Application of new biosorbent based on chemicaly modified *Lagenaria vulgaris* shell for the removal of copper(II) from aqueous solutions: Effects of operational parameters*

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Abstract

In the present study, a low cost biosorbent derived from the *Lagenaria vulgaris* plant by xanthation, was tested for its ability to remove copper from aqueous solution. The effect of contact time, initial pH, initial concentration of copper(II) ions and adsorbent dosage on the removal efficiency were studied in a batch process mode. The optimal pH for investigated metal was 5. A dosage of 4 g dm⁻³ of xanthated *Lagenaria vulgaris* biosorbent (xLVB) was found to be effective for maximum uptake of copper(II). The kinetic of sorption of metal was fast, reaching at equilibrium in 50 min. The kinetic data were found to follow closely the pseudo-second-order model. The adsorption capacity of 23.18 mg g⁻¹ copper(II) ions on xLVB. The presence of sulfur groups on xLVB was identified by FTIR spectroscopic study. Copper removal efficiency was achieved at 81.35% from copper plating industry wastewater.

Keywords: xanthated Lagenaria vulgaris, copper(II) ions, biosorption.

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Copper is widely used in electrical wiring, plumbing, gear wheel, selenium rectifier and roofing industries, due to its excellent properties such as electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation [1]. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paperboard mills, wood pulp production, and the fertilizer industry. Copper(II) is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment [2].

The conventional methods for removing copper(II) from aqueous solutions include precipitation, oxidation/reduction, electrochemical treatments, evaporative recovery, coagulation/flocculation, filtration methods, ion-exchange and membrane technologies. These processes may have different limitations: high cost, process complexity and sludge formation, or may be ineffective, especially when the metals in solution are in range of 1-100 mg dm⁻³ [3–5]. Biosorption processes are being employed as an attractive alternative SCIENTIFIC PAPER

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technique for the decontamination of industrial effluents and for the recovery of the retained metals [6]. The major advantages of biosorption over conventional methods include low cost, high efficiency, minimization of chemical or biological sludge and possibility of bio– sorbent regeneration [7]. A low cost sorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry [8]. Recently, Bailey *et al.* [9] reviewed a wide variety of low cost sorbents for the removal of heavy metals.

Among the adsorbents used to remove heavy metals, those containing sulfur-bearing groups have a high affinity for heavy metals but low affinity for light metals. From the different sulfur bearing compounds, xanthates are found to be the most prominent because they are easy to prepare with relatively inexpensive reagents, highly insoluble and have high stability constants of metal complex formed according to HSAB classification system. *Lagenaria vulgaris* biosorbent is mostly composed of cellulose and lignin. These components contain many hydroxyl functional groups, which makes it a potential matrix to synthesize xanthate [10–12].

The objective of this research was to investigate the copper removal efficiency of xanthated *L. vulgaris* biosorbent (xLVB) by adsorption from aqueous media. The effect of contact time, initial pH, initial concentration of copper(II) ions and adsorbent dosage were examined. Batch experiments were carried out to investigate the

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adsorption kinetics and isotherms of Cu(II) ions adsorption onto xLVB from aqueous solutions.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade and were used without further refinement. HNO₃, NaOH, CS₂, Cu(NO₃)₂ were purchased from Merck (Germany). All solutions were prepared with deionized water. Standard metal stock solution was prepared by dissolving given amounts of analytical grade Cu(NO₃)₂. All standard solutions were stored in a refrigerator at 4 °C.

Preparation of xanthated biosorbent

Lagenaria vulgaris is a creeping, hardy plant. It belongs to the Cucurbitaceae family. The outer shell is recognized to be hard and ligneous covering the spongy white pith characterized by bitter taste [13]. The experiments in this study have been carried out using a shell of *L. vulgaris*, grown in the south area of Serbia (near the town of Niš) at about 200 m altitude. Plants were grown under controlled conditions with irrigation and without fertilization, planted at the same time in mid-April and harvested in the mid-October, also all at the same time.

