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Removal of dissolved copper(II) and zinc(II) by aerobic granular sludge

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Abstract This study investigated the adsorption kinetics of dissolved copper(II) and zinc(II) by aerobic granular sludge. Two series of batch experiments were conducted at different initial copper(II), zinc(II) concentrations (C_o) and initial granule concentrations (X_o). Results showed that the biosorption kinetics of individual copper(II) and zinc(II) by aerobic granules were closely related to C_o and X_o. The maximum biosorption capacity of individual copper(II) and zinc(II) by aerobic granules was 246.1 mg g^{-1} and 180 mg g^{-1}, respectively. In order to theoretically interpret the results obtained, two kinetic models previously developed for biosorption were employed and compared in this study. It was found that the model proposed by Liu *et al*. (2003) could fit the experimental data very well, but the second-order model failed to fit the data in some cases. It appears that aerobic granules would be potential biosorbent with high efficiency for the removal of dissolved copper(II) and zinc(II) from wastewater.

Keywords Aerobic granules; biosorption kinetics; copper(II); initial conditions; zinc(II)

Introduction

Heavy metals are often detected in industrial and domestic wastewater sometimes. Toxic metals such as Copper(II) and Zinc(II) were discharged into environment from mining, mining and surface finishing industries, paper, petroleum, copper and brass plating (Figueira *et al*., 2000; Auku and Kutsal, 1998). At acidic pH Zn(II) is the predominant species and zinc hydrolyses could be negligible. However, the formation of $Zn(OH)_2$ complexes prevents further adsorption of Zn(II) at basic pH range (Karithikeyan *et al*., 2003; Mohan and Singh, 2002). Cu(II) ions precipitated because of the concentration of OH^- ions in the biosorption medium when pH value was higher than 5.5 (Sağ and Kutsal, 2000). One has been looking for inexpensive technologies with less-than-optimal efficiencies as a strategy for countering economic restraints to the control of metal pollution. Biosorption is an innovative technology for the removal of heavy metals from aqueous solutions. A wide application of this alternative process is strictly related to the selection of efficient and low cost metal biosorbents. To date, a vast array of biomaterials have been tested as biosorbents for heavy metal removal, such as marine algae, fungi, wasted activated sludge, digested sludge and so on (Khoo and Ting, 2001; Kaewsarn, 2002; Chang *et al*., 1997). However, most biosorbents currently used are in form of suspended biomass. The major problems associated with the suspended sludge are separation of the used biosorbent from the treated effluent and difficulty in maintenance of biosorbent stability. Consequently, these drawbacks indeed limit application of biological process in the removal of metals from wastewater. Aerobic granules are microbial aggregates with spherical outer shape, compact structure and excellent settling ability. Similar to any biological processes, aerobic granules have to be discharged from bioreactor regularly, which can be regarded as secondary waste. This study thus looked into the feasibility of using waste aerobic granules as a novel type of biosorbent for the removal of copper(II) and zinc(II) from aqueous solution.

Materials and methods

The aerobic granules used for biosorption tests were collected from a laboratory-scale, sequencing batch reactor (SBR) fed with acetate as sole carbon source. The operational conditions and set-up of the reactor can be found elsewhere (Tay *et al.*, 2001). The average diameter of the mature aerobic granules was about 1.0 mm. Copper(II) and zinc(II) were used as model metals. The concentrated solutions of copper(II) and zinc(II) were prepared by dissolving $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ into de-ionized water, respectively. Two series batch experiments were carried out. (i) The initial individual metal concentration (C_o) varied in the range of 2 to 100 mg/L, while the initial granule concentration (X_o) was kept at 100 mg dry weight/L. (ii) In this series of tests, the initial aerobic granules concentration (X_o) ranged from 50–300 mg/L, but the initial individual metal concentration (C_o) was maintained at 100 mg/L. All batch tests were conducted in 1 L glass beaker with gentle agitation at a temperature of 26°C. Each test lasted 3 to 4 h, and initial pH was controlled at around 5. Soluble Cu^{2+} and Zn^{2+} concentrations were analyzed using Inductively Coupled Plasma Emission Spectrometry (ICP) (Perkin-Elmer P400).

