EVALUATION OF ANAEROBIC SLUDGES AS METAL BIOSORBENTS AND DEVELOPMENT OF A BIOTECHNOLOGICAL PROCESS FOR METAL ION REMOVAL FROM SELECTED WASTEWATER

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EVALUATION OF ANAEROBIC SLUDGES AS METAL BIOSORBENTS AND DEVELOPMENT OF A BIOTECHNOLOGICAL PROCESS FOR METAL ION REMOVAL FROM SELECTED WASTEWATER

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Dissertation submitted in compliance with the requirements for the Master's Degree in Technology in the Department of Biotechnology, Technikon Natal, Durban.

I hereby declare that the dissertation represents my own work.

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12-8-97
DATE

I hereby approve the final submission of the following dissertation.

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this 14 day of March , 1997 at Technikon Natal.

DEDICATION

To my mother and father

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ABSTRACT

As a result of rapid expansion of the industrial sector and increasing population, the environment has been under phenomenal stress. The volume of sewage and other effluents has increased tremendously in the last century. Globally, approximately 12 million tonnes of dry sludge biomass is produced and discarded of by landspreading, landfilling, incineration or dumping in lagoons and oceans. The discharge of industrial effluents into receiving waters has been documented to be the cause of severe environmental contamination. Heavy metals have been the cause of particular environmental concern. Their toxic and carcinogenic potentials at low concentrations, as well as the large quantities disposed to the environment, have prioritised them as leading contaminants. Current technologies of remediating heavy metal containing effluents are expensive and, in most cases, ineffective. Locally, most industries are merely diluting their effluents, thus resulting in the loss of valuable water resources. Waste sludges have shown the ability to adsorb heavy metals from their aqueous environment. Therefore, the current study attempted firstly, to compare biosorptive capacities of various waste sludges for a range of heavy metal ions, and secondly, to establish a relationship, if any, between biosorptive capacity and sludge surface charge. Finally, a laboratory scale biosorption process, encompassing desorption and recovery of metal ions from sludge surfaces, would have to be developed. Effluents used included pure, metal solutions of divalent zinc, cadmium, copper, nickel, trivalent and hexavalent chromium. In addition, synthetic effluents comprising a cocktail of the above-mentioned metal ions as well as an industrial effluent from a metal plating company were used. Five waste digested sludges were prepared and challenged against pure metal solutions to determine and compare their respective biosorptive capacities. Mechanisms of biosorption were elucidated using the Langmuir adsorption isotherm model. Sludge surface charge was determined using the millivolt quantification method. Upscaling of bioreactor trials to fully mixed laboratory scale was also investigated. These experiments encompassed the use of three sludges showing the greatest potential for biosorption and desorption using the selected mineral acid, H_2SO_4. In addition, a simultaneous fully mixed biosorption and desorption process was designed and optimised. Subsequent trials involved comparing the latter process with a packed bed configuration whereby biomass was immobilised using polysulfone resin. The overall comparative adsorptive capacities of the sludges (S1-S5) for metal ions in single solutions was S3 > S2 > S4 > S5 > S1. Surface charge determination showed S3 to contain the most electronegative charge, with other sludges following in the same descending order as mentioned above. These findings supported the theory of a direct correlation between sludge surface charge and biosorptive potential. The affinity series of the sludges for metal ions followed the descending order of $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cr^{6+} > Cr^{3+}$. Fully mixed studies, using mixed synthetic effluents, resulted in lower biosorptive capacities being recorded by the three selected sludges ie., S2, S3 and S4, as compared to single solution experiments. Biosorption studies with industrial effluent, containing Zn^{2+} as the most prevalent metal at 119.4 $mg.\ell^{-1}$, resulted in S3 biosorbing a maximum of 4.5 $mg.g^{-1}$ of the cation. Sulphuric acid (H_2SO_4) at 0.2*N*, hydrochloric acid (HCl) at 0.2*N* and acetic acid (CH_3COOH) at 0.4*N* were tested for their desorptive efficiencies. Sulphuric acid proved to be the most effective desorbing agent. Using S3 as biosorbent and 0.2*N* H_2SO_4 as desorbent, the manipulation and operation of a simultaneous process proved to be successful since both biosorption and desorption occurred concurrently, thus reducing time required for successful remediation considerably. Immobilised biomass, in a packed bed configuration, produced acceptable final effluent regarding standards as stipulated by the Durban

Municipality for trade effluents. However, biosorption capacity of the sludge was compromised, with subsequent reductions in desorption being recorded, when the process was compared to fully mixed trials. Affinity series determined for the packed bed process was $Cr^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Cr^{6+} > Ni^{2+}$.

Waste digested sludge has shown potential as metal biosorbent on an industrial scale. The present findings have succeeded in demonstrating a novel laboratory scale biotechnological process for the remediation of metal laden industrial effluents.

PREFACE

Some of the material presented in this dissertation has been presented and published elsewhere.

Naidoo, D., Bux, F. and Kasan, H.C. 1995. Assessment of waste digested sludges as a biosorbent of metal ions from solution. Presented at Biotechnology for Africa "95" Conference, 13 - 15 November, 1995. University of Pretoria, South Africa.

