Waste activated sludge remediation of metal-plating effluents

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Abstract

Waste activated sludge is capable of binding and removing metal ions from solution. Sludge was exposed to an industrial metal-plating effluent, containing a range of heavy metals, in order to assess its bioadsorptive capacity. Experiments were conducted in fully mixed reactors on a batch basis. Greatest affinity was shown for the Zn cation which consistently proved to be present in untreated waste water samples in the highest concentration. Although Zn dominated the forward adsorption reaction, ionic competition amongst the other metals analysed showed Cr^{3+} and Cu to be the most weakly bound, often displaced to the soluble phase by other metal contaminants. Three agents viz., HCl, H_2SO_4 and NaCl, were assessed for their ability to desorb immobilised metals from the surface of the sludge biomass. Based upon performance and cost, H_2SO_4 showed greatest potential for further experimentation and process optimisation. This study shows that waste activated sludge, with further process optimisation, is suitable as a bioadsorbent material for the remediation of metal-plating effluents.

Introduction

The presence of heavy metals in the environment at concentrations above critical values stipulated by national and international regulatory bodies is considered unacceptable. In the local context, heavy metals in various water bodies are of major concern since South Africa is primarily a water-scarce country with extensive industrialisation and an ever-increasing population density, the majority of whom have no access to a reliable water service. Also, specific industries producing similar effluents are not localised in their various topographical regions. The problem of waste containment and recovery therefore becomes more of a diffuse than point-source pollution problem which increases treatment costs considerably.

Many workers have shown the ability of micro-organisms and/or their derivatives to bioadsorb a range of metal cations from both single and mixed-metal solutions (Oliver and Cosgrove, 1974; Sterritt and Lester, 1981; Bux et al., 1994; Duncan et al., 1994). Extensive research has established that certain microbial biomass types are able to passively bind and accumulate soluble metal species, even when metabolically inactive or dead. However, many of these studies have been conducted only from the perspective of investigating the influence on bioadsorptive capacities of single microbial species when exposed to either homogenous or heterogenous metal effluents (Tsezos and Volesky, 1982; Mattuschka and Straube, 1993; Duncan et al., 1994). Few studies have been performed to determine the bioadsorptive capacity of mixed cultures or activated sludge.

Heavy metal removal during biological treatment of waste waters is known to occur quite efficiently (>50%) (Sterritt et al., 1981). The extent of adsorption of metal salts by activated sludge *in situ* can amount to as much as 10 to 20% of total solids for Zn and Cd; 12.5 to 34% for Cu and Ni; and 18.4% for hexavalent Cr (Hanel, 1988). If, however, elevated concentrations of such metals are allowed to enter waste-water treatment installations, activated sludge may be subject to toxic shock syndrome, thereby inhibiting the sludge biomass from performing its primary function of C and nutrient removal. This will result in the production of treated waste water of inferior quality and perhaps the requirement of a major plant overhaul with resultant economic implications. It is therefore of utmost necessity that such nocuous effluents are treated at their source before discharge to the sewage system. To this end, environmental biotechnologists must become more innovative in their approach to dealing with industrial pollutants and offer industry cheaper alternatives to conventional chemical and physical remediation techniques. This in turn may improve the industrial sector's attitude and sense of responsibility towards the environment and discourage practices such as illegal waste dumping.

Biosorption experiments using various biomass types have demonstrated a certain degree of selectivity with respect to the metal bound (Gadd, 1990). Other contaminating metals present in a waste stream can interfere with the ability of the biosorbent to accumulate the desired metal. This observation has significant consequences when considering the use of a biosorbent to remove metals from heterogenous metal effluents. Bux et al. (1994) showed sludge biosorption to be of a partially non-specific nature, with greatest affinity shown for those metals present in the highest free metal-ion concentrations. They also determined that activated sludge, when exposed to various homogenous metal solutions, showed a definite order of preference for the cations i.e. $Cu>Cd>Zn>Ni>Cr^{3+}>Cr^{6+}$.

Various researchers have stated that in order to be practical for industrial application, a potential bioadsorbent material should have regenerative capacity for use in a continuous/semi-continuous system (Gadd, 1992; McHale and McHale, 1994). If, however, a cheap and abundant supply of waste biomass is used to immobilise the contaminating metals, destructive recovery techniques such as dissolution in strong acids still remain viable options. Recovery of biomass-bound metal-ions through destructive techniques implies the continuous generation of waste material which will require disposal after each treatment cycle.

