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Biosorption properties of cadmium (II) and Zinc(II) from aqueous solution by tea fungus

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ABSTRACT

The study evaluated the sorption of Cd(II) or Zn(II) ions from aqueous solution by a new biosorbent, dead tea fungus. The rate and extent of accumulation were affected by pH, initial metal ion concentration and contact time. The maximum removal of Cd(II) or Zn(II) were found to be 32 mg L^{-1} at pH 9 and 39 mg L^{-1} at pH 10, respectively. The equilibrium process was described well by the Langmuir isotherm model with maximum sorption capacities of 35 and 40 mg g^{-1} of Cd(II) and Zn(II) on tea fungus, respectively, which in agreement with the experimental data. The removal process was rapid and equilibrium was established in less than 30 min. Good correlation coefficients were obtained when the pseudo-second-order kinetic model of this process was assumed. Dead tea fungus was found to be an efficient biosorbent of metal ions from the effluent of electroplating industry.

Keywords: Tea fungus; Cadmium; Zinc; Biosorption isotherm; Kinetic; Electroplating wastewater

1. Introduction

The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even if they are present at relatively low concentrations in environment[0] [1–3]. Various industries, including metal plating, electroplating, mining, batteries and pigments manufacturing, are among the major sources of pollution by heavy metals [4-5].

Cadmium and zinc are commonly found in effluents discharged from processing ores after mining, acid mine drainage, galvanizing plants and municipal wastewater treatment plants. They are not biodegradable and are elevated through the food chain via bioaccumulation, therefore there is significant interest regarding their removal from wastewaters [6].

Removal of heavy metals from aqueous solutions by biosorption plays an important role in water pollution control [7]. It has been reported that heavy metal ions can be removed by inexpensive biological materials such as fungi, bacteria and algae [8–10]. Biosorption is a rapid, reversible and economical technology in contrast to traditional methods used for removal of heavy metals from aqueous streams such as chemical precipitation [11,12].

The present work investigated the potential use of the dead tea fungus as metal sorbent for cadmium and zinc from aqueous solutions. Tea fungus was chosen as a biosorbent because of the relative lack of information about its sorption ability in literature. We studied the influence of parameters affecting biosorption process

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such as pH, initial metal ion concentration, contact time and used the Langmuir and Freundlich isotherm models to evaluate the equilibrium adsorption data. The study was concluded with an attempt to use tea fungus to treat Cd(II) and Zn(II)-containing wastewater from an industrial electroplating process.

2. Materials and methods

2.1. Biosorbent

The strain used in this study was waste tea fungus, obtained from the Culture Research Center of CAS, PR China. The cultures were dried at 60 °C, passed through a 1-mm sieve and the oversize product stored dry until use.

2.2. Metal solutions

All the chemicals used were of analytical grade. Stock solutions of Cd(II) and Zn(II) used in this study was prepared by dissolving accurate quantity of their chloride (Cd(II) added as $CdCl_2{\cdot}H_2O$ and Zn(II) as $ZnCl_2$) in deionized water. Other concentrations prepared from stock solution by dilution with tap water varied between 20 and 1000 mg L^{-1} and the pH of the working solutions was adjusted to desired values with 0.1 M HCl and 0.1 M NaOH. Fresh dilutions were used for each experiment.

2.3. Experimental methods

The effect of pH on biosorption capacity of dead tea fungus was determined by equilibrating the biosorption mixture containing dead tea fungus (0.5 g) and metal solutions (100 mL of 100 mg L^{-1} solution) at different pH values (pH 5–13). At each pH a set of parallel experiments with one being a replicate without tea fungus added were carried out. The difference in metal concentration between parallel runs with and without fungus was used in calculation of the mass of adsorbed metal.