Results

Kinetics studies

According to the first-order reversible reaction kinetics, Liu *et al.* (2003) proposed the following model to describe heavy metal biosorption on the surface of aerobic granules:

$$Q_t = Q_e\,(1 - e^{-kt}) \tag{1}$$

where Q_t is the metal concentration on the aerobic granule surface at time t, mg metal per g granules. Q_e is the biosorption capacity at the equilibrium. k is the overall biosorption rate constant of the metal, min^{-1}. Eq. (1) was used to fit the experimental results obtained (Figures 1 and 2). It can be seen that Eq. (1) prediction is in good agreement with the experimental data. In study of biosorption, the second-order equation proposed by Benguella and Benaissa (2002) was also applied with the following form:

$$\frac{dQ_t}{dt} = k_2\left(Q_e - Q_t\right)^2 \tag{2}$$

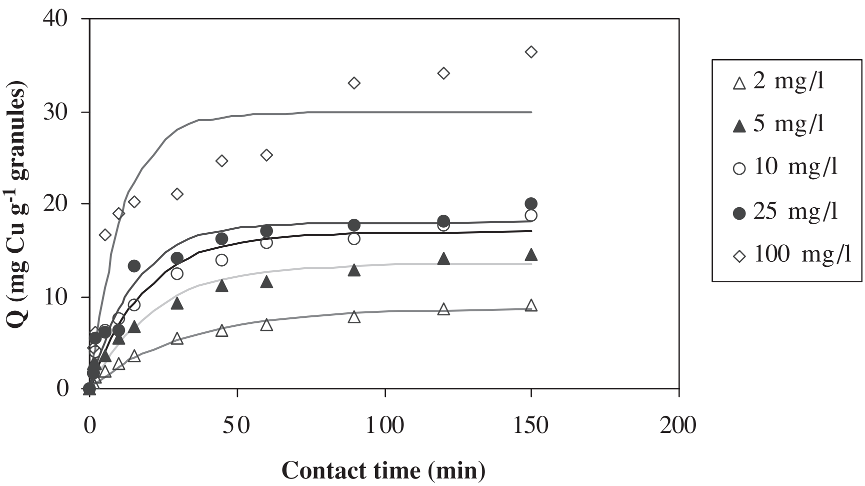

Figure 1 Biosorption profiles of copper(II) at different initial copper(II) concentrations. Eq. (1) prediction is shown by solid curve

Integration of Eq. (2) yields

$$Q_t = Q_e \frac{Q_e k_2 t}{1 + Q_e k_2 t} \tag{3}$$

where k_2 is the rate constant of the second-order adsorption, g mg^{-1} min^{-1}. An example of curve fitting by two models is given in Figure 3 for an initial copper(II) concentration of 50 mg/L.

Effect of initial metal concentration on its biosorption kinetics

Figures 1 and 2 show the respective biosorption profiles of Cu^{2+} and Zn^{2+} at different initial metal concentrations. The zinc(II) biosorption by aerobic granules reached the equilibrium

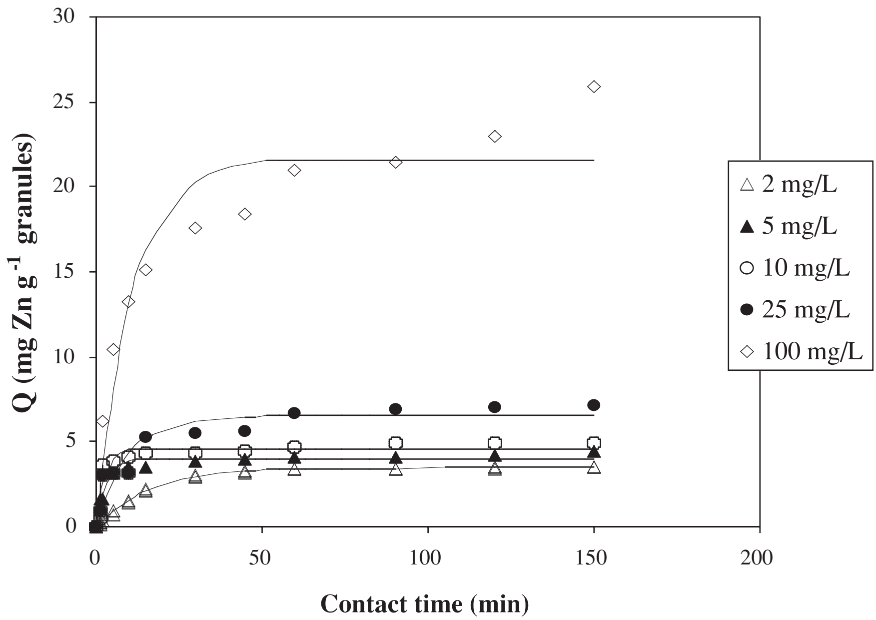

Figure 2 Biosorption profiles of zinc(II) at different initial zinc(II) concentrations. Eq. (1) prediction is shown by solid curve

