

## **Removal Cu(II) ions from water using sulphuric acid treated *Lagenaria vulgaris* Shell (Cucurbitaceae)**

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### **Abstract:**

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Removal of Cu(II) ions from water solutions by sulphuric acid treated *Lagenaria vulgaris* shell (ccLVB) was studied. Batch experiments were done by shaking a fixed mass of biosorbent (1.0 g) with 250 cm<sup>3</sup> of 50.0 mg dm<sup>-3</sup> Cu(II) solutions, at pH ranged from 2 up to 6. Metal concentration in the filtrates as well as in the initial solution was determined by flame atomic absorption spectrometry. Results show that efficiency of Cu(II) ions uptake by sulphuric acid treated *Lagenaria vulgaris* shell is significantly greater than raw *Lagenaria vulgaris* biosorbent. In addition, there is no significant effect of initial pH of solution on Cu(II) ions uptake by ccLVB and obtained biosorbent can be applied in a wide range of pH.

**Key words:** Biosorption, *Lagenaria vulgaris*, Cu(II), pH, kinetics

## **Introduction**

Rapid industrialization throughout the world has generated huge volumes of wastes containing toxic materials, such as heavy metals, dyes, phenols and surfactants. The presence of heavy metals in wastewaters and surface waters is major concern of the public health and the environment. The increased use of metals and chemicals in the industrial processes have resulted in the generation of large quantities of aqueous effluents that contain high levels of metals, creating serious environmental disposal problems (Yu et al., 2000).

The main sources of copper pollution are metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, etc. (Dundar et al., 2009). Copper usually occurs in nature as oxides and sulfides. In acidic environments, a free aqueous Cu<sup>2+</sup> ion dominates. At pH 6–8, the predominant species are Cu<sup>2+</sup>,

Cu(OH)<sub>2</sub>, CuHCO<sub>3</sub><sup>+</sup>, CuCO<sub>3</sub> and CuOH<sup>+</sup>, while at pH > 10 the major species are Cu(OH)<sub>3</sub><sup>-</sup> and Cu(OH)<sub>4</sub><sup>2-</sup>. Copper may be found as a contaminant in food, especially shell- fish, liver, mushroom, nuts and chocolate. Copper is essential to human life and health, but in large amount it is toxic as well. Excess copper in the human body can cause stomach and intestinal distress such as nausea, vomiting, diarrhea and stomach cramps (Nuhoglu et al., 2002).

Various methods have been used to remove heavy metals from wastewater, such as reduction and precipitation, coagulation, flotation, adsorption on activated carbon, ion exchange, reverse osmosis and electrodialysis (Dang et al., 2009). Some of these processes are expensive, or have other disadvantages, such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, dependence of metal concentration in wastewater, and production of toxic

sludge or other waste products that also need disposal (Antunes et al., 2003).

In recent years, biosorption has been suggested as cheaper as and more effective than many chemical or physico-chemical technologies. (Krishnani et al., 2008) Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Ucun et al., 2002).

Various biomasses are used as potential sorbents, such as fungi, bacteria, algae, agricultural waste and waste from food industries, wood sawdust and bark, in their natural form or in chemically or physically modified form (Basso et al., 2002). Lignocellulosic fiber is an unconventional low-cost sorbent that has been examined for potential use in removing heavy metals. However, the ion exchange or adsorption capacity of lignocellulosic fiber is lower than that of other sorbents. As a result, attempts have been made to modify various lignocellulosic fibers with different chemicals (Min et al., 2004).

In this study, *Lagenaria vulgaris* was used as a potential biosorbent for removal of Cu(II) ions from water. Biosorbent was prepared by sulphuric acid treatment of plant shell to improve sorption characteristics.

## Materials and methods

### Preparation of biosorbent

*Lagenaria vulgaris* (Cucurbitaceae family) is a creeping, hardy plant. It is found growing mainly on alluvial sandy soil and red loam, on flat areas and moderate slopes, and in higher-lying areas, and needs light and warmth. The outer shell is hard and ligneous, covering the spongy white pith characterized by its bitter taste. The experiments in this study were carried out using the shell of *Lagenaria vulgaris* grown in the southeastern area of Serbia without irrigation and fertilization, at an altitude of 200 m.

Raw *Lagenaria vulgaris* shell was air dried, washed with distilled water and grounded. Grounded biomass was rinsed with 0.3 M HNO<sub>3</sub> for a 24 h. Acid treated material was washed with a deionised water to remove excess of acid and stirred on a magnetic stirrer with 0.1 M NaOH for a 30 min. Neutralized biomass was washed with deionized water and dried in a oven on 55±5°C. Obtained biosorbent was fractionized using standard sieves (Endecott, England) and particles with size from 0.8 up to 1.25 mm are used in this study. This

material is designated as aLVB (Mitic-Stojanovic et al., 2011).