The aims of this study were therefore to optimise laboratory conditions for maximum sludge biosorption of metals from a metal-plating industrial effluent, and to assess the desorptive characteristics of three potential desorbents for metal recovery.

Materials and methods

Acquisition and preparation of sludge biomass and industrial effluent

Waste activated sludge samples were collected on a weekly basis from the drying beds of a water-treatment facility dealing exclusively with domestic waste. Dependant on prevailing weather conditions and time of collection, sludge was at varying solids concentrations and therefore required standardisation, using drying techniques, prior to experimentation. All samples were dried overnight in an oven at 105^0C which provided a biomass source of extended shelf life.

Industrial effluent samples (100 ℓ) were collected from the final effluent sump of a metal-plating company producing approximately 50 m^3 effluent/d. Metal species in the various samples were identified and their respective initial concentrations determined using direct flame atomic absorption spectrophotometry (AAS) before the bioadsorption cycles were initiated. When required, initial Zn concentrations were increased using AR grade $ZnSO_4.7H_2O$ (BDH, England). If too alkaline (pH>6), effluent was acidified to 6>pH>4 using concentrated HCl in order to separate the precipitated metal-hydroxide complexes and return insoluble metal ions to the dissolved state. Regulating the pH of untreated samples in the acidic range ensured that competition between the sludge surface and other ligands i.e. hydroxyl ions, was minimised. Care had to be taken not to decrease the pH beyond an order of 4 as sludge surfaces are susceptible to dissolution at these low values which negatively affects its bioadsorptive capacity.

Bioadsorption

All experimentation was conducted on a batch basis. Sludge was added to a 40 ℓ perspex bioreactor containing 30 ℓ effluent, resulting in a final solids concentration of 25 to 30 g·ℓ^{-1}. Once sludge was introduced to the effluent, agitation commenced for a 90 min biosorption cycle. Triplicate samples (20 mℓ) were taken at 15 min intervals and placed in acid-washed scintillation vials. Samples were analysed immediately using direct flame AAS. Heavy metals analysed included Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Ni^{2+} and Zn^{2+}. Hexavalent Cr, analysed using the SABS 206 method, was not detected due to the metal-plater reducing chromium on-line using sodium metabisulphite. Differences in aqueous phase metal concentrations, both before and after treatment, were attributable to the sludge biomass. This value gave a rapid indication of process efficiency. Metal-loading capacity of sludge was calculated as follows:

$$q = (C_i - C_f).V/m$$

where:

q = metal-loading capacity of biosorbent (mg·g^{-1})
C_i = initial metal concentration (mg·ℓ^{-1})
C_f = final metal concentration (mg·ℓ^{-1})
V = batch effluent volume (ℓ)
m = dry mass of biomass (g).

Desorption

Once the bioadsorption cycles were completed, treated effluent was decanted from the reactor vessel and the remaining sludge triple-rinsed using deionised water in order to flush out or dilute any non-bound metal. Desorbent was added to the vessel at a ratio of 1:3 (desorbent:effluent treated, v/v) in order to obtain a concentrated metal solution of substantially smaller volume. Three desorbents were assessed for their eluting properties viz., hydrochloric (HCl; 0.2M) and sulphuric (H_2SO_4; 0.1M) acids and sodium chloride (NaCl; 2.0M). Triplicate samples of desorbent were taken at both zero and 15 min and the various metal species were analysed using AAS. Eluting efficiencies of the three desorbents were expressed as a percentage of initial biosorbent loadings and were determined as follows:

desorption efficiency = (quantity desorbed/quantity adsorbed) x 100%

Results and discussion

Although a mixed-metal industrial effluent was used for the duration of this study, Zn was repeatedly recorded in the highest free metal-ion concentration in the untreated effluent i.e. in effluent samples prior to bioadsorption. Metal species and their respective initial concentrations found in a typical effluent sample are shown in Table 1. Consequently, Zn appeared to dominate the forward adsorption reaction:

$$M + B \leftrightarrows MB$$
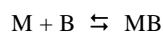
where:

M = metal
B = bioadsorbent
MB = metal-bioadsorbent complex.