Bux, F., Atkinson, B.W. and Kasan, H.C. 1996. An investigation of the efficacy of waste digested sludges as metal biosorbents. Presented at the Ninth Biennial Congress of the South African Society for Microbiology, 8 - 16 July, 1996. University of Pretoria, South Africa.

Bux, F., Naidoo, D. and Kasan, H.C. 1996. Laboratory scale biosorption and desorption of metal ions using waste sludges and selected acids. South African Journal of Science, 92(11/12): 527-529.

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TABLE OF ABBREVIATIONS

AAS	-	atomic absorption spectrophotometer
ECP	-	extracellular polymers
CH_3COOH	-	acetic acid
COD	-	chemical oxygen demand
EDTA	-	ethylene diaminetetraacetic acid (disodium salt)
HCl	-	hydrochloric acid
H_2SO_4	-	sulphuric acid
ID	-	internal diameter
r.p.m.	-	revolutions per minute
UF	-	ultrafiltration

CHAPTER 1

1.0 GENERAL INTRODUCTION

1.1 ANAEROBIC DIGESTION TREATMENT PROCESS

The most widespread and important process involving anaerobic bacteria is anaerobic digestion. This process is principally applied to sludges derived from sewage treatment. Anaerobic treatment of sewage has been practised for 100 years, the first fairly primitive process being described in 1881 (McCarty, 1982). This process, and others developed in the late nineteenth century, treated whole sewage and were something like the modern septic tanks, which are still widely used to treat sewage from isolated rural dwellings. Normally, anaerobic digestion is used to treat sewage sludge which consists mainly of primary sludge, 4 - 9% w/v solids, together with humus or surplus activated sludge, 2 - 4% w/v solids. Primary sludge is the settleable portion of sewage and contains faecal matter, disintegrated paper, sanitary products and some kitchen refuse (Holland *et al.*, 1987).

In general sludge digestion is performed in closed, mixed, heated tanks. Most often, tanks are heated at 30 - 35°C for mesophilic and 50 - 60°C for thermophilic digestion. Digesters are usually cylindrical, constructed of reinforced concrete and sealed by fixed or floating lids. The volume varies but can be greater than one million gallons (4 500 m^3). Briefly, the process of anaerobic decomposition involves four discrete stages (FIG. 1.1).

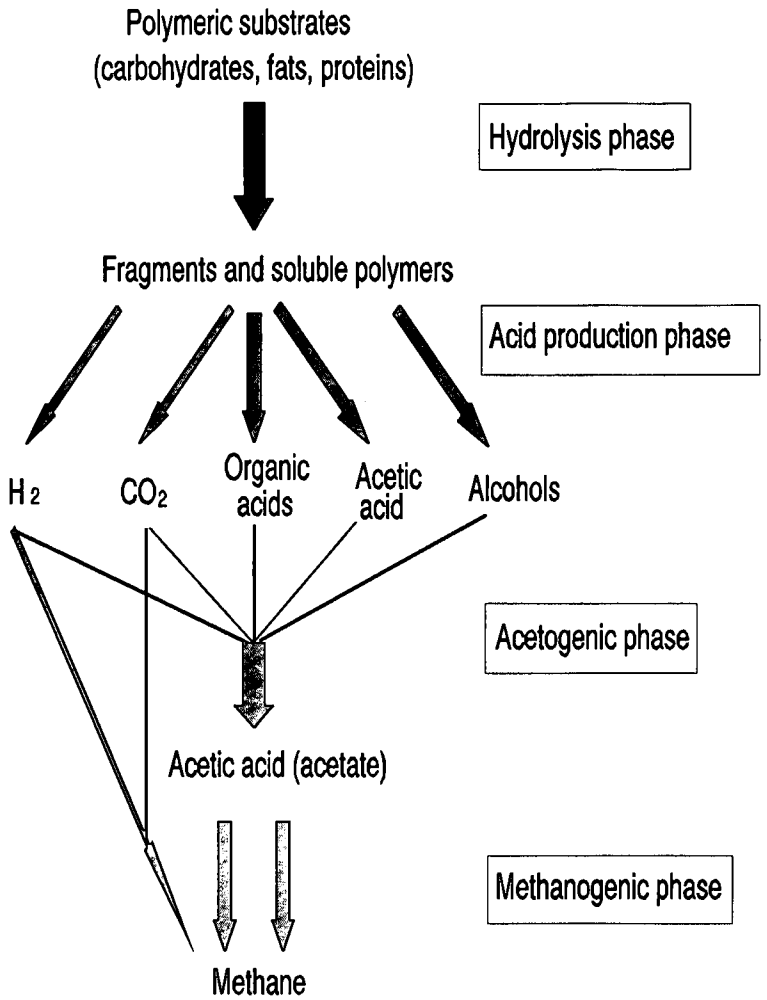

FIG. 1.1 Schematic diagram showing major steps in anaerobic digestion (Li-Yin Lin, 1995).

