

Assessment of acids as desorbents of metal ions bound to sludge surfaces

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Abstract

Waste activated sludge has shown potential for the removal of heavy metals from solution. In order to render bioremediation of metal-contaminated effluents a suitable alternative to costly chemical treatment methods, reusability of the biomass may form an integral part of the process. Four sludges which were pre-exposed to six metal species at varying concentrations were subsequently challenged with three desorbing agents, viz. acetic acid, hydrochloric acid (HCl) and deionised water. Results showed that sludges which presented superior biosorption of metals in solution also showed superior desorption characteristics. Desorption was acid-dependent rather than sludge-dependent. Acetic acid was the most efficient desorbent for Cu and Ni and HCl was most efficient for trivalent Cr, Cd and Zn. Comparatively, the efficiency of deionised water as a desorbing agent, could be regarded as negligible.

Introduction

The economical and ecological implication of a successful biotechnological process for the remediation of metal-contaminated effluent would depend on optimum biosorption by way of superior biosorbents and moreover the ease of metal recovery for subsequent reclamation and most important, the ability to regenerate biomass for reuse in multiple adsorption-desorption cycles. From an economic standpoint, regeneration of biosorbent lowers waste treatment costs for users and can enhance profitability for biosorbent producers. Adsorption and desorption are usually coupled processes. Desorption is also known as elution, particularly in processes involving adsorbents in column configurations.

Studies have been conducted previously on assessing the feasibility of a variety of desorbing agents (Huang and Morehart, 1990). Strandberg et al. (1981), investigated uranium recovery by *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*. They employed several desorbing agents to recover metals from these cells after biosorption. *S. cerevisiae* cells were exposed to 0.1 M nitric acid, 0.1 M disodium ethylenediamine tetra-acetic acid (EDTA) and 0.1 M ammonium carbonate for 16 h and obtained only 59, 72 and 84% removal, respectively. They also attempted desorption with two other agents, viz. sodium citrate 0.1 M and potassium oxalate 1.0 M and obtained 57 and 14% removal, respectively. They did, however, report increased adsorption by biomass desorbed with ammonium carbonate, sodium citrate and potassium oxalate. Although nitric acid and EDTA decreased final adsorption of uranium, initial uptake rates were enhanced. Swalaha (1993) showed EDTA to be not as efficient and economically feasible when compared to other desorbents.

During comparison of 0.01 M EDTA with 0.1 M HCl, Mathackal et al. (1991), found HCl to be the most efficient desorbent since a small amount of Cu still remained bound to the biomass after treatment with EDTA. They postulated that the high concentrations of protons made available by the HCl may dislodge Cu from active

sites thereby making the bond between Cu and the biosorbent labile. EDTA desorption was attributable to direct competition between ligands and EDTA for Cu ions since EDTA forms a strong complex with Cu with a strong stability constant. Therefore, for present application the use of HCl was favoured when compared with EDTA. Previous research had investigated a range of desorbents. Hydrochloric and acetic acids presented superior desorption for the removal of metals investigated at concentrations of 2.5% acetic acid and 0.2 N HCl respectively (Bux et al., 1994).

The present communication forms part of a larger ongoing study focused on the development of a biotechnological process for the remediation of metal-contaminated industrial effluents. This process seeks to exploit the ability of waste sludge biomass to act as a metal biosorbent. However, metal ions bound to sludge biomass need to be desorbed in order to facilitate reuse of the biomass and either disposed of or further treated to promote complete recovery of metals. Therefore, the objective of the present study was to investigate the efficiency of desorption of the following desorbing agents, viz. deionised water, acetic acid and HCl for sludge-bound metal ions, viz. Cu^{2+} , Cr^{3+} , Cr^{6+} , Cd^{2+} , Ni^{2+} and Zn^{2+} .