Kinetics study was carried out at times 5–30 min with 5 min time intervals and in accordance with the procedure described above. The initial metal concentration 100 mg L^{-1} and biosorbent concentration 5 mg L^{-1}, at pH 9 and 10 (Cd(II) and Zn(II), respectively) were used in this part. For the assessment of effect of initial metal ion concentration on biosorption at optimum pH and contact time, the solutions of Cd(II) or Zn(II) ranging from 20 to 1000 mg L^{-1} was prepared and used in experiments. At the end of the experiment each suspension liquid was decanted and filtered through a 0.45 μm cellulose acetate filter and the supernatant was analyzed for residual metal ion concentration.

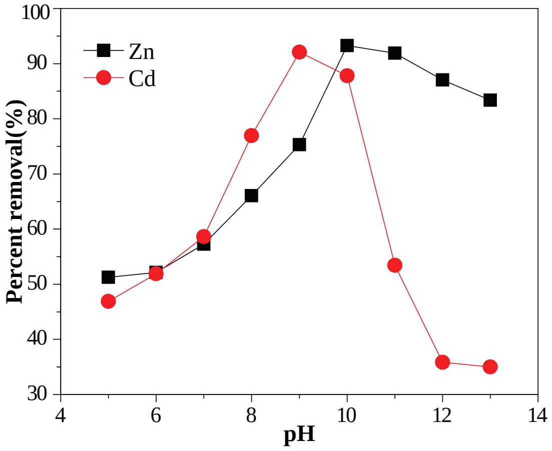

Fig. 1. Effect of pH on Cd(II) and Zn(II) ions removal by tea fungus. Initial metal ions concentration = 100 mg L^{-1} and the biosorbent concentration = 5 g L^{-1}.

The solutions were analyzed for metal concentration using an inductively coupled plasma-atomic emission spectrometer (Intrepid II XSP).

3. Results and discussion

3.1. Effect of pH

Biosorption of heavy metal ions onto the surface of the fungus is influenced by initial pH of the biosorption medium. Batch equilibrium studies were carried out at different initial pH values ranging from 5 to 13 in order to evaluate the effect of pH on the percent removal of Cd(II) and Zn(II). The results presented in Fig. 1 showed that maximum uptake of Cd(II) and Zn(II) were observed at pH 9 and 10, respectively, at initial metal concentration of 100 mg L^{-1} and fungus concentration at 5 g L^{-1}. At pH 5–7 a little biosorption occurred. Under highly basic conditions (pH 11–13) biosorption uptake of Cd(II) and Zn(II) were lower than at pH 9 and 10, respectively. Maximum biosorption uptake of 92% and 93% for Cd(II) and Zn(II) were reached for pH 9 and 10, respectively.

The pH dependence of metal uptake could be related to solubility of metals and the ionization state of the various functional groups on the fungus cell walls. At low pH, the fungal surface groups are mostly protonated, and many of them (carboxyl groups in particular) are neutral thus interaction between wall elements and metal cation or cationic species may be weaker. At higher pH values these groups are deprotonated and many will carry negative charges which interact strongly with cations or still cationic species.

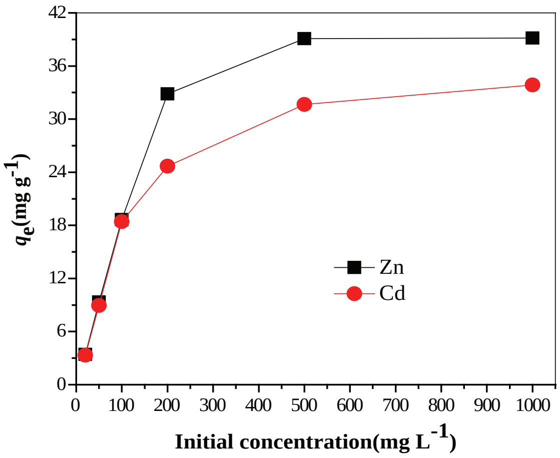

Fig. 2. Effect of initial metal ion concentration on Cd(II) and Zn(II) removal by tea fungus. The biosorbent concentration = 5 g L^{-1}; pH 9 and 10, respectively; contact time = 20 min.