The first stage is the hydrolysis of high molecular weight carbohydrates, fats and proteins which are often insoluble, by enzymatic action into soluble polymers. The second stage involves acid-forming bacteria which convert the soluble polymers into a range of organic acids (acetic, butyric and propionic acids), alcohols, hydrogen and carbon dioxide. Acetic acid, hydrogen and carbon dioxide are the only end products of acid production that can be converted directly into methane by methanogenic bacteria. A third stage is present when the

organic acids and alcohols are converted to acetic acid by acetogenic bacteria. It is in the final phase, which is perhaps the most sensitive to inhibition, that methanogenic bacteria convert the acetic acid to methane.

Although methane is also produced from hydrogen and carbon dioxide, in practice approximately 70% of the methane produced is from acetic acid. Obviously the methanogenic stage is totally dependent on the production of acetic acid and so it is the third stage, or acetogenic phase, that is the rate-limiting step in any anaerobic process (Li-Yin Lin, 1995). The mean retention time of sludge in the digester is generally in the order of 20-30 days for mesophilic and 10-20 days for thermophilic digestion. A large number of anaerobic processes are available, including upflow anaerobic sludge blanket, anaerobic lagoons, digesters and filters (Holland *et al.*, 1987).

Generally, in sewage sludge digestion, the organic matter content is approximately halved. Digested sludge is much less viscous and malodorous than primary sludge and is more easily dewatered or disposed of to land as a fertilizer or soil conditioner. Most of the organic fraction is converted to gas of variable composition, which generally contains 50 - 70% methane and 30 - 50% carbon dioxide (Bolton and Klein, 1971).

1.2 CLASSIFICATION AND DISPOSAL OF WASTE SLUDGES

1.2.1 Waste sludge classification

According to the Health Act, 1977 (Act 63 of 1977), all local authorities were required by law to apply reasonable, practicable measures to maintain its district in a hygienic condition and to prevent the occurrence of nuisances, unhygienic or offensive conditions. In general, these duties also pertain to sewage purification and sludge treatment, storage, processing, utilisation and disposal. Therefore, according to the Department of National Health and Population Development (1991), waste sludges may be differentiated into four categories in decreasing order of its potential to cause odour nuisances and fly breeding as well as to transmit pathogenic organisms to man and his environment. The four categories are:

Type A : Unstable with a high odour and fly nuisance potential, high content of pathogenic organisms.

Type B : Stable with low odour and fly nuisance potential, reduced content of pathogenic organisms.

Type C : Stable with insignificant odour and fly nuisance potential, containing insignificant numbers of pathogenic organisms.

Type D : Sewage sludge is of similar hygienic quality as Type C but since it is produced for unrestricted use on land at a maximum application rate of 8 dry t/ha/yr, the metal and inorganic content is limited to acceptable low levels. (Dept of Nat. Health and Pop. Dev., 1991).

1.2.2 Legislation for disposal

Sludges can be further differentiated into domestic and industrial types depending on the source of the influent. Valuable sludges comply favourably with DNH requirements and are normally distributed to agricultural users at a nominal price. These act, in themselves, as regulatory mechanisms and sludges are used to improve soil textures and reduce quantities of commercial fertilisers used. Potentially valuable (Type A and B) sludges require many more restrictions on their use. These restrictions are currently under review. Toxic and hazardous sludges contain compounds harmful to the environment and the DNH guidelines acknowledge that strict control is required during their use and disposal. These sludges must be disposed at registered disposal sites (McConkey, 1991). The nature of sludge disposal methods in 1981 was: land application 42%; landfill 15%; incineration 27%; ocean disposal 4% and lagoons 2% (Ekama, 1992).

Thus, it is evident that the disposal of waste sludges presents definite problems for municipalities. Therefore, if potential re-use for such waste matter could be established, eg., application as biosorbents to remediate metal contaminated effluents, the potential environmental and economical implications would be advantageous.

1.3 HEAVY METALS

1.3.1 Heavy metal contamination

The presence of heavy metals in sewage is concomitant with the practices of a modern industrial society. Their presence in the environment, however, at concentrations above critical values established by national and international agencies, is now considered as being unacceptable. Toxic metals (including heavy metals) enter waste water from a variety of sources, both domestic and industrial. Many industrial uses of heavy metals involve the discharge of metal laden effluents to the sewage system. Metals from other sources, for example the combustion of carbonaceous fuels, may ultimately reach sewage systems in urban runoff (Brown and Lester, 1979).

The major industrial sources of metals in waste waters in the South African context is from the metal plating industries, mines and paint manufacturers (Bux and Kasan, 1996). Several countries, including the U.S.A. have standards for metals in industrial discharges, or a trade effluent policy as in the U.K. These measures reduce the quantities of metals discharged to municipal sewers, but they do not eliminate them, and they have no effect on the contributions from domestic sources, run-off (both urban and rural) or atmospheric deposition. Thus, it is inevitable that as long as heavy metals are produced, there will be a certain irreducible quantity present in waste waters (Lester, 1983). Research by Rossin *et al.*, (1983) in the UK suggested that approximately 7 800 tons/year of heavy metals are removed in sewage treatment. If this were to represent 75% of the total heavy metal load, then approximately 2 600 tons/year (25%) would be present in final effluents. With recent

trends toward rapid global industrialisation, these figures could be much higher. Apart from Zn, which is the most abundant metal in effluent, a significant proportion of the total discharge is due to Pb, a metal of considerable importance not only because of its toxicity but also because of its ambiguity in raw sewage, arising from urban and road run-off and a variety of industrial processes (McKenzie and Purves, 1975).