Materials and methods

Pretreatment of materials

Polypropylene centrifuge tubes, vials and all glassware were soaked for 24h at ambient temperature in 5% (v/v) Extran MA-01 alkaline (Lasec, South Africa) before use to remove any resident metal. Vials and centrifuge tubes were then rinsed three times in deionised water and dried. Glassware, including pipettes were subjected to stringent acid wash procedure, i.e. rinsing in 50% (v/v) nitric acid (HNO_3) (Unilab, South Africa), followed by 50% (v/v) HCl (Unilab, South Africa) and finally rinsing in triple deionised water.

Preparation of solutions

Aqueous metal stock solutions of 1 000 $\text{mg}\cdot\text{l}^{-1}$ were prepared in 1 l volumes for immediate use as required for the initial phase of

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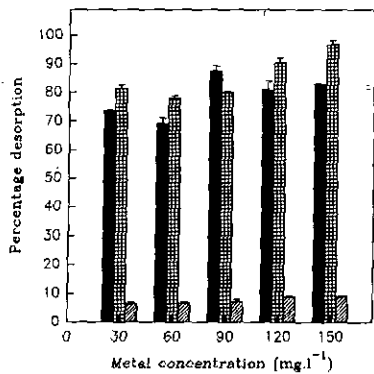


Fig. 1.

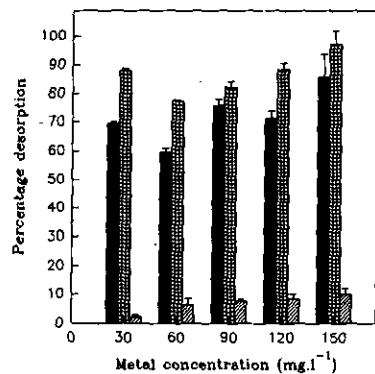


Fig. 2.

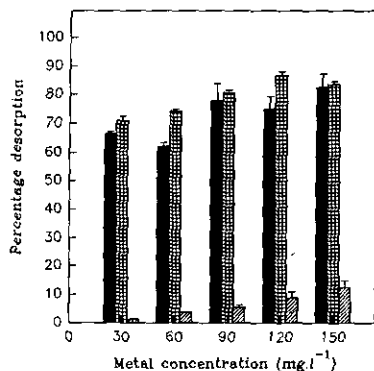


Fig. 3.

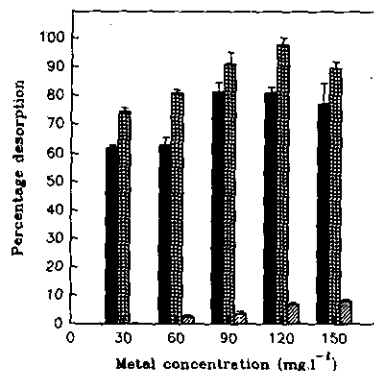


Fig. 4.

Figures 1 - 4

Percentage desorption of Zn from metal-laden sludges 1, 2, 3, and 4 respectively by acetic acid (■), hydrochloric acid (▣) and deionised water (▤)

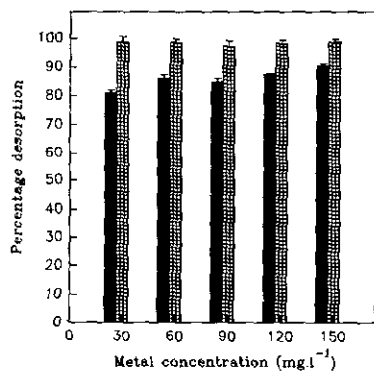


Fig. 5.

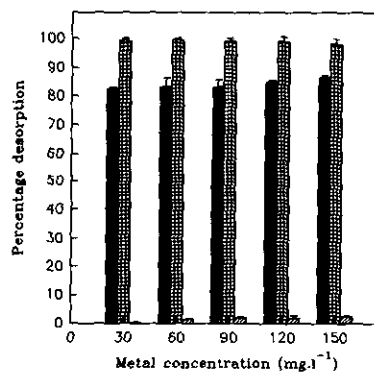


Fig. 6.