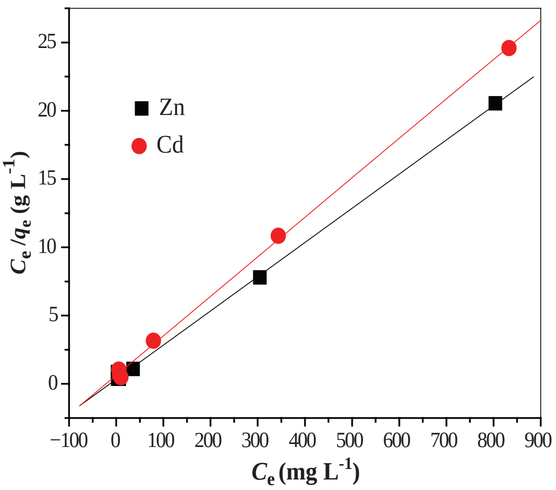

Fig. 3. Langmuir adsorption isotherm of Cd(II) and Zn(II) ions on tea fungus.

At even higher pH values both Zn and Cd cations are expected to be converted to anionic species, and interactions between anionic surface groups and anionic metal species should be weaker again. Our data show (see Fig. 1) that at high pH there is a significant drop in sorption of Cd and less apparent drop in sorption of Zn. This is contrary to known difference in tendency of both metals to exist in the form of anionic species in strongly basic solutions. Zinc is an amphoteric element and zinc hydroxy complex anions such as hydroxyzincates are the predominant species at pH above 11 [13], while stability of similar cadmium anions may be lower at that pH.

3.2. Effect of initial metal ions concentration

The biosorption experiments with dead tea fungus were conducted using metal ion solutions ranging from 20 to 1000 mg L^{-1} at pH 9 and 10 for Cd(II) and Zn(II), respectively. The biomass exhibited quite fast metal loading capacity for Cd(II) and Zn(II) in the first 20 min, which was found to be 32 and 39 mg g^{-1} biomass at the initial concentration all of 500 mg L^{-1} for Cd(II) and Zn(II), respectively. Then the biosorption capacity reached a saturation value and did not change further with initial metal ion concentration (Fig. 2).

3.3. Adsorption isotherms

Analysis of the obtained equilibrium data is essential to develop an equation that precisely represents the results and can be used for design purposes. There are two widely accepted and easily linearized adsorption isotherm models, Langmuir and Freundlich models, both commonly used in the literature. These two isotherm equations were tested in the present study.

Langmuir equation is applied to quantify adsorption capacity and is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (1)$$

where C_e and q_e are equilibrium solute concentration (mg L^{-1}) and equilibrium adsorption capacity, respectively (mg g^{-1}), q_m and b the Langmuir constants representing adsorption capacity (mg g^{-1}) and energy of adsorption (mg^{-1}), respectively.

The Freundlich isotherm was tested in the following linearized form:

$$\ln q_e = \ln K + \left(\frac{1}{n}\right) \ln C_e. \qquad (2)$$

where q_e is the amount of metals adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of metals in solution (mg g^{-1}), K and $1/n$ the Freundlich constants, which represent the adsorption capacity (mg g^{-1}) and adsorption intensity of these sorbents, respectively. The constants K and $1/n$ are evaluated from the intercept and the slope of the straight lines using a least-square fit program.