L. vulgaris shell was roughly crushed, washed with deionized water and grounded by laboratory mill. Biomass was soaked in 0.3 M HNO₃ for 24 h to remove metals bio-accumulated in the plant during growing. After that, biomass was washed with deionized water to remove excess acid and treated with 0.1 M NaOH in period of 30 min. Excess alkali was removed by thoroughly washing and sorbent was dried in the oven at 55 ± 5 °C to constant weight. Dried biomass was fractionised using standard sieves (Endecotts, England). The prepared adsorbent was abbreviated as basic *L. vulgaris* biosorbent (LVB) hereafter for convenience.

Xanthation was carried out by following procedure: LVB, with granulation from 0.8 to 1.25 mm, was soaked in 4 M NaOH and stirred for 3 h and another 3 h after adding CS₂. Xanthated material was allowed to settle for 1 h and separated by decantation and filtration. After that, the biomass was washed with deionized water. Xanthated *L. vulgaris* biosorbent (xLVB) prepared on this way was additionally washed in two times with acetone and dried at room temperature. As a result, xLVB was prepared for removing heavy metals from aqueous solutions.

Batch biosorption experiments

The stock solution of Cu(II) was prepared in 1.00 g dm^{-3} concentration using Cu(NO₃)₂ and working standard solutions were prepared just before use by the appropriate dilution of the stock solutions. The pH of

each solution was adjusted to the required value with 0.1/0.01 mol dm⁻³ NaOH/HNO₃ solutions pH-metrically (Senslon5, HACH, USA), before biosorption treatment.

Studies on the adsorption of metal ions by xLVB were carried out in batch conditions, by agitating 250 cm³ of 50.0 mg dm⁻³ metal ion solutions of Cu(II), contacted with 1.00 g biosorbent. A parallel experiment was a blank system, a treatment of the same solution without biosorbent. We used the blank system for testing the loss of metal on glass dishes. At required time intervals, 4.0 cm³ of samples were withdrawn and analyzed using a flame atomic adsorption spectrometer AAnalyst 300 (Perkin Elmer, USA). The amount of metal adsorbed q_t (mg g⁻¹) was determined by using the following equation:

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

where c_0 and c_t are the initial and final concentrations of the metal ion in solution (mg dm⁻³), V is the solution volume (dm³) and m is the mass of the sorbent (g).

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

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

RESULTS AND DISCUSSION

Contact time effect

The effect of contact time on the removal efficiency of Cu(II) ions by xanthated *Lagenaria vulgaris* biosorbent (xLVB), was investigated in time intervals 0, 1, 5, 10, 20, 40, 60, 90, 120 and 240 min.

Typical biosorption kinetics exhibit a rapid initial uptake, followed by a slower process. The experimental results show that maximum adsorption efficiency was observed in the first 20 min of sorbent-sorbate contact, when removal of Cu(II) ions was 81.92%. The sorption equilibrium was attained after about 50 min of contact time, when 97.92% of total Cu(II) ions were removed. The initial concentration of Cu(II) ions decreased from 50.0 to level of 1.04 mg dm⁻³ when equilibrium was attained. To the end of the treatment, changes of metal concentrations in the solution are negligible. It can be seen that after 240 min of treatment, 98.92% of total Cu(II) ions were removed from aqueous solution (Figure 1).

The effect of contact time on the adsorption of Cu(II) by unmodified *L. vulgaris* biosorbent indicated that initial concentration of metal ions decreases from 50.0 to 29.38 mg dm⁻³ after 50 min of contact time when equilibrium was attained. It can be seen that xLVB gave significantly better removal efficiency than unmodified biosorbent: 98.92 with regard to 62.59%.



Figure 1. Removal of Cu(II) ions from aqueous solutions by xLVB. Initial pH: 5, [Cu(II)]₀ = 50.0 mg dm³, sorbent dose: 4.0 g dm³, temperature: 25.0±0.5 °C.

