Kinetics of copper(II) and chromium(VI) biosorption by dried waste tea fungal biomass from aqueous solution

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Abstract

The potential of dried waste tea fungal biomass to remove Cu(II) and Cr(VI) from aqueous solution was investigated at different biomass concentrations. Two kinetic models such as Lagergren and Elovich models and the intraparticle diffusion model were selected. The highest uptake observed were for Cu(II) at 20.09 mg g^{-1} of fungal biomass and 32.50 mg g^{-1} for Cr(VI), respectively. The application of the Lagergren and Elovich equations showed a better fitting of experimental data to the second equation. The intraparticle diffusion is involved in the adsorption proces in he case of Cr(VI) system.

Keywords: Biosorption, Copper(II), Chromium(VI), Waste tea fungal biomass

Introduction

Heavy metal pollution in wastewater has always been a serious environmental problem because heavy metals are not biodegradable and can be accumulated in living tissues. Copper(II) and chromium(VI) are widely used in various important industrial applications. Copper at excessive concentration is toxic to living organism of humans and other creatures, especially fish [1]. The effects of acute copper poisoning in humans are very serious, in particular possible liver damage with prolonged exposure. Strict environmental regulations have enhanced the demand for new technologies for metal removal from wastewater to attain toxicity driven limits [2]. Chromium, with its great economic importance in industrial use, is a major metal pollutant of the environment. The discharge of effluents by a variety of industries such as textile, dyes and pigments production, leather tanning, electroplating and metal finishing may contain undesirable amounts of Cr(III) and toxic Cr (VI) compounds due to EPA (US Environmental Protection Agency) at concentrations ranging from tens to hundreds of mg L^{-1} [3]. Biosorption, which uses the ability of biological materials to remove and accumulate heavy metals from aqueous solutions, has received considerable attention in recent years because of a few advantages compared to traditional methods. Literature shows that a wide variety of microorganisms, including bacteria, algae and fungi, and agricultural wastes are capable of sorbing Cu(II) cations and Cr(VI) anions [4-9]. Among these microorganisms, fungal biomass seems to be a good sorption material, because, it can be produced easily and economically using simple fermentation techniques with a high yield of biomass and economical growth media. Fungal biomass is also available as a by-product or waste material from various fermentation processes. Furthermore, since dead fungal biomass is of little use and is abundant, it may be good source of biomaterial for the removal of Cu(II) and Cr(VI) from industrial wastewater [3, 10].

Despite the quite extensive literature available on metal biosorption by different biosorbents, little attention seems to have been given to the study of single-metal biosorption by waste tea fungus (waste by-product from tea fungus fermentation of black tea during preparation of Kombucha beverage) as biosorbent. The use of the pretreated waste tea fungal biomass as biosorbent for arsenic removal was investigated by Murugesan *et al*.[11].

The present work investigates the potential use of dried waste tea fungal biomass as metal sorbent for removal of Cu(II) and Cr(VI) from aqueous solution. Waste tea fungal biomass was chosen as a biosorbent because of the relative lack of information abouth its sorption ability. Two kinetic models such as Lagergren and Elovich models and the intraparticle diffusion model were selected. This information will be useful for further applications of system design in the treatment of practical waste effluents.

Material and methods

Tea fungal biomass as biosorbent

The tea fungus (a simbiont of yeasts *Saccharomycodes ludwigii, Saccharomyces cerevisiae, Saccharomyces bisporus, Torulopsis* sp., *Zygosaccharomyces* sp. and a bacterium genera *Acetobacter*) was obtained from Markov *et al.* [19] of the *Faculty of Technology* in Novi Sad (Serbia). The tea fungal biomass was washed with an adequate amount of distilled water to obtain it free from the media components and then dried at 105^{o}C until the constant weight. The dry tea fungal biomass was ground using a laboratory mill.

Preparation of metal solutions

The stock solutions of Cu(II) and Cr(VI) (0.25 mol L^{-1}) were prepared by dissolving $CuSO_4$ x $5H_2O$ or $K_2Cr_2O_7$ in distilled water. Other concentrations were obtained by dilution and the pH values in adsorbate solutions was adjusted to desired values with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. Fresh dilutions were used for each experiment. All the chemicals used were of analytical grade.