Speciation plays a significant role in bioadsorption experiments and processes in mixed-metal effluents when one considers metal-ion radii and ionic charge. For electrical attractions between adsorbates and adsorbents, ions with similar ionic radii but higher ionic charge are more strongly attracted to sites of opposite charge i.e. biomass. For ions of similar charge, hydrated radius determines order of preference for adsorption with ions of smaller ionic radii being able to approach closer to potential adsorption sites (Bux et al., 1994). However, although Cr and Cu had the smaller radii of the metals analysed (0.69Å), high initial loading enhanced the removal of Zn from solution. Adsorbed Cr and Cu were subsequently returned to the aqueous phase or not sorbed at all. Competitive adsorption, therefore, seems to be more dependent upon metal loading than chemical characteristics of the various elements.

As Zn was present in the highest free metal-ion concentrations, the bioadsorption process was maximised for its removal

| TABLE 1 TYPICAL METAL-ION COMPOSITION OF INDUSTRIAL EFFLUENT SAMPLE FROM METAL-PLATING PLANT ANALYSED BEFORE TREATMENT (NO CHEMICAL ADDITION)	
Metal species	**Concentration (mg·ℓ^{-1})**
Zn^{2+}	43.4
Ni^{2+}	8.5
Cd^{2+}	1.7
Cu^{2+}	10.5
Cr^{total}	14.1
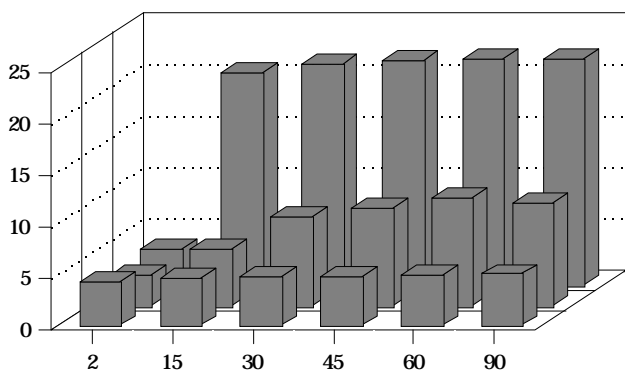
Figure 1
*Zn sorption capacity (mg·g⁻¹) of waste activated sludge
in a metal-plating effluent at initial metal concentrations
of 124.5 mg·ℓ⁻¹ (▨), 901.0 mg·ℓ⁻¹ (▦) and
1 223.0 mg·ℓ⁻¹ (▨)*
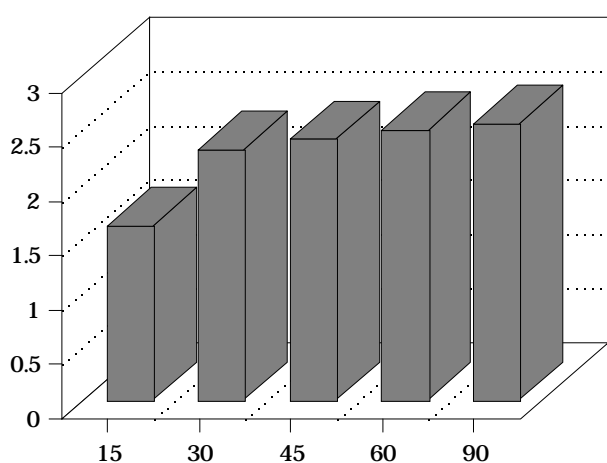
Figure 2a
*Zn sorption capacity (mg·g⁻¹) of activated sludge in a
mixed-metal industrial effluent*
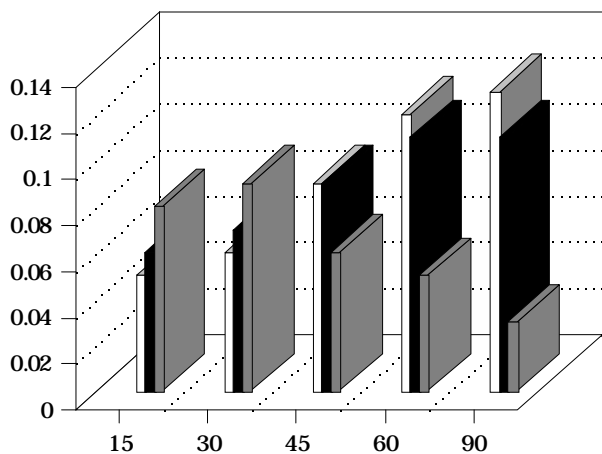
Figure 2b
*Metal sorption capacity (mg·g⁻¹) of activated sludge in a
mixed-metal industrial effluent.
Ni = (▢); Cd = (■); Cr (III) = (▨)*