Effect of pH

Generally, the pH of solution is recognized as a very important parameter that governs the adsorption process. It was established that pH affected the surface change of the adsorbent. The influence of initial pH on the removal of Cu(II) ions from aqueous solution was investigated at five different initial pH values: 2, 3, 4, 5 and 6. An increase in the solution pH from 2 to 5 led to an increase of removal efficiency for the adsorption of Cu(II) ions (Figure 2), and then slightly decreases at pH 6. Values for removal efficiency at pH 6 (results not shown) were obtained by subtraction change of Cu(II) concentration in the blank from residual concentration in biosorption treatment. At pH value 5, removal efficiency achieved maximum values (98.92%). When the pH decreased, concentrations of protons increased and competition in binding the active sites on the surface of biosorbent, between the H^+ and metal ions, started. Protonated active sites were incapable of binding the bind metal ions, leading to free ions remaining in the solution.

With the increase of pH, the overall surface on xLVB became negative and adsorption was increased. The competing effect of hydronium ions decreased and the positively charged metal ions took up the free binding sites. Dominant species of copper in the pH range 3–5 are Cu^{2^+} and $CuOH^+$, while the copper at above 6.3 occurs as insoluble $Cu(OH)_{2(s)}$ [14–16]. Above pH 6, insoluble copper hydroxide starts precipitating from the solution [17]. For these reasons, further metal sorption studies were carried out at pH 5, which is well below the pH level where Cu(II) ions are precipitated.

During the adsorption process on xLVB, the equilibrium pH values increased because the buffer solution is not used in any experimental solutions (Figure 3). This phenomenon can probably be explained by releasing OH^- from $CuOH^+$ at pH between 5 and 6 [15]. In addition, Na^+ were also released into the solution according to ion exchange, then combined with OH^- to form alkali, which strengthened the alkalinity of the solutions [11].

Effect of initial Cu(II) concentration

Biosorption of metals by any biosorbent is highly dependent on the initial concentration of metal ions [18]. The effect of concentration on sorption of Cu(II) was investigated with initial Cu(II) concentrations of 10, 20, 50, 100, 200 and 400 mg dm⁻³. The experiments



Figure 2. Effect of initial pH on the removal efficiency of Cu(II) ions from aqueous solutions by xLVB. [Cu(II)]₀ = 50.0 mg dm⁻³, sorbent dose: 4.0 g dm⁻³, temperature: 25.0±0.5 °C.



Figure 3. A plot of pH_{initial} and pH_{equilibrium}; [Cu(II)]₀ = 50.0 mg dm³, sorbent dose: 4.0 g dm³, temperature: 25.0±0.5 °C.

were performed by adding 250 cm³ solution of each concentration to six different 250 mL flasks each containing 1.0 g of biosorbent. The results are shown in Figure 4. When the initial metal ions concentration was increased from 10 to 400 mg dm⁻³, at pH 5, the loading capacity of adsorbent increased from 2.59 to 23.18 mg of Cu(II) per gram of xLVB (Figure 4). Examination of this parameter is important because wastewater from various processes such as electroplating processes contains metal ions in a wide range of concentrations [19,20].



Figure 4. Effect of initial metal concentration on the removal efficiency of Cu(II) ions from aqueous solutions by xLVB. Initial pH: 5, sorbent dose: 4.0 g dm⁻³, temperature: 25.0±0.5 °C.

Effect of adsorbent dosage

For the assessment of adsorbent dosage of the adsorption, 50.0 mg dm⁻³ Cu(II) solutions were stirred for 240 min with different amounts of xLVB (0.5, 1, 2, 4

and 8 g dm⁻³). The results of experiments with varying biosorbent concentration are presented in Figure 5. With an increase in biosorbent concentration from 0.5 to 8 g dm⁻³, the percentage of biosorbed Cu(II) removal increased from 12.74 to 98.98% as the number of possible binding sites is increased. It is obvious that the removal efficiency is not increased considerably when biosorbent concentrations are higher than 4.0 g dm⁻³. Thus, the optimum dosage of xLVB for biosorption of Cu(II) ions was found to be 4.0 g dm⁻³.