Biosorption experiments

The biosorption experiment was performed by mixing 0.25; 0.5 or 1.0 g L^{-1}, respectively, of dried tea fungal biomass in 200 mL of synthetic metal ion solutions with concentration 0.4 mmol L^{-1} at pH 4 for Cu(II) and pH 2 for Cr(VI), respectively. Batch experiments were carried out at 25^{o}C in Erlenmeyer flasks on a rotary shaker at 200 rpm. The contact time was varied up to 250 min. Samples were taken at certain time intervals, filtered by using filter paper Watman N^{o}1 to remove the suspended biomass and analyzed for residual Cu(II) and Cr(VI) concentrations. The concentrations of heavy metal ions before and after biosorption were determined using an atomic absorption spectrophotometer (Varian AA-10).

The sorption capacity of tea fungal biomass can be calculated based on the mass balance principle where:

$$q\ (\text{mmol g}^{-1}) = V\ (C_o - C)\ /\ m \qquad (1)$$

where q is the amount of metal uptake per unit mass of biosorbent (mmol g^{-1}), C_o and C (mol L^{-1}) are the initial and residual concentrations of metal ion, respectively, V is the volume of the solution (L^{-1}); m is the dry mass of the biosorbent (g).

Each batch of experiments was carried out in duplicate and the average results are presented herein.

Results and Discussion

Biosorption rate

The biosorption rates of Cu(II) and Cr(VI) ions on waste tea fungal biomass at three different biomass concentrations 0.25; 0.5 and 1.0 g L^{-1}, respectively, were shown in Fig.1, and Fig. 2. Rapid uptake of metal species was occurred within 20 min for Cu(II) and 40 min for Cr(VI), respectively, and an equilibrium was reached in 120 min for both metal ions. After this equilibrium period the amount of adsorbed metal ions did not change significantly with contact time. This rapid initial uptake was similar to the previous reports on the biosorption of heavy metals by different sorbents [13, 14]. It was noticed that lower tea fungal biomass concentrations resulted in higher rates and amounts of Cu(II) and Cr(VI) adsorption, respectively. Similar observation were made in the case of copper and chromium uptake by *Aspergillus carbonarius* [15]. Higher uptake at lower biomass concentrations could be due to an increase metal to biosorbent ratio which decreases upon an increase in biomass concentrations [2]. The highest uptake were observed were for copper 20.09 mg g^{-1} of fungal biomass and 32.50 mg g^{-1} for chromium, respectively.

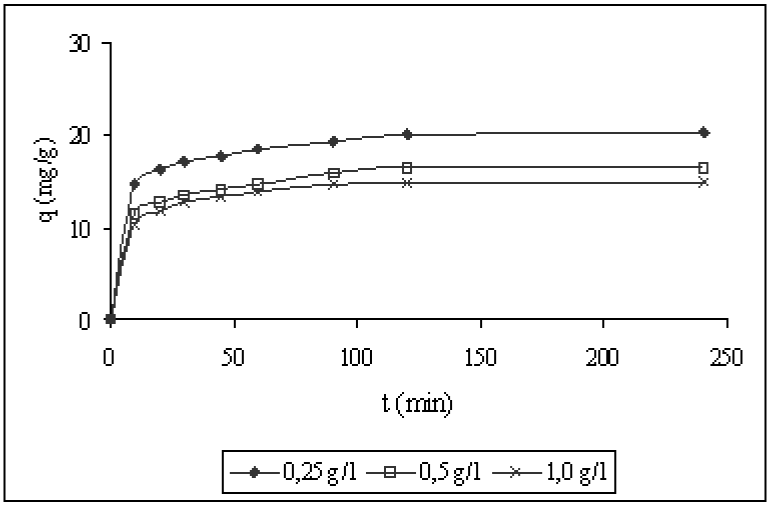

Figure 1. Copper (II) adsorption kinetics at different doses of tea fungal biomass (C_o= 0.4 mmol L^{-1}, pH 4)

