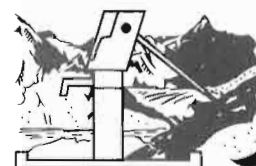




## WATER, ENVIRONMENT AND MANAGEMENT

### Potential application of waste sludges

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#### INTRODUCTION

The activated sludge process is an efficient biological method for the stabilisation of domestic and industrial wastewater. A consequence of this process is the production of substantial quantities of waste activated sludge (WAS) which can be used as fertiliser due to the high nitrogen and phosphate content. However, sludges are often contaminated with metal-ions. These sludges cannot be used as fertiliser due to the possible entry of metal-ions into groundwater and toxicity to plants and animals. Current methods available for the disposal of metal contaminated sludges include dumping at sea, incineration and burial in landfill sites. Each of these methods necessitates financial costs for the disposal of waste sludges.

Legislation governing protection of the environment is becoming progressively stricter. The treatment and disposal of industrial effluents is receiving increasing attention on a global basis. Conventional methods used for removing metals from industrial effluents include chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, application of membrane technology and evaporative recovery. These methods may be ineffective or extremely expensive especially when metals are dissolved in large volumes of solutions at relatively low concentrations (around 1 to 100 ppm). Therefore, the objective of the present study was to determine the potential of waste activated sludges for the biosorption and removal of metal-ions from solution.

#### MATERIALS AND METHOD

##### *Materials*

All glassware was soaked in 1% (v/v) Superdecontamine 33 (Lasec, South Africa) overnight before rinsing in 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally rinsing in deionised water. Chemicals,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  were of Analar grade (BDH, England).

Stocks of  $1000\text{mg.l}^{-1}$  of each metal were prepared. All subsequent solutions were prepared from these stocks. Metal concentrations were determined by flame atomic absorption spectrophotometry (AAS) using a Varian Spectra AA-10 (Varian Techtron, Australia). Return activated sludges were obtained from the Umhlatuzana Treatment Works, which operates parallel industrial and domestic treatment units. Sludges were stored overnight at  $4^\circ\text{C}$  prior to use.

##### *Biosorption by activated sludges*

Mixed liquor suspended solids (MLSS) of each sludge was determined by drying triplicate 100ml quantities of each, overnight at  $105^\circ\text{C}$  in pre-weighed porcelain dishes. Sludge concentration was adjusted to  $25000\text{mg.l}^{-1}$  MLSS by centrifugation at  $3200 \times g$ . Working solutions of each metal were prepared immediately prior to use and triplicate 8ml quantities of each were dispensed into 15ml conical polypropylene capped centrifuge vials. Aliquots of 2ml of the  $25000\text{mg.l}^{-1}$  sludges were dispensed into the tubes before sealing. This dilution factor reduced the metal concentrations in the vials to 25, 50, 75 &  $100\text{mg.l}^{-1}$  and resulted in a sludge MLSS concentration of  $5000\text{mg.l}^{-1}$ . Controls comprised 8ml of each metal solution at each concentration and 2ml of deionised water substituted for sludge. Tubes were incubated at 120 rpm (reciprocal agitation) for 3h at  $25^\circ\text{C}$ . After incubation, tubes were centrifuged at  $4000 \times g$ . Supernatants were decanted into polypropylene vials and free metals were determined by AAS.

#### RESULTS

Sludge-bound metal values were computed by subtracting supernatant values from those determined for appropriate controls. In addition, percentage metal removal by sludge from solution was calculated by relating bound metal to total metal concentrations exposed to the sludge. The results for each sludge used are shown in Figures 1 and 2.

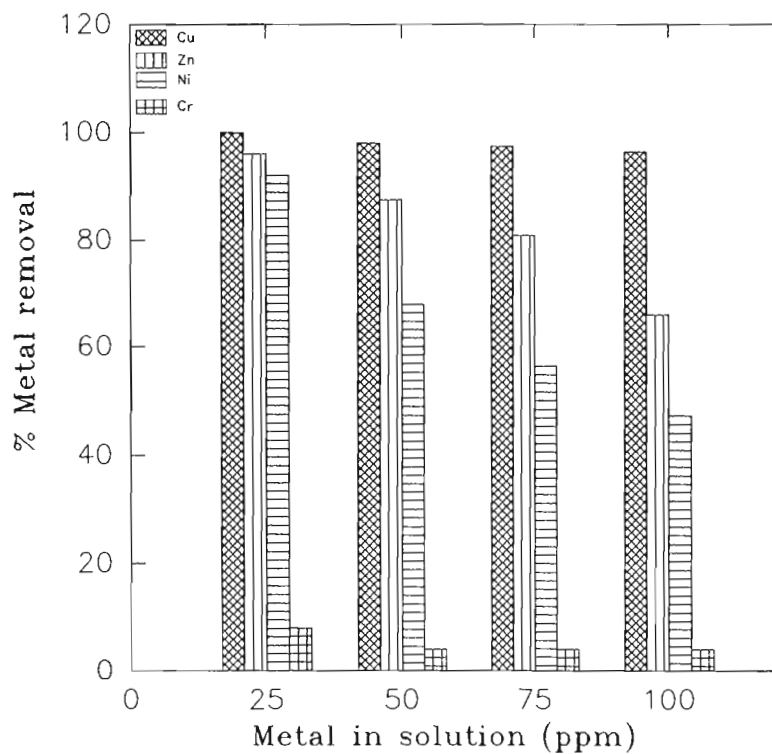


Fig. 1. Biosorption and removal of four metal-ion species by industrial activated sludge.