Kinetic study

One of the most important features of the biosorbent is the rate at which the solid phase adsorbs metal ions from the aqueous solutions and attains equilibrium. In our case, two different kinetic models were applied in order to establish which of them shows the best fit with experimental results. All kinetic data for the adsorption of Cu(II) ions onto xLVB are reported in Table 1. Comparison of the r^2 values for different models suggested that metal sorption by xLVB followed the pseudo-second-order reaction.

It can be seen from Figure 6 that the adsorption of Cu(II) on xLVB at an initial metal ion concentration of 50.0 mg dm⁻³ can attain equilibrium within 50 min. The fast adsorption rate reflect good accessibility of the binding sites of xLVB to Cu(II) ions. Data were modeled using pseudo-second-order model, which assumes that the rate is proportional to the square of the number of remaining free surface sites [21].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(3)

The plot of t/q_t versus t (Figure 6) is a straight line where the slope and intercept are respectively $1/q_e$ and $1/(k_2q_e^2)$. The rate constant, k_2 , and the equilibrium sorption capacity, q_e , are calculated from these para-



Figure 5. Effect of sorbent dosage on the removal efficiency of Cu(II) ions from aqueous solutions by xLVB. Initial pH: 5, $[Cu(II)]_0 = 50.0 \text{ mg dm}^3$, temperature: $25.0\pm0.5 \text{ °C}$.

meters [22]. Obviously, the biosorption process could be well described by the pseudo-second-order equation, indicating the process mechanism to be chemical adsorption.

Sorption isotherms

Sorption equilibrium can be described by a number of models available in the literature. In this study, the equilibrium data obtained for the adsorption of Cu(II) ions were analyzed by considering the Langmuir, Freundlich and Temkin isotherm models. The isotherm parameters for the adsorption of Cu(II) ions onto xLVB are given in Table 2. The Langmuir adsorption model provides the best fit with experimentally obtained data ($r^2 = 0.9984$, Figure 7).

The linear form of Langmuir isotherm equation is given as:

$$\frac{c_{\rm e}}{q_{\rm e}} = \frac{c_{\rm e}}{q_{\rm max}} + \frac{1}{q_{\rm max}K_{\rm L}}$$
(4)

where $q_e \text{ (mg g}^{-1}\text{)}$ is the amount of metal removed per gram of sorbent, $q_{\text{max}} \text{ (mg g}^{-1}\text{)}$ is the maximum sorption capacity, $c_e \text{ (mg dm}^{-3}\text{)}$ is concentration in the equilib-

rium solution, and $K_{\rm L}$ (mg dm⁻³) is the Langmuir constant related to the adsorption energy [22–24]. The biosorption followed the Langmuir isotherm model with the maximum biosorption capacity of 23.18 mg g⁻¹.



Figure 6. Pseudo-second-order kinetic model of adsorption Cu(II) ions onto xLVB. Initial pH: 5, [Cu(II)]₀ = 50.0 mg dm⁻³, sorbent dose: 4.0 g dm³, temperature: 25.0±0.5 °C.

Table 1. Kinetic model parameters for adsorption of Cu(II) onto xLVB

Kinetic model	Parameter	Value	
Pseudo-first-order	k_1 / g mg ⁻¹ min ⁻¹	0.0576	
	r^2	0.9452	
	$q_{\rm e}$ / mg g ⁻¹ (exp)	11.7375	
	$q_{\rm e}$ / mg g ⁻¹ (calculated)	6.2361	
Pseudo-second-order	k_2 / g mg ⁻¹ min ⁻¹	0.0306	
	r^2	0.9991	
	$q_{\rm e}$ / mg g ⁻¹ (exp)	11.7375	
	$q_{ m e}$ / mg g ⁻¹ (calculated)	12.0700	