Prepared biosorbent was soaked with concentrated sulphuric acid for a 2 h. Temperature of mixture was held on 40°C. After treatment, obtained black powder was washed with deionised water, and 0.1 M NaOH was added in small portions until pH reached 7-7.5. Then, biomass was washed with deionized water, filtered and dried in an oven on 55±5°C. Result of this process is the most similar to thermal carbonization, and we call it „cold carbonization“. Obtained material is designated ccLVB.

### Batch experiments

The batch experiments are conducted by stirring a fixed mass of biosorbent (1.0 g) with 250 cm<sup>3</sup> of 50.0 mg dm<sup>-3</sup> Cu(II) into glass beaker. The initial pH of solutions was adjusted using HNO<sub>3</sub> or NaOH (0.01, 0.1M) in range from 2 up to 6. The mixture was agitated for 240 min to reach equilibrium state and filtered through filter paper (Wathman No2). Samples (5 cm<sup>3</sup>) were taken at the beginning (before adding the sorbent) and at predetermined time intervals (1, 2, 5, 10, 20, 40, 60, 90, 120 and 240 min) for the residual Cu(II) ion concentration in the solution. To preserve aliquots, 0.1 ml of concentrated HNO<sub>3</sub> was added. Metal concentration in the filtrates as well as in the initial solution was determined by flame atomic absorption spectroscopy (Model AAnalyst 300, Perkin Elmer, USA).

### Determine of pH<sub>pzc</sub>

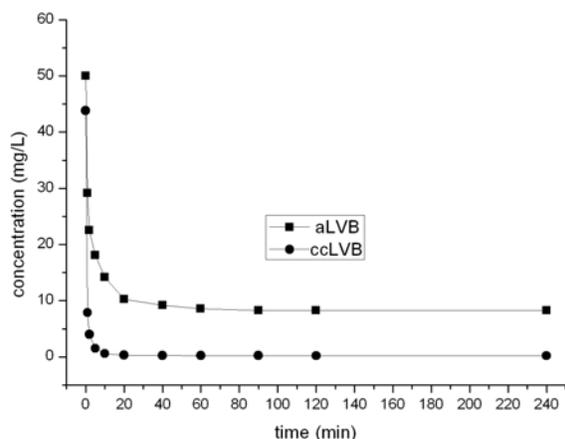
Point of zero charge was determined by pH drift method (Yang et al., 2004; Aziz et al., 2009) with some modifications for LVB. As inert electrolyte was used 0.01M KNO<sub>3</sub>. The pH of test solutions were adjusted in range between 2 and 10 using 0.01M HNO<sub>3</sub> and 0.01 M KOH. A 0.2 g of biosorbents were added to 50 ml of test solutions into stopped glass tubes and equilibrated for 24 h. The final pH (pH<sub>f</sub>) was measured after 24 h and plotted against the initial pH (pH<sub>i</sub>). The pH at which the curve crosses line pH<sub>i</sub> = pH<sub>f</sub> was taken as pH<sub>pzc</sub>. pH was measured by SensIon3 (Hach, USA), which was calibrated before every measure.

## Results and discussion

### Effect of contact time

To determine the effect of contact time on copper biosorption, 250 ml of Cu(II) ions solution, concentration 50.0 mg dm<sup>-3</sup>, was treated with 1.0 g of *L. vulgaris* shell biomass at 25±0.5°C and initial

pH 5.0. The residual concentration of Cu(II) ions was determined after 1, 2, 5, 10, 20, 40, 60, 90, 120 and 240 min. Results are shown on **Figure 1**.



**Figure 1.** Effect of contact time on Cu(II) ions biosorption removal ( $c_{\text{Cu(II)}} = 50 \text{ mg dm}^{-3}$ ,  $\text{pH}_i = 5.0$ ,  $c_{\text{LVB}} = 4.0 \text{ g dm}^{-3}$ ,  $T = 25 \pm 0.5^\circ\text{C}$ )

