Effects of power of ultrasound on removal of Cu(II) ions by xanthated *Lagenaria vulgaris* shell

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ABSTRACT

This study was aimed at removal of Cu(II) ions from aqueous solutions by ultrasound-assisted sorption onto xanthated *Lagenaria vulgaris* shell (xLVB). Sorption kinetics, isotherms and ultrasonic power were investigated. Sorption isotherm data were best fitted by the Langmuir model. The acoustic power was an important factor for the enhancement of the removal of copper. The maximum sorption capacity in the presence of ultrasound was much greater than in absence of ultrasound. The sorption process in the presence and absence of ultrasound obeyed to the pseudo-second order kinetics, indicating that the rate-limiting step might be a chemical reaction between the sorbent and the sorbate. The intraparticle diffusion and Boyd model indicated that that the intraparticle diffusion was not the only rate-limiting step in the sorption of Cu(II) ions on xLVB but that the other processes also control the rate of sorption.

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1. Introduction

One of the most important global environmental problems is water pollution, especially pollution by heavy metals. The improper disposal of heavy metals leads to pollution. This is especially significant because of the facts that heavy metals are non-degradable, hence are accumulated in living organisms by food chains. Copper and its salts are widely used industrial chemicals as agricultural fungicides, petroleum refining, electroplating baths, mining etc. (Huang et al., 2007; Al-Asheh et al., 2002). Excessive sorption of copper can cause serious health problems such as heart, liver, kidney, pancreas and brain damage, intestinal distress and anemia (Abu-Al-Rub et al., 2006). The toxic heavy metals must be effectively removed from the wastewaters, because of its numerous consequences to human and overall environment. The most common used methods for reducing heavy metal concentration are chemical precipitation, chemical oxidation and/or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery (Canizares et al., 2005; Feng et al., 2000; Kumano et al., 2006; Ozaki et al., 2002; Trivunac and Stevanovic, 2006). However, there are numerous disadvantages of these technology processes: incomplete metal removal, high costs because of requirements for expensive equipment and monitoring system, low efficiency (Brady et al., 1999). Alternative technology for conventional wastewater treatment is sorption, as efficient, clean and cheap technology.

Although in literature there are no numerous information and studies about the removal of metal ions from aqueous solution by sorption combined with ultrasound, this technique is used in industry, especially in wastewater treatment.

Present study deals with investigation of ultrasound-assisted biosorption of Cu(II) ions from aqueous solutions on xanthated *Lagenaria vulgaris* shell. Therefore, the overall objective of the study was to evaluate the effects of power of ultrasound on the process equilibrium and kinetics and to define the best isotherm and kinetic sorption models. Also, there are no records about the influence of US on Cu(II) ions removal by xanthated biomass.

2. Experimental

2.1. Reagents and biosorbent

All chemicals were of reagent grade and used without further refinement. HNO_3, $NaOH$, CS_2 and $Cu(NO_3)_2$ were purchased from Merck (Germany). All solutions were prepared with deionized water. Standard metal stock solution was prepared by dissolving given amounts of pure $Cu(NO_3)_2 \cdot 3H_2O$. *L. vulgaris* shell was treated with diluted nitric acid and after that by sodium hydroxide,

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producing a basic *L. vulgaris* biosorbent (LVB). Xanthation was carried out by treatment of LVB with carbon disulfide in alkaline medium. This synthesis and characterization are discussed in previous research (Kostić et al., 2014).

2.2. Batch biosorption experiments

Batch sorption experiments were conducted in ultrasonic bath (Sonic, Serbia; total nominal power: 50 W) that operates at 40 kHz frequency (The experimental setup is shown in supplementary Fig. S1). The temperature in the ultrasonic bath was held at 20 °C ($\pm$0.2 °C) by recirculating water from a thermostated bath Julabo F12-ED (Refrigerated/Heating Circulator, Germany). Sorption experiments were performed in 400 cm^{-3} glass vessel, placed in ultrasonic bath with mechanical stirrer immersed in (200 rpm). Working standard solutions were prepared just before use by the appropriate dilution of the stock solutions (1.00 g dm^{-3}). All experiments were performed with 4.0 g dm^{-3} quantity of dried biosorbent suspended in 250 cm^{-3} of Cu(II) solutions in a concentration range between 10 and 400 mg dm^{-3} of Cu(II) ions at initial pH 5.0 $\pm$ 0.2. At pH value 5.0 removal efficiency achieved maximum level, which was explained in previous research (Kostić et al., 2013). Samples (4.0 cm^3) were taken before mixing the sorbent 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 concentration in the solution. The concentrations of residual Cu(II) ions in the solution were determined by an atomic adsorption spectrometer Analyst AA 300 (Perkin Elmer, USA). The amount of metal sorbed q_t (mg g^{-1}) (Meitei and Prasad, 2014) and the removal efficiency (RE) (Li et al., 2013) of metal ions was calculated using the Eqs. (1) and (2), respectively.