Equilibrium model	Parameter	Value
Langmuir isotherm	$K_{\rm L}$ / dm ³ mg ⁻¹	0.2886
	$q_{\rm max}$ / mg g ⁻¹	23.175
	r ²	0.9984
Freundlich isotherm	$K_{\rm F}$ / dm ³ g ⁻¹	6.839
	п	4.066
	r ²	0.8310
Temkin isotherm	K _t	1.0036
	$b_{\rm T}$ / kJ mol ⁻¹	0.9599
	r ²	0.9643

Table 2. Equilibrium model parameters for adsorption of Cu(II) onto xLVB



Figure 7. Langmuir isotherm for Cu(II) adsorption onto xLVB. Initial pH: 5, [Cu(II)]₀ = 50.0 mg dm³, sorbent dose: 4.0 g dm³, temperature: 25.0±0.5 °C.

Analysis of Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of xLVB is shown in Figure 8. In xLVB spectrum, the broad and intense absorption peaks at around 3414.9 $\rm cm^{-1}$ correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in cellulose and lignin [25]. The peaks at 2922.1 cm⁻¹ are attributed to the symmetric and asymmetric C-H stretching vibration of aliphatic acids [26]. The peaks at 1654.0 and 1458.8 cm^{-1} are due to asymmetric and symmetric stretching vibration of C=O in ionic carboxylic groups (-COO⁻), respectively. Aliphatic acid group vibration at 1267.8 cm⁻¹ may be assigned to deformation vibration of C=O and stretching formation of -OH of carboxylic acids and phenols [27]. The broad peak is at 3414.9 cm⁻¹ in the xLVB, which indicates that the hydroxyl groups have com-



Figure 8. FTIR Spectrum of xLVB.

bined with CS₂. The presence of sulfur groups in the xLVB has been identified by the appearance of peaks at 533.5, 1025.7 and 1158.9 cm⁻¹ corresponding to ν_{c-s} , ν_{c-s} and ν_{s-c-s} [11].

Testing under copper plating industry effluent condition

In recent years, the production of metal-containing waste has been continuously increasing. The level of copper in electroplating effluent is from less 100 to almost 1000 mg dm⁻³ while pH ranged from 2.5 to 5.0 [19,28]. The Environmental Protection Agency (EPA) sets a limit of 1.3 mg dm⁻³ of copper in drinking water and the allowed industrial discharges level of copper should not exceed 1 mg dm⁻³, otherwise the water has a metallic taste [29]. Therefore, the concentration of this metal must be reduced to the level that satisfies environmental regulations for various bodies of water.

The applicability of the xanthated *L. vulgaris* biosorbent (xLVB) was demonstrated by removing Cu(II) from copper plating industry wastewater. The metal content of copper plating industry effluent is shown in Table 3. For preparing a model effluent, copper plating industry wastewater was diluted to have a new solution with 50.0 mg dm⁻³ of copper. To determine the dependence of metal sorption on time, 1.0 g of xLVB was exposed to a 250 cm³ model effluent with initial pH 5.0. Despite the presence of competitive effect of cadmium, chromium, zinc and nickel metal ions, about 81.35% reduction in Cu(II) concentration was achieved as a result of treatment with developed adsorbent. It was observed that the copper removal efficiency decreased by 17.57% comparing to a single metal solution of copper.

Table 3.	The metal	content of	copper	plating	industry	effluent
						-3

Metal ion	Concentration, mg dm^{-3}	
Cu(II)	380.0	
Cd(II)	6.0	
Cr(VI)	41.0	
Zn(II)	130.0	
Ni(II)	116.0	
Na ⁺	600.0	
K ⁺	18.0	
Ca ²⁺	16.0	
рН	3.8	