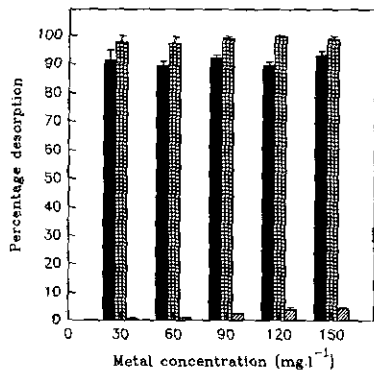


Fig. 7.

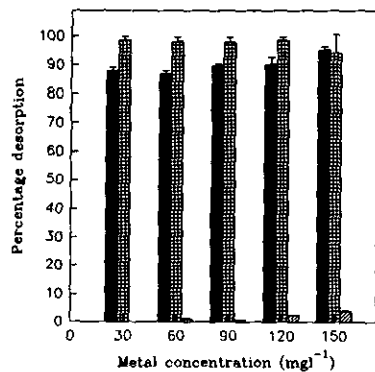


Fig. 8.

Figures 5 - 8

Percentage desorption of Cd from metal-laden sludges 1, 2, 3, and 4 respectively by acetic acid (■), hydrochloric acid (▣) and deionised water (▤)

the experiment, i.e. biosorption. Lower concentrations were prepared from the stock solution. Chemicals, $K_2Cr_2O_7$ (BDH, England), $CrK(SO_4)_2 \cdot 12H_2O$ (BDH, England), $CuSO_4 \cdot 5H_2O$ (BDH, England), $Zr(SO_4)_4 \cdot 7H_2O$ (BDH, England), $(CH_3COO)_2Cd \cdot 2H_2O$ (BDH, England) and $NiCl_2 \cdot 6H_2O$ (Hopkins and Williams, England) were of Analar grade. Chemical agents for the desorption process were freshly prepared as required. The chemicals used were 0.2 N HCl, (BDH, England) and 2.5% acetic acid (BDH, England) and deionised water.

Sludge collection and preparation

Four sludges were selected for investigation, namely, Amanzimtoti, S1; New Germany, S2; Hammarsdale, S3 and Southern Works, S4. Five litre volumes of return activated sludge (RAS) were obtained from the wastewater treatment installations in glass bottles and processed as required. Dry mass determinations of all sludges were performed by drying overnight at 105°C. Sludges were concentrated to 25 000 mg.l⁻¹ by centrifugation using a J6B Beckman centrifuge at 3 500 x g for 30 min and pellets subsequently resuspended in 100 ml deionised water and stored at 4°C for further use.

Biosorption procedure

Heavy metal species used in experiments included Cu^{2+} , Cd^{2+} , Cr^{3+} , Cr^{6+} , Ni^{2+} , Zn^{2+} . These were prepared from refrigerated 1 000 mg.l⁻¹ stock solutions when required at final concentrations of 30, 60, 90, 120 and 150 mg.l⁻¹ and at a pH of between 5 and pH 6. Experiments were performed in triplicate for each metal at all concentrations. Aliquots of 8 ml of metal solution were dispensed into polypropylene centrifuge tubes. This was followed by addition of 2 ml of 25 000 mg.l⁻¹ sludge, producing a final concentration of 5 000 mg.l⁻¹ of sludge per tube. The tubes were capped, agitated using a vortex mixer and incubated in a shaking incubator at 25°C at 150 r.min⁻¹ for 3h at a slant. This was followed by centrifugation at 4 000 x g for 30 min using a J6B centrifuge. Supernatant liquids were decanted into scintillation vials and analysed for metal ions using a Varian atomic adsorption spectrophotometer. The

remaining sludge pellets were immediately subjected to the desorption procedure. There was an average increase of 0.5 to 0.7 pH units at equilibrium after adsorption.

