Competitive adsorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions onto *Eichhornia crassipes* in binary and ternary systems

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ABSTRACT

A batch sorption technique was used to study the biosorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions onto the vastly abundant water hyacinth weed, *Eichhornia crassipes* biomass in binary and ternary systems at a temperature of 30 °C and pH 4.84. Mutual interference effects were probed using equilibrium adsorption capacity ratios, q'_e/q_e, where the prime indicates the presence of one or two other metal ions. The combined action of the metals was found to be antagonistic, and the metal sorption followed the order $Pb^{2+} \gg Cd^{2+} \gg Zn^{2+}$. The behaviour of competitive biosorption for Pb–Cd and Pb–Zn combinations were successfully described by the Langmuir Competitive Model (CLM), whilst the model showed poor fitting to the Cd–Zn data. In conclusion, Pb^{2+} ions could still be effectively removed from aqueous solution in the presence of both Cd^{2+} and Zn^{2+} ions, but removal of the Cd^{2+} and Zn^{2+} ions would be suppressed in the presence of Pb^{2+}.

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1. Introduction

In recent times, research activities on biosorption of heavy metals have focused on sorption from multi-component systems (Marques et al., 1999; Hasan et al., 2007; Çeribasi and Yetis, 2001; Fagundes-Klen et al., 2007; Ghani-Abdel et al., 2008; Pérez-Marín et al., 2008; Plazinski and Rudzinski, 2009). Studies on multi-metal systems have shown competitive interactions amongst metals for binding onto sorption sites. The mutual interference effects depend on the metals under study. For example Figueira et al. (1997) showed that 1.5 mM Fe caused 24% reduction in cadmium biosorption but a similar concentration Cd caused up to 45% reduction in sorption of Fe by *Sargassum* sp. from a binary system. Srivastava et al. (2006) reported that the equilibrium metal removal decreased with increasing concentrations of the other metal ion and the combined action of Cd(II) and Zn(II) ions on the biomass was found to be antagonistic.

Among plants that have been studied for their uptake of heavy metals from aquatic systems, *Eichhornia crassipes* has been shown to possess the ability for the sorption of several heavy metals (Aowal and Singh, 1982; Attar and Maly, 1982; Muramoto and Oki, 1983; Stratford et al., 1984; Delgado et al., 1993; Zaranyika and Ndapwadza, 1995; Schneider et al., 2001; Soltan and Rashed, 2003; Wang and Lewis, 1997; Verma et al., 2007). Ambe et al.

(1985) used a tracer technique and Mössbauer spectroscopy to study the distribution and chemical states of iron and cobalt in living *E. crassipes* cultivated with a nutrient solution containing isotopes of the metals. Their results showed that both metals tended to accumulate mainly in the roots of the weed. On studying the contribution of *E. crassipes* grown under different conditions to Fe-removal mechanisms in constructed wetlands, Jayaweera et al. (2008) concluded that *E. crassipes* grown under nutrient poor conditions was ideal for the removal of Fe from wastewater. Lu et al. (2004) showed that Cd and Zn had effects on *E. crassipes* relative growth and the living plant was a moderate accumulator of both ions. Schneider et al. (1995) reported that *E. crassipes* roots accumulated very high levels of several divalent metal ions in the living plant. The potential of using the living plant to remove toxic metals from petroleum refinery effluents was investigated by Ismail and Beddri (2009), who reported limited success for the case of Fe and Zn and acknowledged the need for further research on the area.

It is evident from reported findings that very limited work has been carried out on biosorption using non-living forms of *E. crassipes.* Low et al. (1995) investigated the potential of the non-living biomass as a biosorbent for methylene blue and Victoria blue dyes from aqueous solution and indicated high adsorption capacities. In our paper on single component biosorption studies (Mahamadi and Nharingo, 2007), we showed that *E. crassipes* had a greater quest for cadmium than green alga samples.

Cleary, although several studies have documented that *E. crassipes* is good metal accumulating plant, none of these have documented the removal of these metals in binary and tertiary systems using non-living, dried forms of the plant. Carrying out competitive adsorption studies using *E. crassipes* would therefore

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generate very useful information on the potential of the non-living biomass to remove toxic metals from these systems. The present work has therefore been addressed to the study of sorption dynamics of Pb^{2+}, Zn^{2+} and Cd^{2+} ions during their biosorption by inactive *E. crassipes* roots from binary and ternary systems.

2. Methods

2.1. Materials

Mature plants were collected from Lake Chivero in Harare, washed on-site three times with Lake water and carefully packed in polythene bags previously cleaned by soaking in 10% nitric acid. The plants were then placed in a fishpond filled with tap water at Bindura University of Science and allowed to grow. After four weeks the parent plants were harvested and replaced by daughter plants reproduced during the period. Five grams of NH_4NO_3 fertilizer were added in the pond to promote shoot development. Plants were harvested after four weeks, roots separated and washed three times with running tap water and twice with deionised water. They were then sun dried for two days before being oven-dried at 65 °C for 12 h. Dried samples were crushed, ground with a mortar and pestle and sieved (size fraction of 2.5 mm). The samples were then acid-treated with 0.1 M HNO_3 for 8 h followed by washing with deionised water until a pH of 7 was attained. The biomass was then oven-dried at 65 °C for 24 h. The acid pre-treatment was done to desorb any metal ions adsorbed during plant growth and to remove any debris or soluble biomolecules that might interact with metal ions. The biomass was stored in airtight containers and subsequently used in the adsorption experiments.