The Langmuir constants along with the regression coefficient has been calculated from the corresponding plots (Figs. 3) for biosorption of Cd(II) and Zn(II) on the tea fungus and the results are presented in Table 1. Langmuir model seemed to define the experimental data obtained from this study well with the regression coefficient (R^2) value of 0.9995 and 0.9996 for Cd(II) and Zn(II), respectively. Small b value (0.045 and 0.074)

Table 1
Langmuir constants for biosorption of Cd(II) and Zn(II) ions by tea fungus

Experimental	q_e (mg g^{-1})	q_m (mg g^{-1})	b (mg^{-1})	R^2
Cd(II)	32	35	0.045	0.9995
Zn(II)	39	40	0.074	0.9996

indicated that Cd(II) and Zn(II) ions were bonded strongly to tea fungus. Therefore, biosorption process in this study may be interpreted as monolayer adsorption. According to Langmuir model, sorption occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no further sorption can take place at this site [14].

3.4. Adsorption kinetics

Fig. 4 showed the rates of biosorption of Cd(II) and Zn(II) by dead tea fungus from solutions containing 100 mg L^{-1} of Cd(II) and Zn(II) ions, respectively. Inspection of this figure leads to conclusion that the biosorption equilibrium was established in 20 min for both Cd(II) and Zn(II). This suggested that the biosorption process was quite fast. After this equilibrium period the amount of biosorbed metal ions did not change significantly with contact time and this period may be accepted as the optimum contact time. This trend for metal ions in binding suggests that the binding may take place through interactions with functional groups on the surface of the biosorbent which continues until all the surface groups are involved in interactions with ions [15].

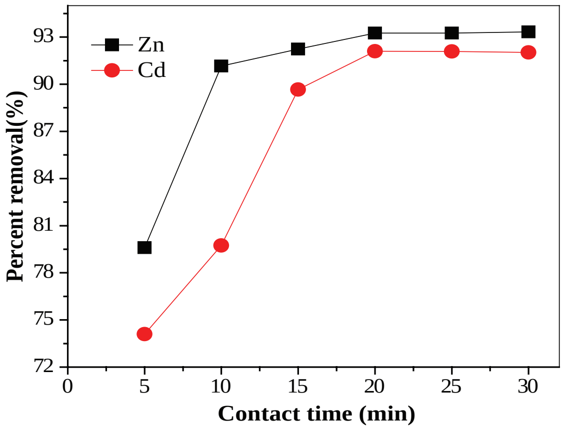

Fig. 4. Biosorption uptake of Cd(II) and Zn(II) on tea fungus. Initial metal ions concentration = 100 mg L^{-1}; the biosorbent concentration = 5 mg L^{-1}; pH 9.0 and 10.0, respectively.

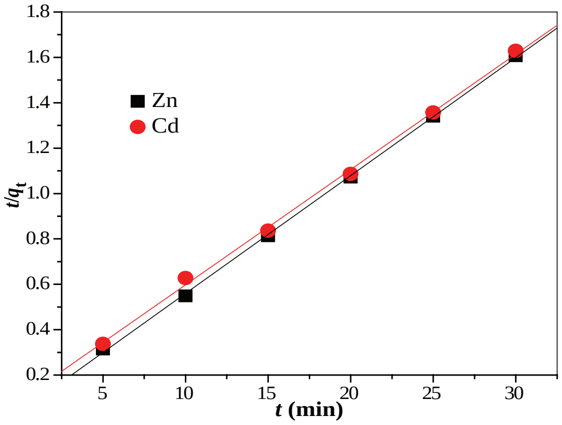

Fig. 5. Pseudo-second-order sorption kinetics of Cd(II) and Zn(II) on tea fungus.

Various sorption kinetic models have been used to describe the removal of metals from solutions. The first-order kinetic process has often been used for reversible reaction with an equilibrium being established between liquid and solid phases. The pseudo first-order rate equation by equation of Lagergren has also been used widely in such a scenario. Elovich-type equation has been used to describe a series of reaction mechanisms, such as solute diffused on interface and activated at surface. Fitting our experimental data to Lagergren and Elovich-type equation, respectively, yielded the regression coefficient (R^2) values that were all lower than 0.9 for both Cd(II) and Zn(II). Over the past few years, a pseudo-second-order kinetic model has been considered to be among the most appropriate [16] and was successfully applied by many authors in their studies of the sorption kinetics of metal ions using several different biosorbent materials [17].