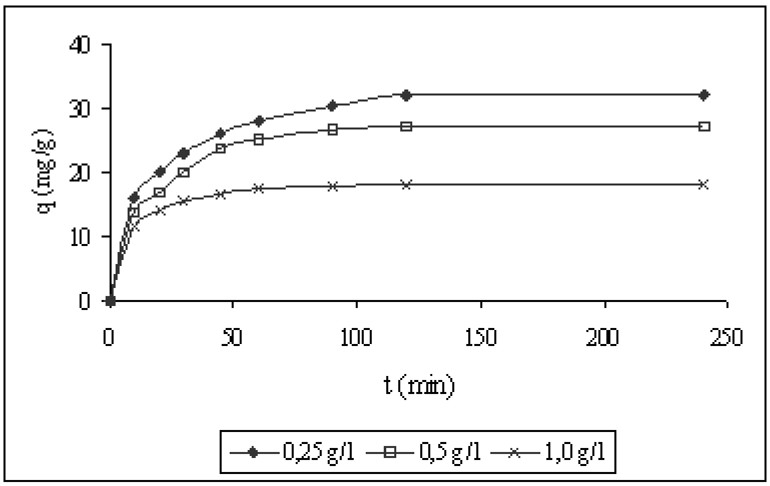

Figure 2. Chromium (VI) adsorption kinetics at different doses of tea fungal biomass (C_o= 0.4 mmol L^{-1}, pH 2)

Biosorption kinetics

Two kinetics models, Lagergren [16] and Elovich [17] are used to examine the controlling mechanism of adsorption process. The first order Lagergren equation is:

$$\log (q_e - q_t) = \log (q_e) - K_{ad}\, t / 2.303 \qquad (2)$$

where q_e is the quantity of adsorbed material (mg g^{-1}) at equilibrium, and q_t is the quantity of adsorbed material (mg g^{-1}) in a given time t (min), and K_{ad} (min^{-1}) is the adsorption rate constant.The Elovich equations is given as follows:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q} \qquad (3)$$

where α is the initial rate (mg g^{-1} min^{-1}) because (dq_t/dt) approaches α when q_t approaches zero and the parameter β is related to the extent of surface coverage and activation energy for chemisorptions (g mg^{-1}). Coefficients in Eqs. 1 and 2 and coefficients of determination (R^2) were computed from linearized forms of these equations by Microsoft Exel package.

The calculated Lagergren and Elovich kinetic constants for biosorption of Cu(II) and Cr(VI) onto dried tea fungal biomass and their corresponding linear regression correlation coefficient values are shown in Table 1 and 2. The rate constants were higher at lower adsorbent concentrations for both Cu(II) and Cr(VI) ions. The Lagergren constants are comparable with the K_{ad} values reported by Murugesan *et al.* [11]. The coefficients of determination R^2 by Lagergren model found as 0.9330 for Cu(II) biosorption onto 0.25 g L^{-1} biomass and 0.8103 for Cr(VI) biosorption. This shows that this model can be applied to predict the adsorption kinetic model in case of Cu(II) biosorption because R^2>0.9. For both metal ions, coefficients of determinatin were found to be above 0.9 by Elovich equation in case of biosorption at 0.25 g L^{-1} biomass. The higher R^2 values confirm that the adsorption date are well represented by Elovich model. These results are in agreement with data given Önal [18].

Table 1. Lagergren and Elovich kinetic constants for biosorption of Cu(II) onto tea fungal biomass

Kinetic model	Adsorbent dosage (g L^{-1})		
	0.25	0.5	1.0
Lagergren			
q_e (mg g^{-1})	5.20	4.51	3.10
$k \cdot 10^{-3}$ (L min^{-1})	15.4	11.5	18.0
R^2	0.9316	0.8070	0.7718
Elovich			
a (mg g^{-1})	10.72	7.52	7.23
k	1.79	1.76	1.55
R^2	0.9749	0.9603	0.9189

Table 2. Lagergren and Elovich kinetic constants for biosorption of Cr(VI) onto tea fungal biomass

Kinetic model	Adsorbent dosage (g L^{-1})		
	0.25	0.5	1.0
Lagergren			
q_e (mg g^{-1})	12.54	8.91	3.72
$k \cdot 10^{-3}$ (L min^{-1})	12.9	16.8	11.3
R^2	0.8103	0.7677	0.6672
Elovich			
a (mg g^{-1})	4.11	3.91	7.74
k	5.56	4.75	2.13
R^2	0.9469	0.8969	0.8707

In many cases of adsorption process for porous solids there is a possibility that intraparticle diffusion will be the rate limiting step and this normally determined by using the equation described by Weber and Morris [19] :

$$K_p = \frac{q}{t^{0.5}} \qquad (4)$$

where q (mg g^{-1}) is the amount adsorbed metal ions at time t and K_p is the intraparticle rate constant (mg g^{-1} $min^{-0.5}$).