Contamination of raw sewage with heavy metals may potentially cause problems of three types:

i) toxic effects on the secondary biological treatment process;

ii) through the discharge of final effluent containing excessive concentrations of heavy metals;

iii) during sludge treatment and disposal; and

iv) effects on surface and ground water quality when sludge is applied to land (Lester *et al.*, 1983).

1.3.2 Legislation

Current South African legislation governing levels of metal species in waste water or effluent draining to any river or natural water source is limited to 0.5 mg.ℓ^{-1} total Cr, 1 mg.ℓ^{-1} Cu and 5.0 mg.ℓ^{-1} Zn, with the sums of Cd, Cr, Cu, Hg and Pb not exceeding 1 mg.ℓ^{-1} when in combination (Government Gazette, 1984). In addition most local authorities have their own standard with regards to trade effluent discharged into the sewage disposal systems. The sewage disposal bylaws of the City of Durban (1994), stipulate maximum concentrations of

metals in trade effluents which could be discharged into sewage disposal systems (TABLE 1.1) (City of Durban, 1994).

TABLE 1.1 Durban City Bylaws pertaining to maximum heavy metal concentrations in trade effluents (City of Durban, 1994).

Metal	Maximum concentration ($mg.\ell^{-1}$)
Copper (expressed as Cu)	50
Nickel (expressed as Ni)	50
Zinc (expressed as Zn)	50
Cadmium (expressed as Cd)	25
Lead (expressed as Pb)	25
Total chromium (expressed as Cr)	25
Mercury (expressed as Hg)	1

The bylaws are presently in the process of being revised and more stringent standards on heavy metals in trade effluents are to be enforced due to limitations on water resources (N., Burgess, 1995 - personal communication). Legislation suggested by the Environmental Protection Agency (Washington, USA) regarding metal species discharged to watercourses is more specific with regard to effect of the metal species and is therefore more stringent. For example, total Cr may not exceed 0.1 $mg.\ell^{-1}$ because of its effect on marine life, although fish appear to be tolerant to it (Murray, 1987).

1.3.3. Environmental Impact

The pollution of receiving waters, in particular rivers, has become the subject of concern globally (Water Research Centre, 1976; Palmer Development Group, 1994). In industralised countries where water resources are limited, sewage effluent may contribute a substantial part of the volumetric flow of lowland rivers. At certain times of the year in some localities of the UK, sewage effluent may represent 90% of the flow in surface waters, which are later abstracted for drinking water (Hawkins *et al.*, 1980). In South Africa there is an estimated 345 670 informal dwellings or "backyard shacks" (DeLoor, 1992). Most of these people live along rivers upon which they depend for "potable" water. In many cases discharge of effluent by industries has caused problems downstream (Palmer Development Group, 1994). In addition, heavy metals present in sewage effluents give cause for concern in four major areas (Water Research Centre, 1976):

i) human health in areas where water re-use is practised;

ii) effects on the use of river waters;

iii) ecological effects on rivers; and

iv) contamination of the hydrosphere.

The toxicity of certain metals and metallards to man and other organisms has long been recognised and has been extensively reviewed (Gottschall, 1976; Cook, 1977; Pickering *et al.*, 1989). The so called "heavy metals" have been the cause of particular environmental concern. These are generally accepted to be chromium, manganese, iron, cobalt, copper, zinc, molybdenum, silver, mercury, lead, cadminium, arsenic and nickel (Englande and

Reimers, 1982). The impact of toxic elements upon the quality of receiving waters is dependent on the use for which they are required. Bacteria have been shown to adapt to growth inhibiting concentrations of metal ions (Mitra *et al.*, 1975). Once acclimated, bacterial cells are capable of accumulating metal, resulting in its incorporation in food chains and transfer to higher organisms by biomagnification (Patrick and Loutirt, 1976). Investigations have been conducted into the toxic effects of such heavy metals on the growth and activity of aquatic bacteria (Bagby and Sherrard, 1981). Pollutant effects on freshwater organisms were measured by (Pickering *et al.*, 1989), who reported deleterious effects of Cr on various organisms to be within 14 - 60 mg.ℓ^{-1}, Cu 0.025 - 35 mg.ℓ^{-1}, Ni 0.02 - 17 mg.ℓ^{-1} and Zn, 0.001 - 48 mgℓ^{-1}. These effects ranged from avoidance to a chemical agent to lethal doses killing 50% of populations.