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

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

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

All the experiments were conducted in triplicate and average values were used in the data analysis using OriginPro 9.0 software (OriginLab Corporation, USA).

3. Results and discussion

3.1. Contact time

To investigate the effect of contact time on Cu(II) ions sorption, experiments were conducted at initial metal concentration of 50 mg dm^{-3} in the presence and absence of ultrasound, the acoustic power used was 50.0 W. In the presence of ultrasound the experimental results show high sorbent efficiency in removing Cu(II) ions: sorption equilibrium was obtained in 20 min of sorbent–sorbate contact, when 97.5% of total Cu(II) ions were removed (Fig. 1). After 180 min, initial concentration of Cu(II) ions decreases and removal efficiency was 98.8%. In the presence of ultrasound a shorter time is required to reach equilibrium. In the silent sorption, equilibrium was attained after about 50 min of contact time and RE was 80.1%. (Kostić et al., 2013). The shorter time to reach equilibrium and the faster rate of removal in the presence of ultrasound and mechanical stirring were attributed to the strong convective currents occurring within the reactor. These effects associated with the hydrodynamic phenomena due to cavitation and mechanical stirring are responsible for the perfect mixing of the vessel content (Hamdaoui et al., 2005).
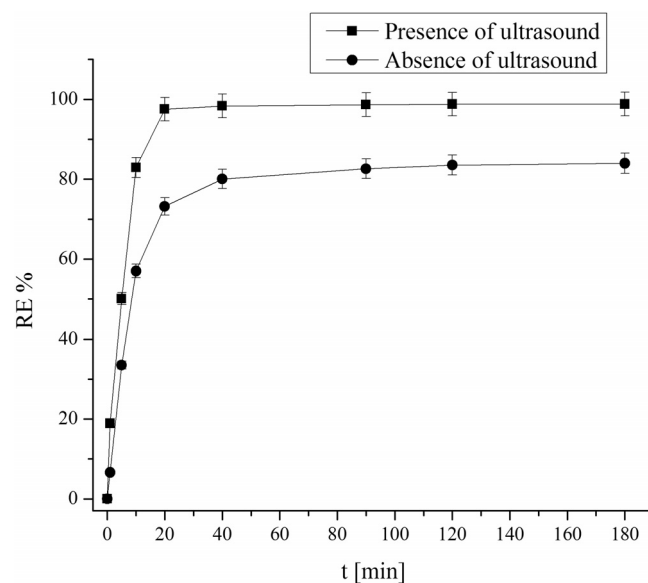

Fig. 1. Effects of the contact time in the presence and absence of ultrasound on the biosorption of Cu(II) ions on xLVB.

3.2. Kinetic study

The reaction kinetic models (the pseudo first-order and pseudo second-order model) were applied to study the reaction kinetics of the sorption process, whereas the intraparticle diffusion model and Boyd's were further tested to determine the diffusion limitations of the sorption of Cu(II) ions onto xLVB.

The original equations for pseudo first-order, pseudo second-order, intraparticle diffusion and Boyd's model are presented in detail in paper by Ho and McKay (1998); Yao et al. (2010); Hossain et al. (2012).

The determination coefficients (r^2) for the pseudo first-order kinetic model (Table 1) obtained for all the studied acoustic power were relatively low. Also, it was found that the calculated q_e values did not agree with the experimental q_e values. This suggests that the sorption of copper did not follow pseudo-first-order kinetics. The experimental data were observed to fit well to the pseudo-second order model. The determination coefficients for the pseudo-second order equation obtained at all the studied acoustic powers were high (from 0.9871 to 0.9970). Also, the q_e^{cal} values are in good agreement with the experimental data. In addition, it can be seen in Table 1. that with an increase in acoustic power, the rate constant of sorption (k_2) increases. In this case of Cu(II) ions sorption from aqueous solution, ultrasound increased significantly the sorption capacity and increase of k_2 was very high 0.0108 and 0.0235 g mg^{-1} min^{-1} for silent and ultrasound-assisted sorption, respectively. Based on the obtained data, the primary benefit of sonication is an increase in the speed of sorption, especially in the initial period. The values of the sorption capacity for sorption of Cu(II) ions by xLVB increased from 11.46 to 12.92 mg g^{-1} while the acoustic power increased from 0 to 50.0 W. As can be seen from Fig. 1, amount of sorbed Cu(II) ions increased from 10.49 to 12.35 mg dm^{-3} with the increase in acoustic power from 0 to 50, indicating significantly influence of ultrasound. This means that ultrasound has an impact on both the rate of reaching equilibrium and the sorption capacity. The removal of Cu(II) ions was higher in the presence of ultrasound than in its absence, due to the cavitation process which increased the diffusion process. In accordance with the pseudo second-order reaction mechanism, the overall rate of Cu(II) sorption processes appear to be controlled by the chemical processes. The mechanism of ion-exchange which is probably