2.2. Equipment

Shimadzu AA-6601F Atomic Absorption and Flame Emission Spectrophotometer, KDB temperature bath supplied by Memmert Holdings, Pvt Ltd., Stuart Scientific shaker and magnetic stirrer hot plate, Vacuum suction pump – KnF neuberger Labort.

2.3. Chemicals

Chemicals used in this work were analytical reagent quality; $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$ $CdCl_2 \cdot 2.5H_2O$, NaOH, supplied by Associated Chemicals (Pvt) Ltd., HCl and HNO_3 supplied by Sky Labs (Lenasia, South Africa).

2.4. Buffer solution

Sodium acetate trihydrate 3.4 g (0.025 mol) and 1.5 ml (0.025 mol) of glacial acetic acid were placed in a 2 L volumetric flask. The mixture was diluted to the mark with deionised water to produce a buffer of pH 4.84. Further pH adjustments were done using acetic acid and 0.1 M NaOH.

2.5. Sorption equilibrium studies

The biosorption experiments were carried out using the batch equilibrium technique (Sharma et al., 2007) at 30 °C, pH 4.84, and agitating rate of 150 rpm for 3 h. The initial and residual metal ion concentrations were determined using a Shimadzu Cooperation model AA-6601F Atomic Absorption/Emission Spectrometer. Spectroscopic grade standards were used to calibrate the instrument ($r^2 \geqslant 0.998$), which was checked periodically through out the analysis for instrument's responds. The difference between the initial metal concentration and the remaining metal concentration was assumed to be bound to the biomass.

2.6. Binary system

In each experiment, 100 mg of the dried biomass sample was brought into contact with a 50 ml buffer solution containing equimolar concentrations of each cation in the 10–60 mg/l range for each of the combinations: Zn–Pb, Cd–Pb and Zn–Cd. Each of the metal ions was analyzed as described above.

2.7. Ternary system

Biosorption in the ternary system was assessed by using composite solutions containing equimolar concentrations of each cation (Pb^{2+}, Zn^{2+} and Cd^{2+}) in the 10–60 mg/l range as described above. The experiments were carried out in similar conditions as those in binary sorption systems. Each of the three cations was analyzed by flame atomic absorption spectrometry as above.

3. Results and discussion

3.1. Mutual interference effects of metal ions on biosorption

The sorption dynamics of the mixture was probed using q'_e/q_e ratios, were the prime denotes the presence of other metal ions. In general, three possible types of behavior are exhibited: $q'_e/q_e > 1$, synergism (the effect of the mixture is greater than that of the individual adsorbates in the mixture); $q'_e/q_e < 1$, antagonism (the effect of the mixture is less than that of each of the individual adsorbates in the mixture) and $q'_e/q_e = 1$, non-interaction (the mixture has no effect on the adsorption of each of the adsorbates in the mixture).

3.2. Binary system sorption

The q'_e/q_e ratios for the sorption of one metal in the presence of another metal are shown in Table 1. The ratios were all <1, indicating that the adsorption of the metals was depressed by the presence of other metal ions in the binary solution, hence the effect of the mixtures seemed to be antagonistic. The q'_e/q_e ratios for the sorption of Pb^{2+} ions in the presence of Cd^{2+} and Zn^{2+} ions were 0.68 and 0.69, respectively. These values indicate that there was no significant difference in the magnitude of suppression of Pb^{2+} ion uptake by Cd^{2+} and Zn^{2+} ions. However, the suppression effect of Pb^{2+} ions on Cd^{2+} ion adsorption ($q'_e/q_e = 0.24$) was much greater than the effect of Zn^{2+} ions ($q'_e/q_e = 0.65$). A similar trend was observed for the effect of Pb^{2+} and Cd^{2+} ions on the sorption of Zn^{2+} ions ($q'_e/q_e = 0.58$ and 0.78, respectively). Thus, these results show that in all cases, there was an inhibitory effect of one metal on binding of the other metal, with Pb showing the greatest effect. Interestingly, the overall adsorption capacities of *E. crassipes* for Pb–Cd (18.96 mg/g) and Pb–Zn (20.65 mg/g) were higher than the adsorption capacities of Cd(II) (9.92 mg/g) and Zn(II) (7.18 mg/g) ions alone, but lower than that of Pb^{2+} ions in the single component system. For that reason, the adsorption sites of Pb^{2+} may partially be overlapped with those of Cd^{2+} and Zn^{2+} in binary systems. However, the overall adsorption capacity for Cd–Zn (12.02 mg/g) was greater than the single component values for Cd^{2+} (9.92 mg/g) and Zn^{2+} (7.18 mg/g), thus suggesting that sorption sites of Cd and Zn are likely to be different. Overall, the sorption order in binary systems was found to be Pb ≫ Cd > Zn.

3.3. Ternary system sorption

The tri-metal biosorption of Pb^{2+}, Zn^{2+} and Cd^{2+} ions by *E. crassipes* was investigated to establish the effect of the presence of two metal ions on the biosorption of each one of them in equimolar