Figs. 3 and 4. show the effect of intraparticle diffusion on biosorption of Cu(II) and Cr(VI) ions at dried tea fungal biomass concentrations of 0.25; 0.5 and 1.0 g L^{-1}, respectively. The kinetics of adsorption may depend on the adsorbent porosity; the matrix must allow the adsorbate to diffuse through it until reaching the active sites [2]. Fig 3. shows that the relationships for dried tea fungal biomass and Cu(II) system for different biosorbent concentrations are not linear over the entire time range, indicating that more than one process is affecting the adsorption. This type of non-linearity has been reported previously by Mohanty *et al.* [20]. In the case of Cr(VI) system, the plot indicated an initial curved portion followed by a linear portion and plateau.

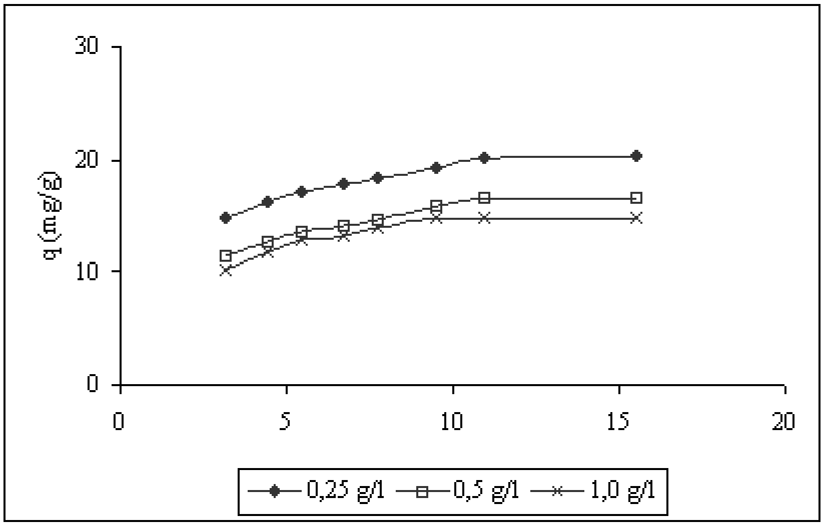

Figure 3. Plot of q vs. $t^{0.5}$ of Cu(II) biosorption onto different tea fungal biomass dosage

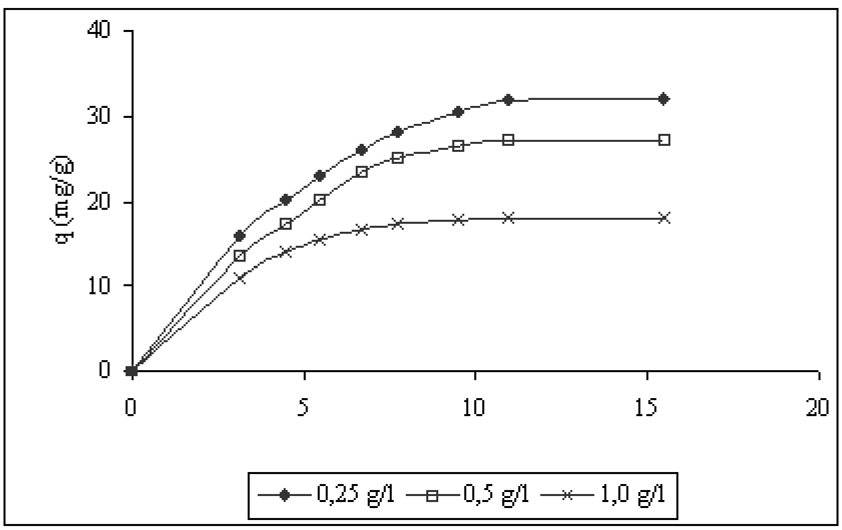

Figure 4. Plot of q vs. $t^{0.5}$ of Cr(VI) biosorption onto different tea fungal biomass dosage

Conclusion

The results obtained in this study on kinetic data could be useful for the design of a wastewater plant. A comparative data of adsorptive capacity indicated that the dried tea fungal biomass surface had more affinity for Cu(II).

Acknowledgements

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