CONCLUSION

Xanthated Lagenaria vulgaris biosorbent (xLVB) was employed as an adsorbent for removal of Cu(II) ions from aqueous solution. The maximum biosorption capacity of biosorbent for the removal of Cu(II) was obtained at pH 5. The loading capacity of xLVB increased from 2.59 to 23.18 mg of Cu(II) per gram of xLVB, as the initial concentration of Cu(II) ions increased from 10 to 400 mmol dm⁻³. The optimum adsorbent dosage was established to be 4 g dm⁻³. Kinetics experiments proved that the biosorption process was rapid with equilibrium attained within 50 min. The kinetics of the process were best described using the pseudo-second order model. The Langmuir adsorption model was used to represent the experimental data and equilibrium data fitted very well to the Langmuir isotherm model ($r^2 = 0.9984$). FTIR Spectra confirm the presence of sulphur groups on the *L. vulgaris* xanthate. Batch studies with 81.35% copper removals from a copper plating industry effluent wastewater revealed the practical utility of the developed biosorbent.

The obtained results and their comparison to various biosorbents reported in the literature showed that xanthated *L. vulgaris* biosorbent (xLVB) was an efficient biosorbent for Cu(II) ions.

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REFERENCES

- Z. Aksu, L.A. Isoglu, Removal of copper(II) ions from aqueous solution onto agricultural waste sugar beet pulp, Process Biochem. 40 (2005) 3031–3044.
- [2] G. DÖnmez, Z. Aksu, The effect of copper(II) ions on the growth and bioaccumulation properties of some yeasts, Process Biochem. **35** (1999) 135–142.
- [3] A. Witek-Krowiak, R.G. Szafran, S. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desalination 265 (2011) 126–134.
- [4] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. 162 (2009) 616–645.
- [5] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.
- [6] B. Volesky, Sorption and Biosorption, BV Sorbex, Inc., Montreal – St. Lambert, Quebec, Canada, 2003.
- [7] M. Zhao, J.R. Duncan, R.P. van Hille, Removal and recovery of zinc from solution and electroplating effluent using *Ayolla filiculoides*, Water Res. **33 (6)** (1999) 1516– –1522.
- [8] K.S. Low, C.K. Lee, S.C Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, Process Biochem. 36 (2000) 59–64.
- [9] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water. Res. 33 (1999) 2469–2479.

- [10] A. Kumar, N.N. Rao, S.N. Kaul, Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal – preparation, characterization and application, Bioresour. Technol. **71** (2000) 133–142.
- [11] G.C. Panda, S.K. Das, A.K. Guha, Biosorption of cadmium and nickel by functionalized husk of *Lathyrus sativus*, Colloids Surfaces, B 62 (2008) 173–179.
- [12] S. Liang, X. Guo, N. Feng, Q. Tian, Application of orange peel xanthate for the adsorption of Pb²⁺ from aqueous solution, J. Hazard. Mater. **170** (2009) 425–429.
- [13] D-L. Mitić-Stojanović, A. Zarubica, M. Purenovic, D. Bojic, T. Andjelkovic, A. Bojic, Biosorptive removal of Pb²⁺, Cd²⁺ and Zn²⁺ ions from water by Lagenaria vulgaris shell, Water SA **37**(3) (2011) 303–312.
- [14] E. Demirbasa, N. Dizgeb, M.T. Sulakb, M. Kobyab, Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, Chem. Eng. J. 148 (2009) 480–487.
- [15] H.A. Eliot, C.P. Huang, Adsorption characteristic of some Cu(II) complexes on aluminosilicates, Water Res. 15 (1981) 849–855.
- [16] M. Asmal, A.H. Khan, S. Ahmad, A. Ahmad, Cole of sawdust in the removal of copper(II) from industrial waters, Water Res. 32 (1998) 3085–3091.
- [17] T. Mathialagon, T. Viraraghavan, Adsorption of cadmium from aqueous solution by perlite, J. Hazard. Mater., B 94 (2002) 291–303.
- [18] N. Ahalya, R.D. Kanamacdi, T.V. Ramachandra, Biosorption of chromium(VI) from aqueous solution by the husk of Bengal gram (*Cicer arientinum*), Eur. J. Biotechnol. 8 (2005) 258–264.
- [19] C. Peng, Y. Liu, J. Bi, H. Xu, A-S. Ahmed, Recovery of copper and water from copper electroplating wastewater by the combination process of electrolysis and electrodialysis, J. Hazard. Mater. 189 (2011) 814–820.
- [20] M. Kul, Ü. Çetinkaya, Recovery of copper by LIX 984N-C from electroplating rinse bath solution, Hydrometallurgy 98 (2009) 86–91.

