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RESEARCH NOTES

Heavy Metal Adsorption Properties of Marine Algae *Durvilliea Potatorum*, *Ecklonia Radiata* and *Laminaria Japonica*

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1 INTRODUCTION

Biosorption of heavy metals using biosorbents derived from suitable biomass is a new technology for the removal and recovery of heavy metals from industrial waste waters. The advantages of the biosorption technology include rapid reduction of dissolved heavy metal ions concentration to 10^{-6} and 10^{-9} levels, use of inexpensive and non-hazardous biosorbents, use of existing adsorption process equipment and therefore low operating costs, high uptake capacity and specificity for selective heavy metal removals, and low interference from other components such as light metal ions that may exist in high concentrations in waste water streams. The limitations of the technology are that large scale production of effective biosorbent materials has not yet been established and that the technology has only been tested for a limited industrial application.

Various types of biomass available from natural sources, from cultivation or as industrial by-products have been studied for their adsorption properties for heavy metals. These include bacteria[1,2], fungi[3,4], algae[5,6] and others[7,8]. They frequently have high capacities for heavy metal uptakes, with reported values typically ranging from 0.05 to 1 mmol • g^{-1}. We have studied a number of biomass types for their heavy metal adsorption properties and identified a group of marine algae (*Durvilliea potatorum*, *Ecklonia radiata* and *Laminaria japonica*; commonly known as brown algae) having much higher heavy metal uptake capac ities than other types of biomass. Biosorbents derived from the biomass of these marine algae generally have heavy metal uptake capacities similar to , or better than synthetic ion exchange resins. For example, the uptake capacity of the biomass of *Ecklonia radiata* for lead at pH 5 is around 1.5 mmol • g^{-1}, while the resin capcity is typically around 1 mmol • g^{-1} (normal range 0.5 — 1 mmol • g^{-1}). The biosorbents have the additional advantage of low

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interference from light metal ions whose relative affinities are much lower than those of heavy metal ions. In this paper we report the adsorption properties of the marine algae biomass for various heavy metal ions. The adsorption properties were also compared with those of fungal biomass, a powdered activated carbon and a natural zeolite.

2 MATERIALS AND METHODS

The raw biomass of *Ecklonia radiata* was collected from New South Wales, Australia; that of *Durvilliea potatorum* was obtained from Tasmania, Australia; that of *Laminaria japonica* was obtained from Dalian, China, and that of *Phellinus badius* was collected from Brisbane, Australia. The samples were dried at 60℃ and ground to granules of 300—600 μm. A coconut base powdered activated carbon (Pica) and an Australian natural zeolite (Zeolite Australia) were purchased from commercial sources. Their average particle size is around 70 μm. All adsorption properties were measured with standard batch equilibrium experiments. Each vial contained 200 mg of biomass and 100 ml of selected heavy metal solutions of known concentration and the contents were shaken at room temperature (21℃) for 24 hours in a rotating shaker. The initial concentrations of the heavy metal ions ranged from 0.2 to 3.5 mmol • L^{-1}. The biomass were removed by filtration through a 0.45 μm membrane filter (Millipore) and the filtrates were analysed for residual heavy metal concentrations by flame atomic absorption spectrophotometry (Varian).

3 RESULTS AND DISCUSSION

The adsorption equilibrium isotherms of various heavy metal ions on the biomass *E. radiata* are shown in Fig. 1. The isotherm curves can generally be fitted with the Langmuir equation (not shown). The adsorption capacities for the heavy metals ranged from about 0.3 mmol • g^{-1} for Ag^{+} to 1.5 mmol • g^{-1} for Pb^{2+}. The values for Pb^{2+}, Cu^{2+} and Cd^{2+} are comparable to those of commercial ion exchange resins. Fig. 1 also shows that the equilibrium isotherms of Pb^{2+}, Cu^{2+} and Cd^{2+} have steep initial slopes, indicating high adsorption affinities of the biomass for the heavy metal ions.

During the experiments for Fig. 1, the solution pH value of the batch system was not controlled. It was observed that the solution pH value tended to drop off with the increasing uptake of heavy metal by the biomass. The final pH value of the solution varied from 5.5 to 4.5. Further experiments revealed that the adsorption of heavy metals is sensitive to pH value. A low pH value of the solution reduces the adsorption capacity. At pH 1 or lower, the adsorption capacities for the heavy metal ions are almost negligible. As the pH value increases, the adsorption capacities increase exponentially, and then level off to reach maximum values at pH 4—5. Details of the pH value dependence of Pb^{2+} biosorption onto biomass of *E. radiata* have been discussed elsewhere[9].