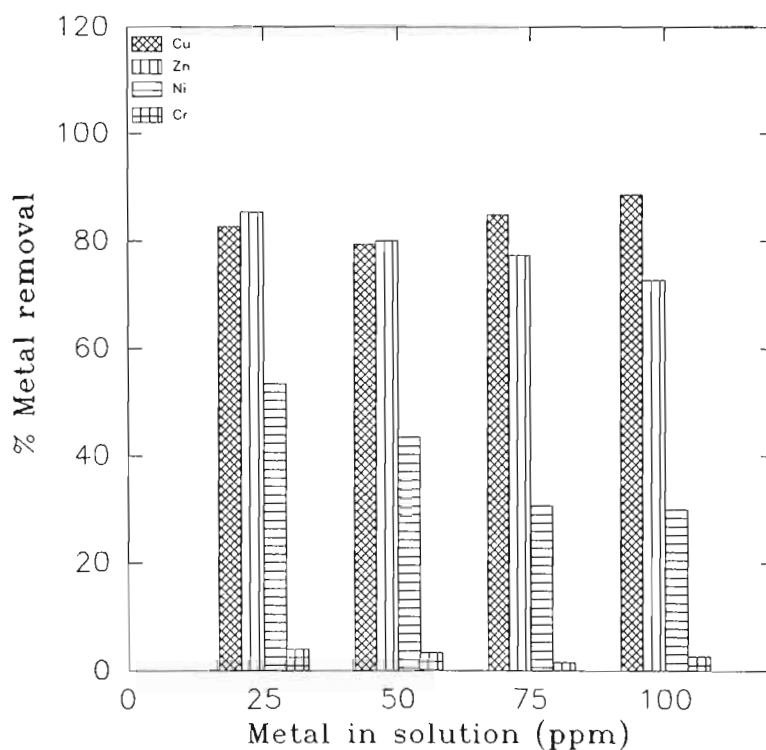


Fig. 2. Biosorption and removal of four metal-ion species by domestic activated sludge.

## DISCUSSION AND CONCLUSIONS

Activated sludge is composed primarily of aggregates of filamentous and eubacteria held together in discreet units called flocs. A large component of the flocs is the extracellular polysaccharides produced by the eubacteria which aid in floc integrity. Settleability is an important characteristic of these flocs and settled floc is termed sludge. Sludge has been shown to have a net negative charge (Morgan *et. al.*, 1990), and therefore is capable of removing cations from solution. Two methods have been proposed for binding of metals to sludges a) chemical adsorption through ion exchange at floc surfaces and b) adsorption of inorganic precipitates (Kasan & Baecker, 1989).

Overall, both the industrial and domestic sludges were capable of metal biosorption and removal from solution. Industrial activated sludge demonstrated higher affinity for metal-ions than domestic sludge. The affinity trend for the four metals was  $\text{Cu} > \text{Zn} > \text{Ni} > \text{Cr}$  for both sludges (Figs 1 & 2). Domestic sludge showed slightly depressed biosorption for Cu at the lower concentrations but at higher concentrations Cu was biosorbed more efficiently (Fig. 2) than the other three species. Copper biosorption was greatest at concentrations of 25 ppm with total (100%) removal from solution at this concentration by industrial WAS (Fig. 1). A decrease in biosorption efficiency was observed as concentration increased for all metals with the exception of Cu bound to domestic sludge which indicated a slight increase in biosorption as metal concentration increased (Fig. 2). This is possibly attributable to the domestic sludge equilibrium being slightly shifted upward as a result of the pressure of the increasing metal concentration. Thus a slightly higher percentage is taken up as concentration increases.

The fact that metal removal efficiency decreased as metal concentration increased, in the other instances, indicates firstly that there are a fixed number of binding sites for metal-ions and secondly, that when saturation occurs, no further metal will be biosorbed. If efficiency of biosorption declines steeply as is the case of Ni biosorption to both sludges it indicates a low number of binding sites and consequently a low saturation point. This is correlated by findings of Esmond & Petrsek (1974) who postulated a "fixed demand" for Ni by municipal activated

sludge. However, the converse holds true for a negligible decline in removal capability as evidenced in the uptake of Cu by industrial sludge (Fig. 1).

Cr biosorption by both sludges was extremely low compared to the other three metals and this is possibly due to the valence of the Cr species used (Cr (VI)) which has a low affinity for binding even though it is highly soluble (Figs 1 & 2).

Current work investigates the extraction of polymers from these activated sludges to determine their role in the biosorption process by subjecting them to similar experiments. It is hoped that waste sludges which are of no significant value will be utilisable as a bioremediative agent for high concentrations of certain metals as well as a polishing method for industrial effluents before discharge. Furthermore, if metals can be cost-effectively recovered or desorbed from the sludges after binding then the potential removal process will provide a further dimension in the use, recycle and, ultimate safe management of metal levels in water.

## REFERENCES

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