Desorption procedure

Centrifuge tubes containing the respective sludge pellets were exposed to 10 ml volumes of each 0.2N HCl, 2.5% acetic acid and deionised water and incubated for 12 h in a shaking incubator at 150 r·min⁻¹. After incubation the tubes were centrifuged for 30 min in a J6B centrifuge at 4 000 x g. Supernatants were decanted into a second set of pre-labelled scintillation vials and analysed for desorbed metal ions using a Varian atomic absorption spectrophotometer. The percentage(%) desorption was calculated using the following formula:

$$\% \text{ desorption} = \frac{\text{quantity desorbed (mg)}}{\text{quantity adsorbed (mg)}} \times 100$$

Results and discussion

One of the most obvious observations of the present study was that there was a definite increase in desorption of metals from sludge that produced superior biosorption. Desorption of Zn and Cd (Figs. 1 to 8) from the four sludges to which it was adsorbed showed general removal trends which were similar among the sludges, i.e. the effect was desorbent-dependent rather than sludge-dependent. Both acetic acid and HCl displayed high overall desorption efficiencies for Zn and Cd from sludges. The contribution of deionised water to desorption was very low in comparison to these two agents. Comparing the two acids, HCl was the better desorbing agent among all four sludges although acetic acid was present in greater concentrations, c.f. 0.2N to 2.5 % (approx. 0.42N). This is most probably due to the fact that HCl is a strong acid (pH 0.75) and liberates more protons to exchange with metal ions bound to the surface of sludge than acetic acid (pH 2.78), which is a weak acid. Desorption of Zn by acids at all concentrations was high indicating that ions were effectively removed. In no instance, however, was all the metal removed from the

Figures 13-16
Percentage desorption of Ni from metal-laden sludges 1, 2, 3, and 4 respectively by acetic acid (■), hydrochloric acid (▣) and deionised water (▤)

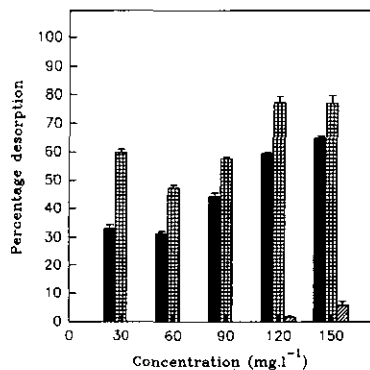


Fig. 9.

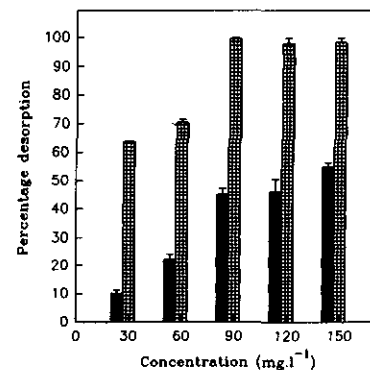


Fig. 10.

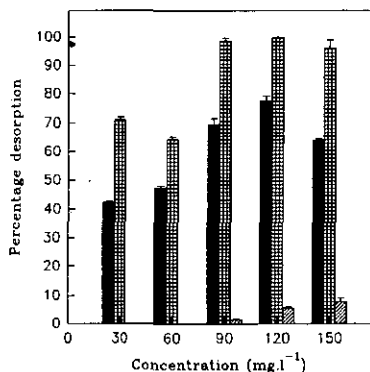


Fig. 11.

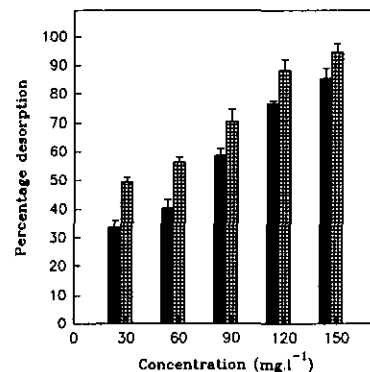


Fig. 12.