- [21] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Can. J. Chem. Eng. 76 (1998) 822–827.
- [22] A. Aziz, M.S. Ouali, E.H. Elandaloussi, L.C. De Menorval, M. Lindheimer, Chemically modified olive stone: A lowcost sorbent for heavy metals and basic dyes removal from aqueous solutions, J. Hazard. Mater. **163** (2009) 441–447.
- [23] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon preparedby chemical activation, J. Hazard. Mater. 165 (2009) 1029–1039.
- [24] M. Iqbal, A. Saeed, S. I. Zafar, FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd²⁺ and Pb²⁺ removal by mango peel waste, J. Hazard. Mater. **164** (2009) 161–171.
- [25] R. Gnanasambandam, A. Protor, Determination of pectin degree of esterification by diffuse reflectance Fourier transform infrared spectroscopy, Food Chem. 68 (2000) 327–332.
- [26] [26] F.T. Li, H. Yang, Y. Zhao, R. Xu, Novel modification pectin for heavy metal adsorption, Chin. Chem. Lett. 18 (2007) 325–328.
- [27] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies, Env. Sci. Technol. 36 (2002) 2067–2073.
- [28] F.J. Cerino-Córdova, A.M. García-León, E. Soto-Regalado, M.N. Sánchez-González, T. Lozano-Ramírez, B.C. García-Avalos, J.A. Loredo-Medrano, Experimental design for the optimization of copper biosorption from aqueous solution by Aspergillus terreus, J. Environ. Manage. 95 (2012) S77–S82.
- [29] H. Harmita, K.G. Karthikeyan, X.J. Pan, Copper and cadmium sorption onto kraft and organosolv lignins, Bioresour. Technol. **100**(24) (2009) 6183–6191.

IZVOD

PRIMENA NOVOG BIOSORBENTA NA BAZI HEMIJSKI MODIFIKOVANE KORE *Lagenaria vulgaris* ZA UKLANJANJE BAKRA(II) IZ VODENIH RASTVORA: UTICAJ PARAMETARA PROCESA

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Kora biljke Lagenaria vulgaris korišćena je za dobijanje novog biosorbenta procesom ksantovanja u alkalnoj sredini. Dobijeni ksantovani materijal primenjen je kao adsorbent za uklanjanje jona bakra iz vodenih rastvora. Ispitivan je uticaj kontaktnog vremena, pH, inicijalne koncentracije bakra(II) i količine adsorbensa na efikasnost procesa uklanjanja metala. Pokazano je da sorpcioni proces dostiže ravnotežu za 50 min, a najveća vrednost sorpcionog kapaciteta (23,18 mg g^{-1}) postignuta je pri početnoj vrednosti pH rastvora 5. Sa povećanjem početne koncentracije metalnog jona od 10 do 400 mg dm⁻³ raste i količina metala adsorbovanog po gramu sorbenta. Rezultati ispitivanja uticaja količine sorbenta na efikasnost uklanjanja bakra(II) pokazuju da je optimalna količina sorbenta 4 g dm⁻³. Kinetika adsorpcije se najbolje opisuje modelom pseudo-drugog reda, dok je najbolje slaganje eksperimentalnih rezultata dobijeno sa Langmuir-ovom adsorpcionom izotermom. Funkcionalne grupe na površini ksantovanog biosorbenta su ispitivane FTIR metodom. Ksantovani L. vulgaris biosorbent može se primeniti za uklanjanje bakra iz otpadnih voda industrija prevlaka bakra sa efikasnošću od 81,35%.

Ključne reči: Ksantovani *Lagenaria vulgaris* • Bakar(II) joni • Biosorpcija