1.4 TREATMENT OF HEAVY METAL EFFLUENTS

1.4.1. Conventional Technology

Industrial and domestic water use results in the discharge of heavy metals in sewage effluents to natural aquatic systems. Recovery of these metals from effluents is essential for two primary reasons. Firstly, heavy metals in high concentrations are toxic to the environment and secondly, recovery of these metals from effluent could have commercial implications. Conventional technology involved different chemical methods to remove metals from waste water, for example hydrosoide and sulphide precipitation, ion exchange, and the addition of natural and synthetic polymers (Jellinek and Sangar, 1972; Wheatland *et al.*, 1975). These methods were only economically viable for very large industrial units. More recent

treatment technologies involve electrodialysis, ultrafiltration processes (Strobuald, 1995) and application of membrane technology (Schoeman and Steyn, 1995). Ultrafiltration (UF) involves the movement of water through a semipermeable membrane. In metal finishing operations, UF is typically employed to concentrate emulsified oils from rinses or to recover valuable detergents from cleaning rinse waters. Electrodialysis involves the use of a "stack" which consists of atlernating ion-exchange membranes that are permeable to either anions or cations. Electrodialysis is being used successfully on the rinses from the following types of electroplating baths : gold, platinium, nickel, tin, copper, silver and palladium (Schoeman and Steyn, 1995). However, these treatment methods have a variety of limitations. Membrane fouling by suspended or precipitated solids represents the single most common cause of system malfunction. In addition, maintenance of these procedures is essential to achieve optimum results. There is no single membrane process optimum for all applications. In the Durban area, the most common method employed to achieve desired heavy metal concentrations in final effluents is simply dilution. This results in the loss of valuable water resources which under the present circumstances is unacceptable. Therefore, processes such as those discussed above, are either ineffective or extremely expensive to operate especially when metals are dissolved in large volumes of solutions at concentrations between 40 - 150 $mg.\ell^{-1}$, which is what the average concentration is before treatment.

1.4.2. Bioremediation of heavy metal effluents

Recent trends indicate global interest toward using biological systems for the treatment of heavy metals in industrial effluents. Fungi and yeasts, in common with other microbial groups such as bacteria, cyanobacteria and algae are capable of accumulating heavy metals

and radionucleotides even from dilute external solutions (Tuovinen and Kelly, 1974; Shumate and Strandberg, 1985; Gadd, 1990). Srivastava *et al.*, (1989) investigated waste slurries generated in fertiliser plants as absorbents for Cl, Hg, Pb, Su, Mo, Ni and Zn. Jang *et al.*, (1990) also attempted Cu recovery with a gel-forming biopolymer, sodium alginate, from a fluidised bed reactor. They achieved 2.682 g Cu removal per g of alginate which steadily decreased to 0,148 $g.g^{-1}$. Brierley *et al.*, (1986) developed a granular biological material patented as AMT-Bioclaim™ whose capacity to remove Ag, Cd, Cu. Pb and Zn at 100 $mg.\ell^{-1}$ is 86, 101, 152, 601 and 137 $mg.g^{-1}$, respectively. Other commercial biosorbents (inactive biomass) presently in use include products such as MRA (caustic treated killed bacteria), AlgaSORB (algae) and Bio-Fix (Peat moss, spirulina and others) (Smith *et al.*, 1994). The technologies discussed thus far for the bioremediation of metal contaminated effluents have been proven to be successful, but at a cost, thus having economical implications on the applicability of the process at industrial scale.

Previous research has shown that substantial quantities of metals present in wastewater may be removed in the activated sludge process of biological waste treatment (Brown *et al.*, 1973 and Stoveland *et al.*, 1979). As discussed previously, large concentrations of heavy metals in effluent are toxic to the microflora at waste treatment processes.

Inactivated non-living biomass can serve as a basis for development of patentable biosorbent materials for concentration and recovery of strategic or valuable heavy metals, nuclear fuels or radioactive elements (Volesky, 1987). Although it is clear that non-living biological based systems offer a competitive alternative to physical and chemical technologies, in most applications the use of such materials as metal sorbents has not been without contention

because the cost of obtaining suitable biomass material in sufficient quantities (Ehrlich and Brierley, 1991). Selection of suitable biosorbents should be based on the following criteria:

a) uptake and release of metal should be efficient and rapid;

b) active biosorbent agent should be produced at a low cost and should be reuseable;

c) particle size, shape and mechanical properties of the biosorbent should be suitable for use in continuous flow systems in freely mixed, packed beds, or fluidised bed configurations;

d) removal of the biosorbent from solution should be cheap, efficient and rapid; and

e) separation of metal from the sorbent (description), should be metal selective, economically feasible and the loss of sorbent should be minimal (Volesky, 1987).

Previous research (Bux *et al.*, 1994) has clearly demonstrated adsorptive capabilities of waste activated sludges in the removal of heavy metals from metal laden solutions. With the exception of absorbent re-use, waste sludges appeared to have satisfied criteria determining good sorbents. Limitations on re-use was attributed to the destructive properties of desorbents (mineral acid). This finding had much positive impact, since a waste product, viz., waste sludges from conventional sewage works which present disposal problems could be applied in remediating metal-ions from contaminated industrial effluents. Unlike conventional and present technology for the treatment of heavy metal effluents, the cost of producing the biosorbent is negligible, since it is waste matter which occurs in abundance, subsequently drastically reducing cost involved in large scale industrial application. One of the sources of waste sludges during waste water treatment is the sludge that is produced during the anaerobic digestion process.