Figures 9-12
Percentage desorption of Cr(III) from metal-laden sludges 1, 2, 3 and 4 respectively by acetic acid (■), hydrochloric acid (▣) and deionised water (▤)

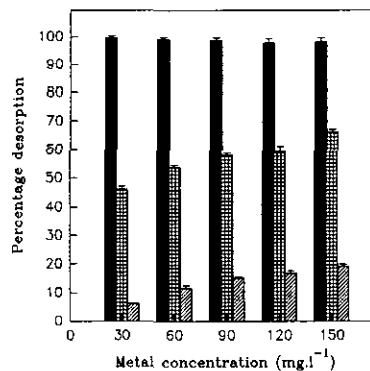


Fig. 13.

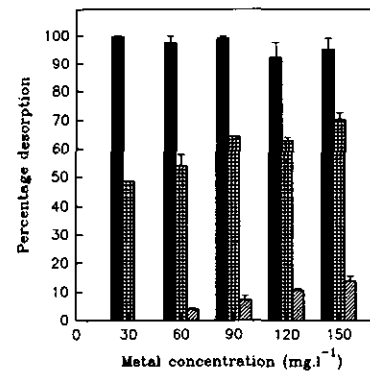


Fig. 14.

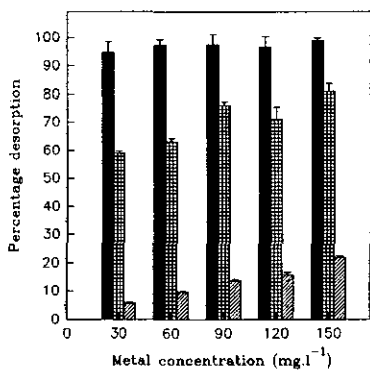


Fig. 15.

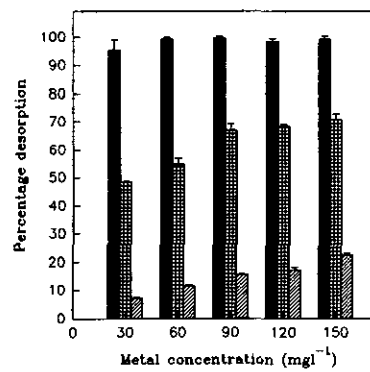


Fig. 16.

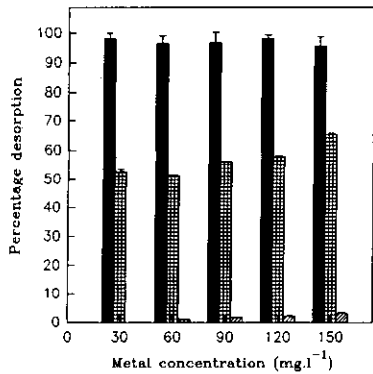


Fig. 17.

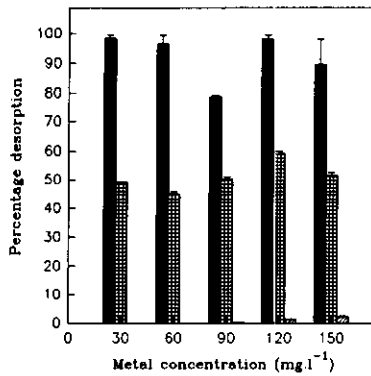


Fig. 18.

Figures 17 -20
Percentage desorption of Cu from metal-laden sludges 1, 2, 3, and 4 respectively by acetic acid (■), hydrochloric acid (▨) and deionised water (▧)

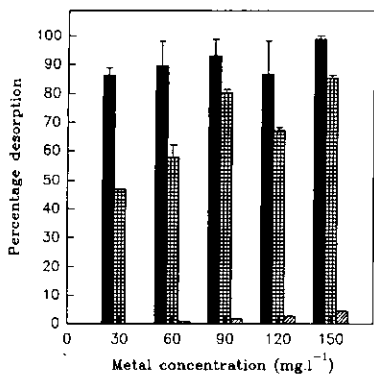


Fig. 19.

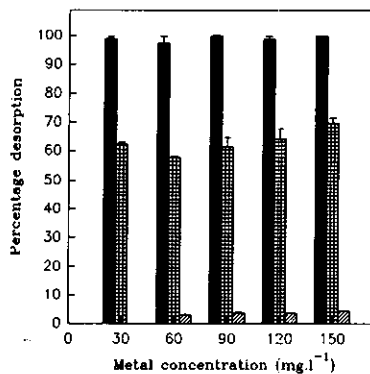


Fig. 20.