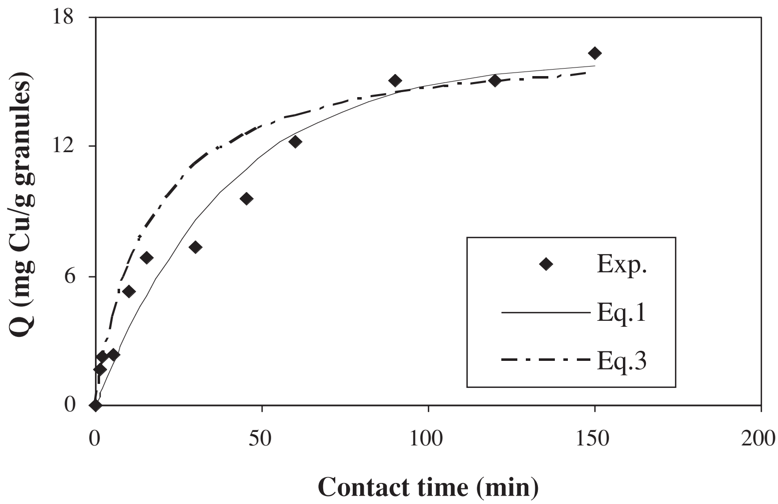

Figure 3 Comparison of Eqs (1) and (3)

within 60 minutes, while the biosorpion equilibrium of copper(II) onto aerobic granules was attained after 100 min contact. It appears from these two figures that at a fixed biomass concentration, the metal biosorption capacity increased with increasing initial metal concentration. Khoo and Ting (2001) also reported that an increase in initial gold concentration led to an increase in the specific gold uptake at a fixed cell loading. Figure 4 further shows the effect of initial copper(II) concentration on the overall biosorption rate constant and biosorption capcity by aerobic granules. It was found that the overall biosorption rate constant determined by Eq. (1) was proportionally related to the initial copper(II) concentration, and a similar trend was observed for the biosorption capacity at equilibrium. For comparison purpose, Figure 5 displays the biosorption of individual copper(II) and zinc(II) under the same conditions. It seems that the affinity between aerobic granules and copper(II) is much higher than that between granules and zinc(II).

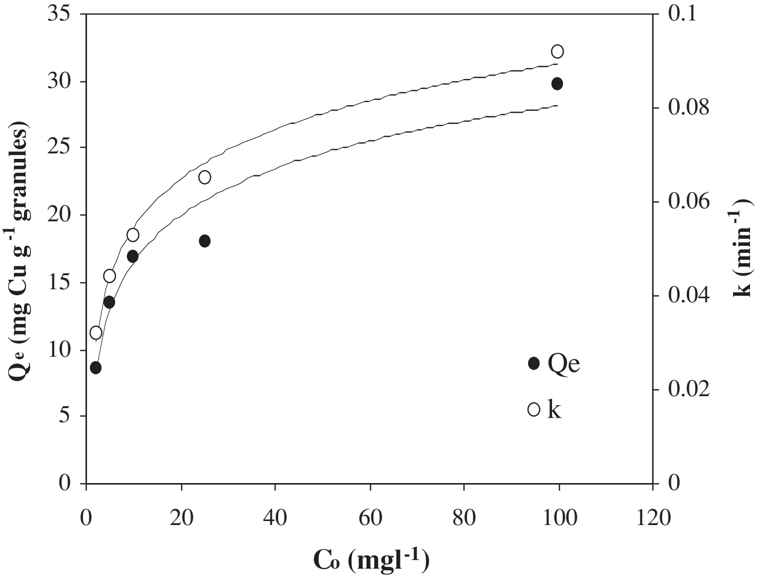

Figure 4 Effect of initial copper(II) concentration on Q_e and k determined by Eq. (1)