1.6 AIMS AND OBJECTIVES

The aims of the proposed study were to investigate the potential for using waste anaerobic sludges as metal biosorbents from solution and to develop a laboratory scale process to exploit the use of sludge for metal ion removal from solution and industrial wastewater.

The objectives of the proposed study were to:

a) determine and compare the biosorptive capacities of various waste digested sludges, when interacting with metal ions in a synthetic effluent;

b) determine the surface charge of sludges under investigation;

c) establish the mechanism involved in sludge-metal interactions;

d) establish possible relationships between the biosorptive capacity of sludges, their relative surface charges and mechanisms of biosorption;

e) select a suitable desorbent that would achieve maximum desorption of sludge-bound metal ions;

f) achieve process optimisation, at laboratory scale, whereby biosorption and desorption could occur in a continuous process;

g) investigate the biosorptive capacity of immobilised waste digested sludge ;

h) determine the efficiency of the packed-bed process as opposed to fully mixed in the removal of dissolved metal ions and improving the quality of the effluent.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 NATIONAL ENVIRONMENTAL PROBLEM AND POLICIES

South Africans are at a significant environmental, social and health risk as a result of uncontrolled waste generation and disposal. The Department of Water Affairs and Forestry has indicated that areas of particular concern are:

a) the lack of effective domestic refuse collection in many towns and informal settlements;

b) illegal dumping of toxic and hazardous wastes (some estimates suggest that less than 50% of the toxic and hazardous waste generated in South Africa reaches the formal waste system);

c) a dire lack of information on which to base implementation options.

Good waste management is important for the sustainable use of the country's limited natural resources and for adequate and sustainable protection of the water, air and soil on which all citizens depend. In addition, there is a need to protect the disadvantaged from the consequences of poor waste management policies and to enforce more effective regulation, mindful of the cost to government and the taxpayer of elaborate and fragmented regulatory controls. There is also the need to ensure that the polluter pays the cost of waste management and disposal. South Africa is a signatory to the Basel Convention and has, in

principle, committed itself to establishing a national waste management strategy. The government is presently in the process of introducing stricter provisions aimed at protecting the environment and therefore is likely to encourage companies to examine their waste streams. In addition, international pressure from consumers and environmentalists has increased significantly, forcing industrialists in Europe, USA and the UK to "clean up their act". Many of them have had to invest substantially in effluent treatment plants and production facilities that produce minimum waste (Jackson, 1996).

Heavy metal effluents which contribute largely to the national effluent problem are generated mainly from two industrial sectors, namely, mining and electroplating. The present area of research focuses primarily on the latter effluent problem. Electroplating is said to be one of the most anti-ecological technologies. The environment is annually polluted with approximately one cubic kilometre of toxic effluents, carrying 50 000 tons of heavy metals and 100 000 tons of acids and alkalis, 25 - 30% of which are released to natural aquifers. Chromium is carcinogenic and cadmium causes liver and kidney diseases. The annual consumption of water by the electroplating industry in South Africa is approximately 9×10^6 m^3 of which 80% is discharged as effluent (Schoeman and Steyn, 1995). In an attempt to reduce water polltion, the industry resorts to dilution of its effluents, with consequent wasteage of scarce water resources. Ideally, this waste should be recycled to decrease water intake by the industry. Recycling of recovered metals (Ni, Cu, Zn, Cr) to the plating process will reduce water pollution and sludge volumes dramatically. Consequently, the pollution load on the environment will be reduced with the application of metal/water recovery technologies.

2.2 BIOSORPTION OF METAL IONS FROM SOLUTION

Most microorganisms, such as fungi, algae, yeast and cyanobacteria, are capable of accumulating heavy metals from dilute external solutions (Shumate and Strandberg, 1985; Trevors *et al.*, 1986). A variety of physical, chemical and biological mechanisms may be involved. Such processes are of current biotechnological interest, not only because the removal of potentially toxic heavy metals and/or radionucleotides from solution can lead to the detoxification of industrial effluents but also because subsequent recovery of accumulated elements is possible after destructive treatments (Hutchins *et al.*, 1986).

Since living and non-living or non-metabolising microorganisms accumulate metals, either type of biomass may be employed for removal of metals from solution. Arguments for use of living systems are based on the consideration that: i) the biolgical adsorbent is now a renewable resource, consequently not requiring replacement when material is metal loaded; and, ii) products of metabolism such as H_2S and HPO_4^{2-}, can be used in the metal immobilisation process. Arguments for using non-living, or non-metabolising biomass are supported by the fact that waste streams are often toxic to living systems, eg., high metal concentrations devoid of nutrients, and can possess extreme conditions over time, all situations which make the maintenance of living systems difficult at best (Kuyucak and Volesky, 1988). Also to be considered in using living systems is the matter of supplying nutrients in a cost effective manner to maintain microbial viability in a waste treatment plant. Unless inexpensive nutrients, such as partially digested sewage sludge or decaying plant materials, are readily available, the maintenance of living microorganisms in waste treatment facilities is impractical. Moreover, nutrient supplemented waste streams may support the

growth and activity of microorganisms other than the bacteria which were originally intended. This contamination can result in the depletion of valuable nutrients and proliferation of undesirable species. Therfore, most biological metal removal systems in, or approaching, commercialisation employ non-living or non-metabolising systems (Kuyucak and Volesky, 1988; Tsezos, 1988).