If a pseudo-second-order equation is allowed in our considerations, the rate equation for the reaction may be represented by the following expression:

$$\frac{t}{q_t} = \frac{1}{k} + \frac{t}{q_e} \tag{3}$$

where t is the contact time (min), q_t and q_e are the quantities of sorbate sorbed at time t and at equilibrium (mg g^{-1}) and k is the sorption rate constant (mg (g min)$^{-1}$). From Eq. (1), a plot of t/q_t versus t should give a straight line to confirm the applicability of the second-order kinetic model (Fig. 5). The rate constant (k) and adsorption at equilibrium (q_e) can be obtained from the intercept and slope, respectively. The results are shown in Table 2. They showed that the sorption process for both Cd(II) and Zn(II) on dead tea fungus followed the pseudo-second-order kinetic.

Table 2
Pseudo-second-order kinetics constants for Cd(II) and Zn(II) on tea fungus

Cd(II)			Zn(II)		
q_e (mg g^{-1})	k (mg (g min)$^{-1}$)	R^2	q_e (mg g^{-1})	K (mg (g min)$^{-1}$)	R^2
20	11.21	0.9992	19	25.50	0.9998

3.5. *Effluent treatment*

The dead tea fungus was used in real life situation to remove Cd(II) and Zn(II) from the effluent of local electroplating industry. The Cd(II) and Zn(II) concentration in effluent were found to be 23.7 and 243 mg L^{-1}, respectively, and pH of the effluent was 1.3.

Two identical samples were used in experiment in a parallel run. The pH of the effluent samples was adjusted to 10.1 using saturated solution of $Ca(OH)_2$. To one of the runs tea fungus was added to give a concentration of 20 g L^{-1}, while the second run was completed without tea fungus added. The results of residual metal content analysis are given in Table 3. It may be calculated that over 99% of Cd(II) and Zn(II) could be removed from the effluent of electroplating industry at pH 10.1 using tea fungus as a biosorbent. The observed outcome could be explained by co-precipitation of cations from basic solutions and their biosorption by dead tea fungus. The other contaminant metals removed from the effluent by the sorbent tea fungus were also shown in Table 3. The treatment of the sludge resulting from such a process might not be very complex as the tea fungus is a biodegradable material.

4. Conclusion

The present work evidenced the possibility of using dead tea fungus for removal of cadmium and zinc from aqueous solutions. We found that the biosorption process is affected by experimental conditions such as pH, initial metal ion concentration and contact time. The equilibrium for the process involving dead tea fungus was described well by the Langmuir isotherm model with calculated maximum sorption capacities of 35 and 40 mg g^{-1} of Cd(II) and Zn(II), respectively, which agree well with experimental data. The initial removal was rapid and equilibrium was established in less than 30 min. Good correlation coefficients were obtained for the pseudo-second-order kinetic model. The biosorbent was successfully applied in the treatment of electroplating industry effluent for removal of Cd(II) and Zn(II). It was noted that the concentrations of Ca(II), Cu(II) and Mg(II), which were present in crude effluent, were also lowered slightly as a result of the treatment. It could be concluded based on these results that dead tea fungus may be used as an inexpensive, effective biosorbent for the removal of Cd(II) and Zn(II) ions from aqueous solutions.

Table 3
Treatment of the effluent of Electroplating industry by dead tea fungus

Cations (mg L^{-1})	Before adsorption (pH 1.3)	After adsorption (pH 10.1)	
		No tea fungus	Tea fungus
Cd(II)	23.7	0.21	0.06
Zn(II)	243	11.1	0.42
Ca(II)	88.0	45.2	12.0
Cu(II)	1.95	0.64	0.15
Mg(II)	9.75	7.62	4.18

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