Fig. 2 shows the adsorption isotherms of Pb^{2+} and Cu^{2+} onto the biomass of three marine algae. The three species belong to the same family of marine algae. Although found in different areas, they have similar chemical constituents and similar biosorption properties. In Fig. 2, the six equilibrium isotherms are much alike, with small variations observed. All three species showed high uptake capacities and binding affinities for the two heavy metal ions. We expect that the other adsorption properties would also be similar among the three species.

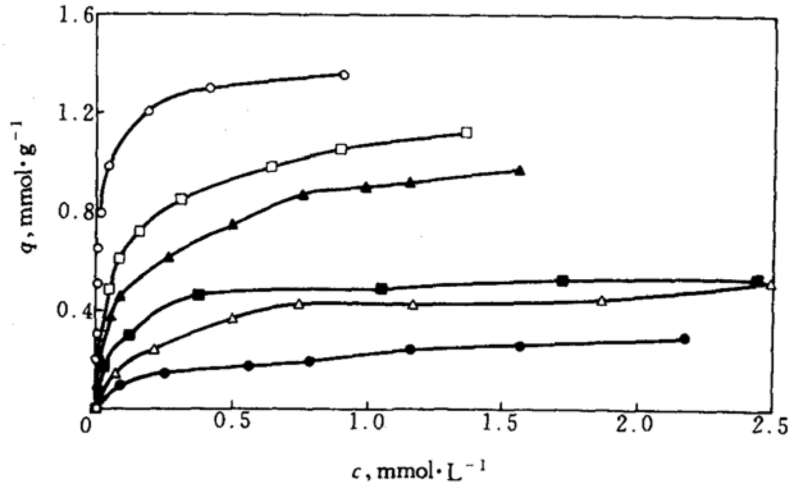

Figure 1 Equilibrium isotherms of various heavy metal ions on *E. radiata*
(biomass 2 g · L^{-1}, solution pH value not adjusted)
○ Pb^{2+}; □ Cu^{2+}; ▲ Cd^{2+}; ■ Fe^{3+}; △ Mn^{2+}; ● Ag^{+}

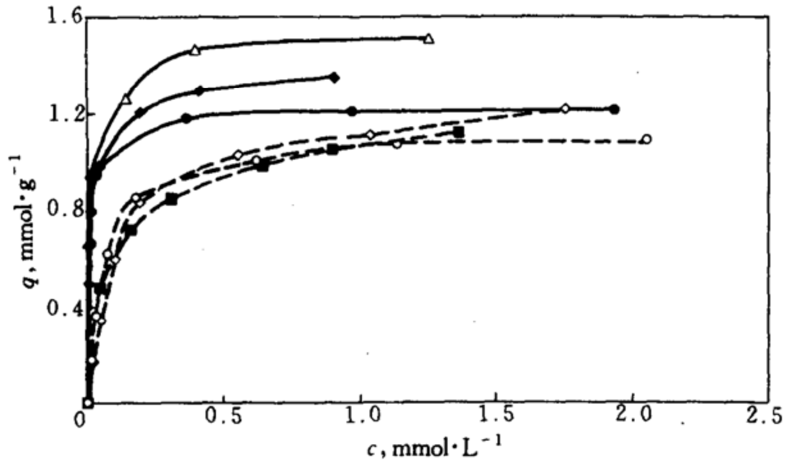

Figure 2 Equilibrium isotherm of Pb^{2+} and Cu^{2+} on *E. radiata* (E. R.), *D. potatorum* (D. P.), *L. japonica* (L. J.) (biomass 2 g · L^{-1}, solution pH value not adjusted)
◆ E. R.-Pb; △ D. P.-Pb; ● L. J.-Pb; ■ E. R.-Cu; ◇ D. P.-Cu; ○ L. J.-Cu

A comparison of the adsorption isotherms between the biomass of marine algae (*E. radiata*) and the biomass of two fungal species (*Phellinus badius* and *Rhizopus arrhizus*), a powdered activated carbon (PAC) and an Australian natural zeolite is given in Fig. 3. The data for *R. arrhizus* were obtained from the literature [10]. The adsorption capacity of the marine algae far exceeds those of the fungal biomass, activated carbon and zeolite. This indicates that highly efficient biosorption systems can be developed for heavy metal removal and recovery.