Although it is quite clear that non-living, biological based systems offer a competitive alternative to physical and chemical technologies in most applications, the use of such material as metal sorbents has not been without contention because of the cost of obtaining suitable biomass material in desired quantities. Therefore, the use of waste sludges which occur in abundance would serve as ideal adsorbent material for removal of metal ions from solution viz., metal bearing effluents. These waste sludges from conventional sewage works consist of a diverse range of microorganisms (Bux and Kasan, 1994b). Previous research has shown that waste sludge biomass possesses metal sorptive capabilities (Lester and Sterrit, 1985; Bux *et al.*, 1994; Bux and Kasan, 1996). Similar to waste activated sludges, waste digested sludges have also shown potential to remove heavy metals from solution (Mehrotra *et al.*, 1987).

2.3 ADSORPTION THEORY

Evaluation of the mechanism of biosorption, determination of binding strengths and capacities of sludges can be ascertained by applying the Langmuir Adsorption Model to sludge-metal interactions. This information can be utilised to select sludges which demonstrate efficient metal removal capabilities and further to use them for specific metal removal processes. The

Langmuir Model of Adsorption provides the basis of deriving a fundamental interpretation of the nature of sludge-metal interaction. Adsorption is frequently used to describe metabolism-independent binding of heavy metals and/or radionucleotides to biomass, although with increasing awareness of the multiplicity of physico-chemical interactions that can occur, it is clear that this term may be rather simplistic (Gadd, 1990). Adsorption involves the accumulation or concentration of substances at a surface or interface; the material being adsorbed is called the adsorbate, and the adsorbing phase is called the adsorbent. The three main types of adsorption involves electrical attractions, van der Waal's attractions and chemical attractions of the solute to the adsorbent. The first type is related to ion exchange and is often called exchange adsorption (Weber, 1972). This type can occur widely in waste sludge biomass, and, indeed, adsorption has been defined as the attraction of positively charged ions to negatively charged ligands on the sludge surface (Brierley and Brierley, 1983; Bux and Kasan, 1994a). Adsorption as a result of van der Waal's forces is often termed physical or ideal adsorption and occurs when the adsorbed molecule can have translational movement within the interface. Chemical attractions occurring between the adsorbate and the adsorbent are termed chemical or activated adsorption. It is often difficult to distinguish between physical and chemical adsorption, and most adsorption phenomena are combinations of the three forms of adsorption described (Weber, 1972). To circumvent this problem of process definition, researchers are using the term biosorption more frequently.

The extent of biosorption of a metal ion by microbial biomass from a single-solute solution is a function of the equlibrium metal-ion concentration in solution, all other solution parameters such as pH and temperature remaining constant. Brunaer *et al.*, (1940, cited by Ruthven, 1984) classified the isotherms for physical adsorption into five classes (FIG. 2.1).

The isotherms for true microporous adsorbents in which the pore size is not very much larger than the molecular diameter of the sorbate molecule, are normally of type I. This is because for such adsorbents there is a definite saturation limit corresponding to complete filling of the micropores. Occasionally if intermolecular attraction effects are large, an isotherm of type V is observed. An adsorption isotherm of type IV suggests the formation of two surface layers either on a plane surface or on the wall of a pore very much wider than the molecular diameter of the sorbate. Isotherms of types II and III are only observed in adsorbents containing a wide range of pore sizes. In each system there is a continuous progression with increasing loading from monolayer to multilayer adsorption and then to capillary condensation (Gasser, 1985).

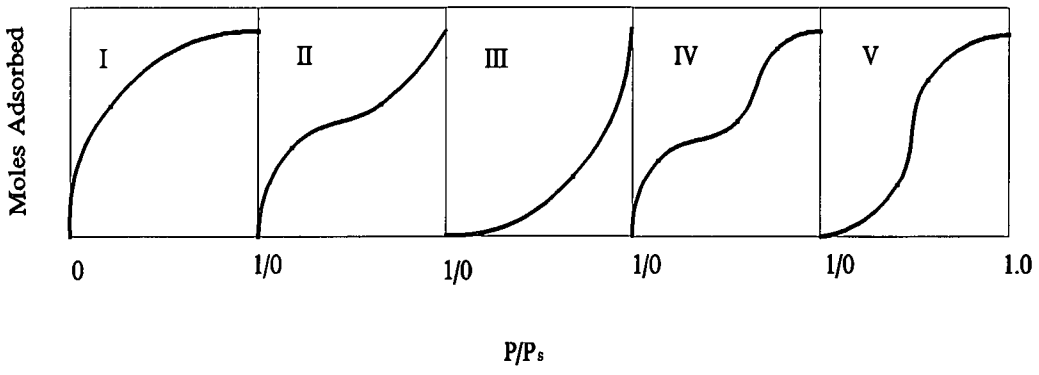

FIG. 2.1 Brunauer classification of adsorption isotherms (Hughes and Poole, 1989).