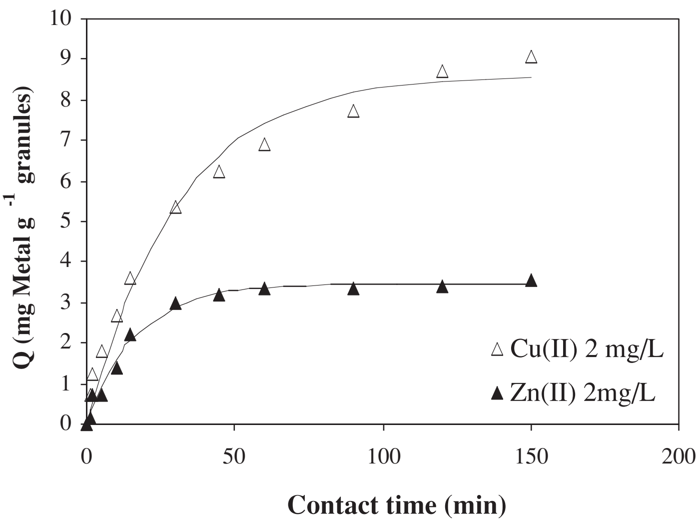

Figure 5 Comparison of copper(II) and zinc(II) biosorption by aerobic granules at an initial metal concentration of 2 mg/L

Effect of initial granule concentration on Cu^{2+} and Zn^{2+} biosorption kinetics

The effect of initial granule concentration on Cu^{2+} and Zn^{2+} uptake was shown in Figure 6. At a fixed metal concentration, an increase in the aerobic granules concentration leads to a decrease in the specific metal biosorption capacity.

Discussion

It can be seen from Figures 1 and 2 that the kinetic model developed by Liu *et al*. (2003) provides a good prediction for the experimental data obtained at various initial metal concentrations, while Tables 1 and 2 summarize the fitting results of two models. It can be seen that the second-order kinetic model (Eq. (3)) can not, and even fails to fit some experimental data obtained. Figure 6 indicates that copper(II) and zinc(II) removal by aerobic granules declines with an increase of the initial granule concentration. Similar trend was also observed in the biosorption of gold by immobilized fungal biomass (Khoo and Ting, 2001) and biosorption of zinc(II) by HZM-1 (Taniguchi *et al*., 2001). It had been proposed that the decrease of the specific uptake capacity at high biomass concentration was mainly due to dilution of the metal with the increased biomass concentration (Taniguchi *et al*., 2001).

Biosorbents currently used are in the form of freely-suspended biomass. Some problems associated with freely-suspended biomass include the need for separation of the suspended biomass from the aqueous medium and the possible clogging of pipelines and filters (Khoo and Ting, 2001). These problems can be overcome by the immobilization of the biomass. However, the immobilization technique is very complex and expensive. Compared with conventional bioflocs, aerobic granules have the advantage of high microbial density and excellent settling ability. In this study, the settling velocity of the used aerobic granules was about 71 m h^{-1}, which was at least 5 times higher than that of microbial flocs. Aerobic

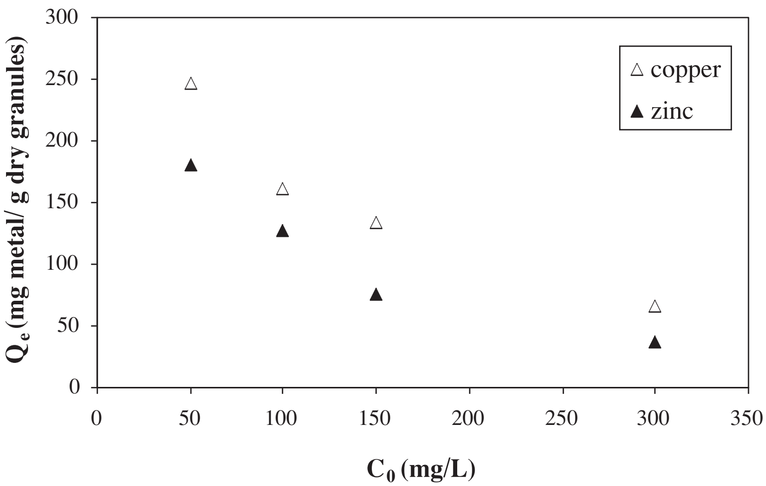

Figure 6 Effect of initial granules concentration on Q_e

Table 1 Comparison of two kinetic models on Cu^{2+} biosorption

Initial copper(II) concentration (mg/L)	Q_e (mg/g)	Eq. (1) k (min^{-1})	R^2	Eq. (3) k_2 (g mg^{-1} min^{-1})	R^2
2	8.7	0.032	0.98	0.0064	0.99
5	13.6	0.045	0.97	0.0043	0.97
10	17.0	0.053	0.96	0.0037	0.97
25	18.0	0.066	0.95	0.0031	0.92
100	29.8	0.092	0.87	0.006	0.64