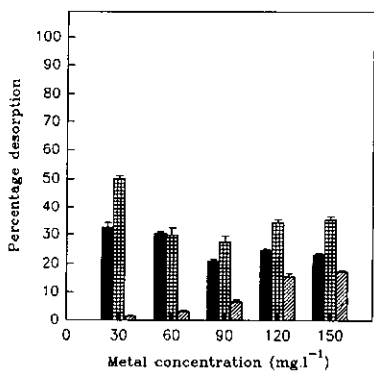


Fig. 21.

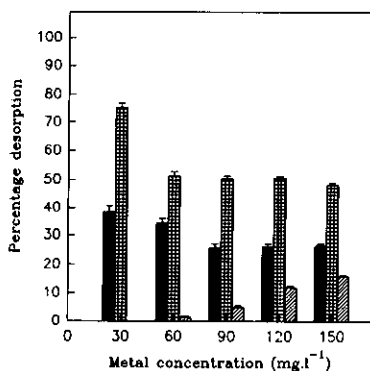


Fig. 22.

Figures 21 -24
Percentage desorption of Cr(VI) from metal-laden sludges 1, 2, 3, and 4 respectively by acetic acid (■), hydrochloric acid (▨) and deionised water (▧)

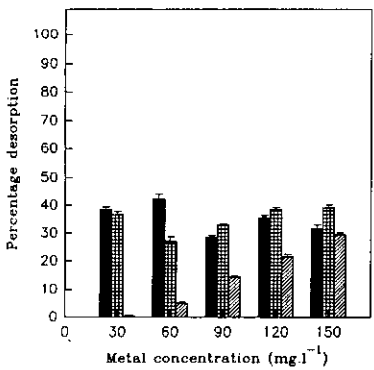


Fig. 23.

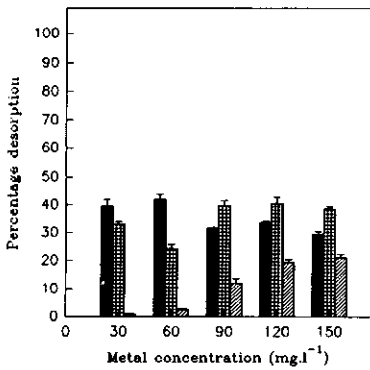


Fig. 24.

sludge surfaces. There was, however, 97% removal of Zn from sludge 4 at 120 mg·L⁻¹ (Fig. 4). Efficiencies of 96% and 97% Zn removal from sludges 1 and 2 at 150 mg·L⁻¹ were also recorded (Figs. 1 and 2). Cd desorption by HCl ranged from 94% to 98%, the former being recorded for sludge 9 at 150 mg·L⁻¹ (Fig. 8) and the latter for sludge 3 at 120 mg·L⁻¹ (Fig. 7). The results indicate that the mineral acid is a highly effective desorbing agent. These findings substantiated previous work by other researchers (Khovrychev, 1973; Tsezos, 1984 and De Rome and Gadd, 1987). Kurek et al. (1982) investigated the desorption efficiencies of 0.1N sodium hydroxide (NaOH) and 5mM diethylene triamine pentacetic acid (DTPA). They reported that the Cd sorbed to bacteria and fungi could be extracted with both agents.

Compared with other agents, Cr³⁺ was more efficiently desorbed by HCl (Figs. 9 to 12). However, the efficiency of desorption was consistently low, increasing as metal ions in solution increased. This could possibly be due to continuous progression with increasing loading from monolayer to multilayer adsorption of Cr³⁺ onto the surface of the sludge. Thus, as more layers are adsorbed, it becomes easier to desorb these surface layers, hence higher efficiencies at higher adsorption concentrations. Notably, in sludges 2 and 3 at higher concentration, desorption by HCl was almost complete. Acetic acid also progressively desorbed more Cr³⁺ from sludge surfaces as concentrations increased, reaffirming the premise that adsorption of Cr³⁺ occurs in layers upon sludge surfaces.