Another unique advantage of heavy metal biosorption using biomass is the low interference effects from light metal ions which may be present in the aqueous phase in high concentration. This is illustrated in Fig. 4 for the case of Cu^{2+} removal using biomass *E. radiata*. As can be seen from Fig. 4, the removal efficiency for Cu^{2+} was not significantly affected by the presence of Na^{+} and K^{+}, even at a concentration of 10 mmol · L^{-1}(10 times that of the initial concentration of Cu^{2+}). The interference effects from Mg^{2+} and Cu^{2+} are about 10% and 20% at a concentration of 10 mmol · L^{-1}. Thus the relative affinities of the light metal ions are low for the biomass of the marine algae.

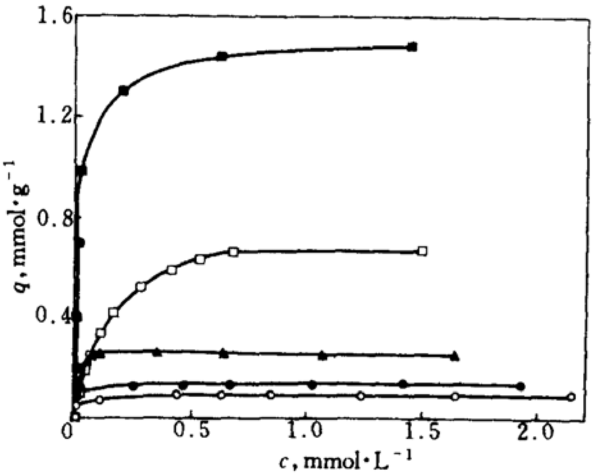

Figure 3 Equilibrium isotherm of Pb^{2+} on different types of adsorbents

(biomass 2 g · L^{-1}, solution pH 5.0)

■ *E. radiata*; □ *P. badius*; ▲ *R. arrhizus*; ● PAC; ○ zeolite

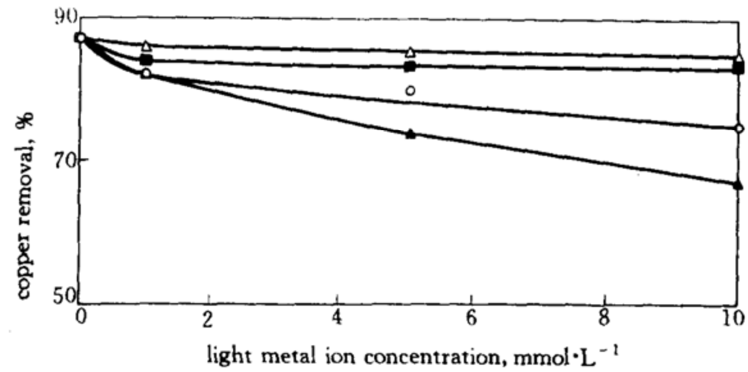

Figure 4 Cu^{2+} removal efficiencies in the presence of light metal ions

(biomass 2 g · L^{-1}, solution pH 4.0, initial Cu^{2+} concentration 1 mmol · L^{-1})

△ Na^{+}; ■ K^{+}; ▲ Ca^{2+}; ○ Mg^{2+}

4 CONCLUSION

This work indicated marine algae *Durvilliea potatorum*, *Ecklonia radiata* and *Laminaria japonica* have high adsorption capacities and binding affinities for many heavy metal ions, especially for Pb^{2+}, Cu^{2+} and Cd^{2+}. The adsorption capacities of the marine algae biomass are comparable to those of commercial ion exchange resins, higher than those of other types of biomass studied, and much higher than those of activated carbon and natural zeolite. In addition, the adsorption affinities of biomass for light metal ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) are much lower and thus interference from these light metal ions are relatively small. A high potential exists for the development of highly efficient biosorbent materials and biosorption technology for the removal and recovery of heavy metals from aqueous solutions.

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NOMENCLATURE

c concentration, mmol • L^{-1}

q the adsorption capacities for the heavy metals, mmol • g^{-1}

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