Table 2 Comparison of two kinetic models on Zn^{2+} biosorption

Initial zinc(II) concentration (mg/L)	Q_e (mg/g)	Eq. (1) k (min^{-1})	R^2	Eq. (3) k_2 (g mg^{-1} min^{-1})	R^2
2	3.5	0.061	0.99	0.018	0.99
5	4.0	0.310	0.95	Failure	
10	4.6	0.416	0.89	Failure	
25	6.5	0.106	0.90	0.007	0.70
100	21.6	0.093	0.94	0.0023	0.68

granules can be completely separated from the treated effluent in one minute after the biosorption tests. The desorption test was also carried out to investigate the possibility of recovering the adsorbed Cu(II) and Zn(II) from aerobic granules. After stirring the contaminated granules gently in 0.1M HCl for 4 hours, more than 90% of adsorbed Cu(II) and Zn(II) could be recovered from aerobic granules into aqueous solution. It is expected that the aerobic granule-based biosorption process could be an efficient and cost-effective technology for the removal of heavy metal from industrial wastewater streams.

Conclusion

It appears from this study that the adsorption capacity of copper(II) and zinc(II) by aerobic granules is strongly related to initial metal and granule concentrations. The excellent settleability of aerobic granules can ensure a rapid separation of biosolids from the treated effluent, which in turn leads to a simple process design. This study shows that aerobic granules could be an effective biosorbent for efficient copper(II) and zinc(II) removal from industrial wastewater.

References

Aksu, Z. and Kutsal, T. (1998). Determination of kinetic parameters in the biosorption of copper(II) on *Cladophora* sp., in a packed bed column reactor. *Proc. Biochem.*, **33**(1), 7–13.

Benguella, B. and Benaissa, H. (2002). Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies. *Water Res.*, **36**(10), 2463–2474.

Chang, J.S., Law, R. and Chang, C.C. (1997). Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa PU21*. *Water Res.*, **31**(7), 1651–1658.

Figueira, M.M., Volesky, B., Ciminelli, V.S.T. and Roddick, F.A. (2000). Biosorption of metals in brown seaweed biomass. *Water Res.*, **34**(1), 196–204.

Kaewsarn, P. (2002). Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp. *Chemosphere*, **47**(10), 1081–1085.

Karthikeyan, G., Anbalagan, K. and Andal, N.M. (2003). Adsorption dynamics and equilibrium studies of Zn(II) onto chitosan. *J. Chem. Sci.*, **116**(2), 119–127.

Khoo, K.M. and Ting, Y.P. (2001). Biosorption of gold by immobilized fungal biomass. *Biochem. Eng. J.*, **8**(1), 51–59.

Liu, Y., Yang, S.F., Xu, H., Woon, K.H., Lin, Y.M. and Tay, J.H. (2003). Biosorption kinetics of cadmium(II) on aerobic granule sludge. *Process Biochem.*, **38**(7), 997–1001.

Mohan, D. and Singh, K.P. (2002). Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from *bagasse* – an agricultural waste. *Water Res.*, **36**(9), 2304–2318.

Sağ, Y. and Kutsal, T. (2000). Determination of the biosorption heats of heavy metal ions on *Zoogloea* and *Rhizopus arrhizus*. *Biochem. Eng. J.*, **6**(2), 145–151.

Taniguchi, J., Hemmi, H., Tanahashi, K., Amano, N., Nakayama, T. and Nishim, T. (2001). Zinc biosorption by a zinc-resistant bacterium, *Brevibacterium sp.* strain HZM-1. *Appl. Microbiol. Biotechnol.*, **54**(4), 581–588.

Tay, J.H., Liu, Q.S. and Liu, Y. (2001). The effects of shear force on the formation, structure and metabolism of aerobic granules. *Appl. Microbiol. Biotechnol.*, **57**(1,2), 227–233.