for application to this particular effluent. Bioadsorption of Zn was progressive whereby a concomitant increase in sludge bioadsorption capacity (mg·g⁻¹) was recorded as soluble metal concentrations increased (Fig. 1). These findings show that sludge either has a high affinity for Zn or shows preference to those metals which are initially present in the greatest concentrations, as was found by Bux et al. (1994). Variances in sludge bioadsorption capacity throughout experimentation were attributed to differences in the concentration of bacterial extracellular polymers at different sludge sampling times. These polymers have a significant influence on metal bioadsorption as they contain chemical groups (carboxyl termini present on amino- and nucleic-acid residues) responsible for metal complexation (Brown and Lester, 1979).

Isothermal studies, used to assess the performance of a potential bioadsorbent, form an integral part of any bioadsorption study. Isotherms, determined previously for waste activated sludge bioadsorption by Bux et al. (1994), can accurately indicate the mechanism involved in microbe-metal interactions i.e. electrostatic, physical or chemical. Desirable isotherms should be steep from the point of origin, indicating a high affinity for the sorbate at low concentrations. Likewise, a high saturation plateau ensures low residual concentrations of a particular metal species in the contaminated effluent once equilibrium is obtained (Volesky, 1987). The mechanism of accumulation also dictates the ease of removal of adsorbate from loaded biomass i.e. the greater the degree of binding, the more stringent the method of recovery required (Gadd, 1992).

Bux et al. (1994) showed that sludge bioadsorption of Zn predominantly resembles a type II isotherm (according to classification by Brunaer (Ruthven, 1984)), which indicates monolayer to multilayer adsorption with increasing metal loading. This may explain why the capacity of sludge to biosorb Zn increased (5 mg·g⁻¹ to 22 mg·g⁻¹) as metal concentrations increased (Fig. 1).

High Zn loading in comparison to the other metals investigated is evident in Figs. 2a and 2b. A maximum of 2.5 mgZn/g biomass was accumulated by sludge at an initial metal concentration of 106 mg·ℓ⁻¹ (spiked with $ZnSO_4.7H_2O$) (Fig. 2a). However, superior Zn bioadsorption could be attributed to the advantage in concentration of the metal species which will enable it to compete more favourably for limited binding sites on sludge surfaces (Lester and Sterritt, 1985). Cheng et al. (1975) emphasized that concentration of metal was an imporatnt factor when comparing bioadsorption of metal in mixed solutions by biomass. Ni and Cd adsorption amounted to approximately 0.12 and 0.1 mg·g⁻¹, albeit initial metal concentrations in the influent to the sorption reactor were only 11 and 2.5 mg·ℓ⁻¹, respectively (Fig. 2b). Total Cr (in trivalent form), at an initial concentration of 0.9mg·ℓ⁻¹, was removed at a maximum capacity of 0.085 mg·g⁻¹ after 30 mins reaction time. However, due to competitive bioadsorption for limited binding sites on the surface of the biomass, the metal was displaced and returned to the aqueous phase (Fig. 2b). Once the bioadsorption cycle was completed (90 min), surface-bound Cr only amounted to 0.03 mg·g⁻¹. Cu was present at a concentration of 3.1 mg·ℓ⁻¹ in the untreated waste water yet quantities removed were negligible. It can therefore be assumed that sludge biomass can effectively be used to remove those metal contaminants which persistently appear in an industrial effluent at elevated concentrations with respect to the other metal constituents.