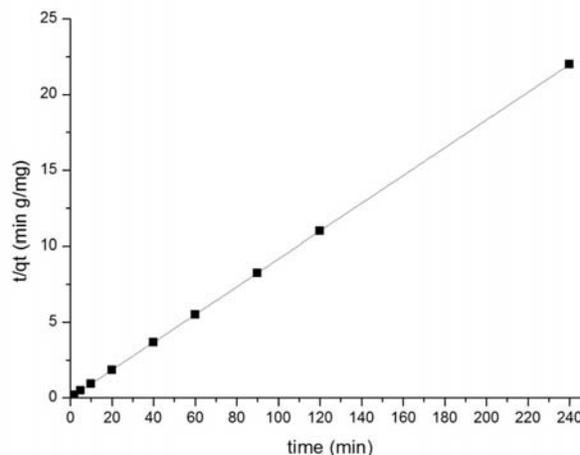
Results show that sorption of copper ions onto the biosorbents was very fast, as the equilibrium state was reached in less than 10 min for ccLVB. At the end of the treatment, after 240 min of contact time, Cu(II) ions removal efficiency is near 100% for ccLVB. Sulphuric acid treatment improves sorption characteristics of *L. vulgaris* shell biomass, because unmodified biosorbent reaches equilibrium within about 30 min with removal efficiency near 90% at the end of treatment (240 min).

Pseudo-second order model was used to describe the kinetics of adsorption of Cu(II) onto ccLVB. The kinetic data were analyzed using linear form of pseudo-second order relation (Ho and McKay, 1999):

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

where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are amounts of Cu(II) ions adsorbed on ccLVB at time  $t$  and at equilibrium, and

$k_2$  ( $\text{min g mg}^{-1}$ ) is the rate constant of process. As can be seen from Figure 2 and Table 1, straight line with correlation coefficient 0.999 show that kinetics of adsorption of Cu(II) on ccLVB can be good fitted by pseudo-second order kinetic model. Kinetic data for aLVB are also good fitted by pseudo-second order kinetic model. In accordance with the pseudo-second order mechanism, the rate of Cu(II) sorption process appear to be controlled by chemical process or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.



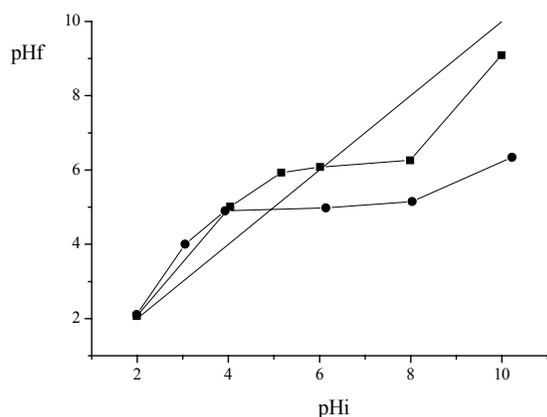
**Figure 2.** Pseudo-second order kinetic model for Cu(II) ions sorption on ccLVB ( $c_{\text{Cu(II)}} = 50 \text{ mg dm}^{-3}$ ,  $\text{pH}_i = 5.0$ ,  $c_{\text{LVB}} = 4.0 \text{ g dm}^{-3}$ ,  $T = 25 \pm 0.5^\circ\text{C}$ )

#### Point of zero charge

The pH at which the sorbent surface charge takes a zero value is defined as point of zero charge ( $\text{pH}_{\text{pzc}}$ ). At this pH, the charge of the positive surface sites is equal to that of the negative ones. At pH values of solution higher than  $\text{pH}_{\text{pzc}}$ , sorbent surface is negatively charged and could better interact with metal positive species while at pH values lower than  $\text{pH}_{\text{pzc}}$ , solid surface is positively charged and could interact with negative species.

**Table 1.** Pseudo-second order kinetic model parameters for Cu(II) ions sorption process on ccLVB

Material	$C_0$ ( $\text{mg dm}^{-3}$ )	$k$ ( $\text{min g mg}^{-1}$ )	$q_{e,exp}$ ( $\text{mg g}^{-1}$ )	$q_{e,cal}$ ( $\text{mg g}^{-1}$ )	$R^2$
ccLVB	50	0.8102	10.90	11.11	0.999
aLVB	50	0.0404	7.97	7.70	0.999

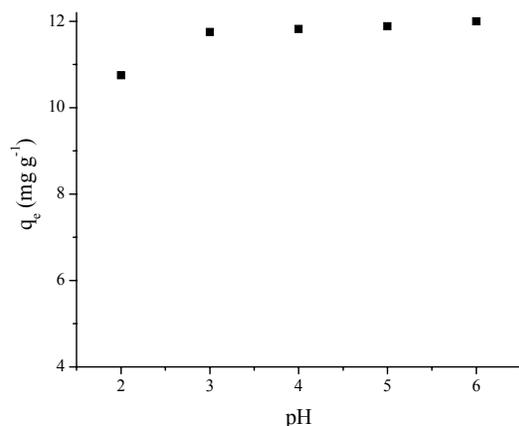


**Figure 3.** Determination of  $\text{pH}_{\text{pzc}}$  using Dirft method

Results in **Figure 3**, show that  $\text{pH}_{\text{pzc}}$  of sulphuric acid treated LVB is 4.95. It is much more acidic in comparison with starting material aLVB, with  $\text{pH}_{\text{pzc}}$  value 6.10. Having in mind applied chemical treatment, increased content of acid groups in LVB structure, probably sulfonic group, is expected.

