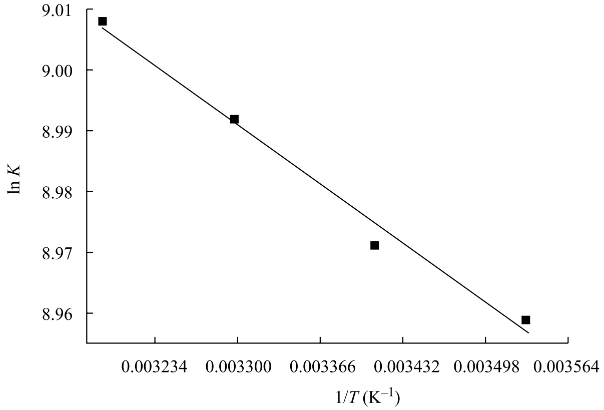


Fig. 6. ln K versus $1/T$ plot for Cu(II) ions adsorption on xLVB ($r^2 = 0.981$)

The $\Delta G°$ values were calculated to be –21.1, –21.9, –22.7 and –23.4 kJ mol^{-1} for Cu(II) ions biosorption at 10, 20, 30 and 40°C, respectively. The negative values of $\Delta G°$ indicate the feasibility of the process and indicate the spontaneous nature of the adsorption. $\Delta G°$ value is more negative with increasing temperature, which suggests that higher temperature makes the adsorption easier. The positive $\Delta H°$ (1.2 kJ mol^{-1}) indicates the endothermic nature of the biosorption processes. The positive value of $\Delta S°=78.8$ J mol^{-1} K^{-1} indicated the increased randomness at the sorbent-sorbate interface during the adsorption of Cu(II) ions by the xLVB.

Batch column system with recirculation of aqueous phase. The effect of flow rate on Cu(II) ion adsorption by xLVB was investigated and varied from 0.5 to 5.0 cm^3 min^{-1}. Figure 7 shows the effect of flow rate and indicates that the flow rate is strongly influenced by Cu(II) ion removal efficiency. The removal efficiency of xLVB significantly decreased from 91.3 to 80.4% with increased flow rate from 1 to 5.0 cm^3 min^{-1}.

Decreasing the removal efficiency of Cu(II) ions was relatively small with the increasing flow rate from 0.5 to 2.0 cm^3 min^{-1}. With a rate increase from 2.0 to 5.0 cm^3 min^{-1}, efficiency declines sharply. Based on this result, the optimum flow rate has a value of 2.0 cm^3 min^{-1}. At higher flow rates, the contact phase is reduced resulting in early breakthrough and less metal uptake. At lower flow rates a large amount of mixing or axial dispersion occurs and thereby increases the metal uptake.

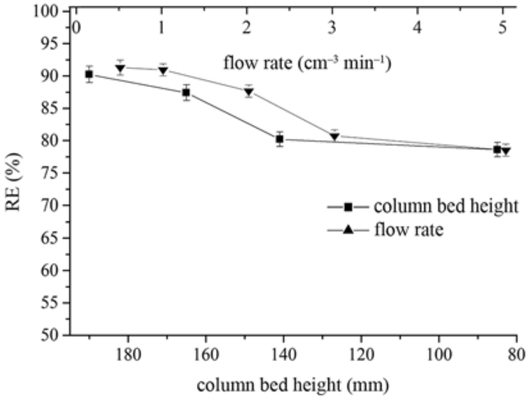


Fig. 7. Effect of flow rate of column and height of packed-bed column on biosorption of Cu(II) ions onto xLVB
$[Cu(II)]_0$ = 50.0 mg dm^{-3}; pH 5.0 ± 0.2; biosorbent dose – 4.0 g dm^{-3}, temperature 20.0 ± 0.2ºC

In this study, the height of packed-bed column was changed from 190 to 85 mm in order to evaluate the effect of height of packed-bed, i.e. column size on biosorption performance (Fig. 7). When the height of packed-bed was decreased from 190 to 85 mm, the biosorption yield decreased from 92.2 to 78.6%. As a result, the maximum loading capacity was observed at the lowest column i.d. (9 mm column i.d. that is packed-bed height of 190 mm) in this experiment. As the column i.d. decreased, height of packed-bed increased and the contact between the biosorbent and Cu(II) ions became better. In applied conditions, for the optimum height of packed-bed column for removal of Cu(II) ions on xLVB, can be recommended value of 165 mm. The probability of the contact of Cu(II) ions with the active centres of xLVB was increased at the biggest height of the packed-bed column. On the other hand, with increasing sorption length the hydraulic pressure increases, due to increased flow resistance through the column. In order to maintain a constant flow rate, which was done in this study, it was necessary to increase the pressure, which required the consumption of the energy.

CONCLUSIONS

In this study, the results show that the biosorption of Cu(II) ions onto xLVB is rapid, with equilibrium achieved after less than 40 min. The influence of solution pH on Cu(II) sorption showed that the process was most efficient at a pH of 5.0, and declines with decreasing pH. The highest sorption capacity of xLVB for the Cu(II) ions was obtained at a biosorbent dose of 4 g dm^{-3}. The equilibrium sorption data fitted to a Langmuir adsorption isotherm and the kinetics for the sorbent–sorbate interaction have been shown to fit a pseudo-second order model. The sorption efficacy increased when the solution temperature increased from 10 to 40°C, indicating that the sorption process is endothermic ($\Delta H°$ is positive). The positive values of $\Delta S°$ showed increased randomness at the solid/solution interface with some structural changes in the sorbate (hydrated metal ions) and biosorbent (xLVB). Possible mechanisms involved in the adsorption of Cu(II) onto the xLVB surface include ion-exchange and physisorption as supported by the effects of pH, FTIR and SEM-EDX analysis. It may be concluded from the reported observations that xLVB biosorbent has the potential to be used as an efficient, low-cost and easily available biosorbent for the removal of Cu(II) ions from wastewater.

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