Zn recovery from the sludge surface was investigated using HCl, H_2SO_4 and NaCl (Table 2). Recovery efficiencies of the two mineral acids were similar and fairly high whilst those of NaCl were comparatively low. Percentage desorption in column three

TABLE 2
SOLID TO LIQUID RATIO (S/L) AND CONCENTRATION RATIO (CR) FOR HYDROCHLORIC AND SULPHURIC ACIDS AND SODIUM CHLORIDE AT INITIAL Zn CONCENTRATION OF 50 mg·ℓ^{-1}

Desorbent	S/L	% desorption	CR
0.1 M H_2SO_4	90	89	0.53
0.2 M HCl	90	85	0.51
2.0 M NaCl	90	33	0.20

TABLE 3
REUSE OF A 0.1M H_2SO_4 SOLUTION IN THREE CONSECUTIVE BIOSORPTION-DESORPTION CYCLES ANALYSING Zn AT INITIAL INFLUENT CONCENTRATION OF 95 mg·ℓ^{-1} (SPIKED)

Cycle number	Biosorption efficiency (% maximum capacity)	Desorption efficiency (% maximum capacity)	Residual Zn loading (% maximum capacity)	S/L (g·ℓ^{-1}) (desorption)	CR
1	58	75	25	90	0.43
2	57	71	29	90	0.40
3	57	34	66	90	0.19

(Table 2) depicts quantities of metal recovered by the three desorbents to those which were initially loaded onto the biomass. When assessing the efficiency of a particular desorbent it is important to consider the process concentration ratio (CR) which is the ratio of the metal concentration in the eluate to the metal concentration used to initially load the biomass (Tsezos, 1984). This value gives an indication of the efficiency of the bioadsorption process as a whole (Table 2). Desorption efficiency of any particular eluting agent is directly proportional to the amount of metal bound to the biomass i.e. biomass containing more metal of any particular species (in this instance, Zn) releases more of that metal back into solution upon desorption. Bux et al. (1995) recorded the same effect. High solid-to-liquid ratios (S/L) of the mass of loaded biomass (g) to the volume of desorbent (ℓ) ensured the production of a highly concentrated, more containable and manageable metal solution which should be the primary objective of desorption (Table 2). Based on cost, H_2SO_4 was selected as the most appropriate desorbent for further study.

In order to make the proposed bioadsorption/desorption process more feasible, a 0.1M H_2SO_4 solution was subjected to a number of desorption cycles to determine its saturation point. A high, sustainable propensity to desorb metals would reduce running costs of the process considerably as the same acid solution could be applied to a number of bioadsorption-desorption cycles before becoming exhausted. Rate and degree of saturation would be dependent upon the quantity of metal which was initially bound to the biomass. It was found that at an initial Zn concentration of 95 mg·ℓ^{-1} in untreated waste-water samples, approximately 55 mg·ℓ^{-1} (58%) was removed from the effluent and bound to the biomass (Table 3). During a subsequent desorption cycle, 75% of the bound Zn (41 mg·ℓ^{-1}) was returned to the soluble phase. This same metal-acid solution was then reused in two further cycles with fresh biomass and effluent on each occasion. All three bioadsorption cycles showed similar percentage Zn biosorbed and it was therefore possible to quantitatively elucidate the acid saturation point. During desorption, the acid became turbid and a gradual increase in its pH indicated a loss of protons, possibly due to the precipitation or accumulation of soluble Zn salts to the surface of the biomass. Protons (H^+), due to their small ionic radii and high mobility, have a high ion-exchange activity (Aldor et al., 1995). This ensured the constant removal of hydrogen ions from the system when desorbed biomass was discarded. Metal concentrations in the acid were drastically reduced during the third cycle (34% of bound metal was desorbed) indicating possible saturation and loss of acid-eluting properties (Table 3). Since metal bioadsorption is a reversible process, desorption efficiency may also have been impaired due to the increasing concentration of metal in the acid i.e. the greater the metal concentration in solution, the greater the motive force for biomass to retain surface-bound metal once a new equilibrium is attained (Aldor et al., 1995). Desorption S/L ratios of 90 g·ℓ^{-1} may therefore have been too high.

Conclusions

Bioadsorption of heavy metals by activated sludge in mixed-metal streams occurs in a non-specific fashion, with preference shown towards those metals which are present in the greatest concentrations. The biomass could therefore be applied to waste streams produced in small volumes yet containing high concentrations of contaminants (metal plating) as opposed to high-volume, low-concentration streams (mining). Sludge-bound metals can also be effectively desorbed using mineral acids although this treatment destroys the integrity of the microbial cell walls, preventing the development of a continuous treatment process. An effluent remediation process utilising sludge

bioadsorbents would therefore have to be designed for a batch procedure unless less destructive methods of biomass regeneration are investigated.

Acknowledgements

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