#### Effect of initial pH

To determine the effect of initial pH on Cu(II) ions removal, experiments were conducted at pH 2, 3, 4, 5 and 6, adjusted with  $\text{HNO}_3$  or NaOH. 1.0 g of ccLVB was added to 250 ml of  $50 \text{ mg dm}^{-3}$  Cu(II) ions solutions. The mixture was agitated for 240 min and aliquots were taken at predefined time intervals. Results are shown in **Figure 3**.



**Figure 4.** Effect of initial pH on Cu(II) ions removal by ccLVB ( $c_{\text{Cu(II)}} = 50 \text{ mg dm}^{-3}$ ,  $\text{pH}_i = 5.0$ ,  $c_{\text{LVB}} = 4.0 \text{ g dm}^{-3}$ ,  $T = 25 \pm 0.5^\circ\text{C}$ )

It is well known that pH has a great importance for cation sorption by biosorbents

because it influences chemical speciation of the metal ions in solution and also on the ionization of chemically active sites on the sorbent (Basci et al., 2004; Goyal et al., 2008; Iftikhar et al., 2009; Dang et al., 2009). In contrast, results in Figure 4, shown that there is a small effect of initial pH of metal solution on sorption of Cu(II) ions onto ccLVB. In pH range from 3 up to 6 almost there is no effect of pH on Cu(II) removal efficiency. Only at the initial pH 2 the efficiency of Cu(II) removal is slightly smaller, for about 10%. Uptake of Cu(II) by ccLVB was favored by pH increasing from 2 to 3 because of different reasons, as in the case of many other biosorbents. The lower sorption of divalent metals observed at low pH values has been attributed to following factors: (a) repulsion between positive charge of the sorbent and free metal cations; (b) competition between  $\text{H}^+$  and free metal cations for the sorbent active sites; (c) lower formation of complexes with metal ions due to protonation of surface functional groups, and (d) combination of several of these factors (Fiol and Villaescusa, 2008; Aziz et al., 2009; Iftikhar et al., 2009). Authors Mitić-Stojanović et al. (2011) were shown that metal ions sorption by untreated *L. vulgaris* biomass is very affected by initial pH of metal solution. They found that sorption efficiency significantly rise with increasing of pH in range from 2 to 5, with maximum at pH 5, which is closely related with obtained  $\text{pH}_{\text{pzc}}$  value of 6.10 for aLVB. However, for sulphuric acid treated LVB results are not completely consistent with observed  $\text{pH}_{\text{pzc}}$ , with value 4.95 (**Figure 3**).

This could mean that mechanism of Cu(II) ions sorption by ccLVB is not strictly of ion-exchange type. Lewis base – Lewis acid interactions between sorbent surface functional groups and metal ions may play a significant role in the copper ions removal by sulphuric acid treated *L. vulgaris* shell biomass. Results can be, also, explained by presence of acidic  $-\text{SO}_3^-$  groups on surface of ccLVB, which cannot be protonated on investigated pH values. In addition, sulphuric acid treatment changes the physical and chemical properties of biosorbent, which results in increase of efficiency for metal ions removal. It can be supposed that conc.  $\text{H}_2\text{SO}_4$  initiated bond cleavage, leading to dehydration and elimination reactions that release volatile products such as water, acetic acid, methanol and other chemical substances (Gerçel et al., 2007). This is followed by partial aromaticity and recombination of species to form a stronger cross-linked solid (Khaled et al., 2008). Ozer et al. (2007) supposed that sulphuric acid reacts with hydroxyl groups in the lignin to form sulphuric esters as a

non-ionic functional group, which may complex cations. Obviously, mechanism of biosorption process is rather complex and involve many different processes: chemisorption, complexation, ion exchange, chelation, physical adsorption, which do not depend of pH on the same way (Sud et al., 2008).

## Conclusion

Sulphuric acid treated *Lagenaria vulgaris* shell is found to be very efficient biosorbent for Cu(II) ions removal from water. Biosorption process was very fast, reaching maximum efficiency (almost 100% of Cu(II) ions was removed from solution) in the first 10 minutes. Sorption kinetic was found to be best-fitted pseudo-second order model, which indicates that process is mostly based on chemisorption. Biosorption on ccLVB is not significantly dependent of initial pH and this material could be used for treatment of acidic wastewater loaded with copper.

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