Desorption of Ni and Cu occurred at high efficiencies by both acids (Figs. 13 to 20). Superior desorption of metal ions was recorded at all concentrations. Previous research (Lawson et al., 1984) suggested that the two major types of adsorption were physical adsorption and chemisorption for Ni and Cu respectively. Physical adsorption occurs at room temperature and the adsorbed layers are more easily desorbed. In contrast to our findings their results showed difficulty in desorbing Cu using EDTA suggesting that Cu was bound to the sludge both by physical adsorption and chemisorption. In contrast to the metals already discussed, Ni and Cu were more efficiently removed by acetic acid than HCl. This could possibly be due to the metal cations being more amenable to form metal-acetate salts than metal-chloride salts. Therefore, since more metal ions form the acetate salt, more exchange of metal ions will occur between the bound metal on sludge and hydrogen cations liberated by acetic acid.

The formation of nickel acetate would be favoured and this is possibly why acetic acid is more efficient at desorbing Ni ions from sludge surfaces. The metals bound to sludge are not inert and can be displaced by a cation forming stronger complexes, i.e. acidification, when protonation of carboxylic acid and phenolic groupings will occur and displace the heavy metal from organic matter (McAdams, 1985). The efficiency of removal of Ni from sludge surfaces by acetic acid ranged from 92% for sludge 2 at 120 mg·L⁻¹ (Fig. 14) to 99% for sludge 4 at 90 mg·L⁻¹ (Fig. 16). Desorption efficiency of Cu, using the same desorbent, ranged between 87% (Fig. 19) for sludge 3 at 120 mg·L⁻¹ and 99% for sludge 4 at 30 mg·L⁻¹ (Fig. 20).

Cr⁶⁺ desorption was low compared with the other five metals. This could be attributed to low initial Cr⁶⁺ concentrations present in the sludge, thus resulting in poor desorption. Also, definite trends were not observed across all sludges for the two acid desorbing agents. HCl was more efficient at desorbing Cr⁶⁺ from sludges 1 and 2 than acetic acid (Figs. 21 and 22). This trend was not repeated in the other two sludges although it seemed that acetic acid was the more efficient desorbent at lower concentrations and HCl at the higher concentrations in sludges 3 and 4 (Figs. 23 and

24). Compared to the other desorbing agents, the efficiency of water as a desorbing agent could be ignored. Increasing desorption was observed as concentrations in solution increased prompting the assumption that Cr⁶⁺ was bound in layers upon the sludge surface.

For maximum benefit, desorption techniques should be highly efficient, economical, and result in minimal damage to the biomass so that subsequent adsorption is unimpaired (McLean and Beveridge, 1990). Research by Tsezos (1984), showed that high concentrations of mineral acids (1M), could cause substantial structural damage to the biomass. For the present application, reduction in the biosorptive capacity of the biomass rendering it ineffective as a biosorbent could be tolerated due to abundance in source of new biomass. In addition, in order for the sludge to be disposed of it has to conform to stringent municipal standards regulating metal content of waste sludges used for application to land (Department of National Health, 1991). The sludges used for this experiment had been tested for their biosorptive capabilities (publication submitted) and therefore were metal-laden. It was also observed that the sludges containing more resident metal, released more metal into the solution when desorbed.

Conclusion

The two acids tested, viz. acetic acid and HCl, as desorbing agents were efficient at removing metal ions from sludge surfaces. Desorption was desorbent-dependent rather than sludge-dependent. Acetic acid was the most efficient desorbing agent for Cu and Ni and HCl for Cr³⁺, Cd, Zn and Cr⁶⁺. Desorbing agents were selective with regard to efficiency of removal of metal ions from sludges. Further research seeks to investigate whether the reuse of sludge biomass as a biosorbent is affected by the use of acids as desorbing agents.

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