The preferred form for depicting this distribution is to express the quantity bound q_e as a function of C, at fixed temperature, the quantity q_e being the amount of solute adsorbed per unit weight of adsorbent and C the concentration of solute remaining in solution at equilibrium. Several types of isothermal adsorption relations may occur. The most common relationship between q_e and C is obtained for systems in which adsorption from solution leads to the deposition of an apparent single layer of solute molecules on the surface or within pores of the solid.

The simplest theoretical model for monolayer adsorption is due to Langmuir. The Langmuir model was originally developed to represent chemisorption on a set of distinct localised sites. The assumptions on which the model is based are:

a. molecules are adsorbed at a fixed number of well-defined localised sites;

b. each site can hold one adsorbate molecule;

c. all sites are energetically equivalent; and

d. there is no interaction between molecules adsorbed on neighbouring sites.

The Langmuir isotherm is characterised by the equation:

$$q_e = \frac{Q^o bc}{1 + bc}$$

(Kinnburgh, 1986)

where:

b = constant related to the energy or net enthalpy (delta H) of adsorption

C = concentration of solute remaining in solution at equilibrium

q_e = amount of solute adsorbed per unit weight solid adsorbent

Q^o = number of moles of solute adsorbed per unit weight of adsorbent in forming complete monolayers (Kinnburgh, 1986).

The Brunauer Emmet and Teller (BET) model represents isotherms reflecting apparent multilayer adsorption. Typical Langmuir and BET isotherms are represented in FIG. 2.2.

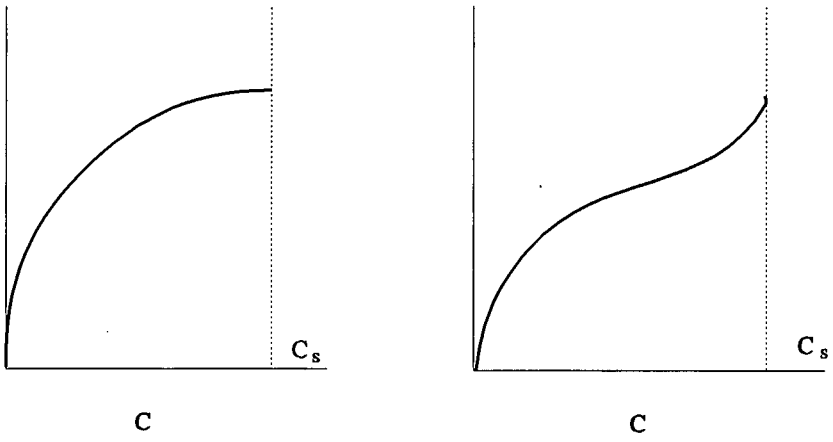

FIG. 2.2 Typical isotherms for Langmuir and BET adsorption patterns. C_s represents saturation concentration at a given temperature (Kinnburgh, 1986).

The BET isotherm is characterised by the equation:

$$q_e = \frac{BCQ^o}{(C_s - C)\,[1 + (B-1)\,(C/C_s)]}$$

(Kinnburgh, 1986)

where:

B = constant expressive of energy of interaction with surface

C_s = saturation concentration of solute in solution at given temperature

This equation can be converted to the Langmuir form if:

a) b is equal to B/C_s;

b) C is taken to be negligibly small compared to C_s; and

c) B is greater than 1 (Weber, 1972).

Two convenient linear forms of the Langmuir equation are (Kinnburgh, 1986):

$$\frac{C}{q_e} = \frac{1}{bQ^o} + \frac{C}{Q^o}$$

(Kinnburgh, 1986)

or

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{bQ^o}\left(\frac{1}{C}\right)$$

(Kinnburgh, 1986)

Linearisation of isotherms allows determination of whether a model will fit experimental data. Linearisation allows simple regression analysis with goodness of fit values indicating how well data fit models. However, linearisation formula should be carefully selected to protect against over optimistic interpretation of goodness of fit by incorporating outliers. In this respect, the first equation tends to exaggerate deviations from the fitted equation and is ideal for application with the Langmuir Model (Kinnburgh, 1986).

2.4 SLUDGE SURFACE CHARGE

Biosorption of metal ions by sludges could be attributed to physico-chemical interactions between metal ions and sludge surfaces (Stoveland and Lester, 1980; Sterrit *et al.*, 1981; Lake *et al.*, 1989). Sludge surfaces are polymeric in nature, comprised of protein, carbohydrate, nucleic acids and lipid (Goodwin and Forster, 1985). Many of the extracellular polymers (ECP) produced by microorganisms possess negatively charged inorganic groups such as carboxylic, aliphatic, aromatic, hydroxyl, sulphate and amino groups, which confer an overall negative charge to sludge floc surfaces. The quantity of bacterial ECP in sludge is controlled by the concentration of various nutrients in the growth medium, sludge retention time and oxidation of polymers by other bacterial species present (Brown and Lester, 1979). The chemical reaction between an anionic bacterial surface (S^-) and a cationic metal ion (M^+) should ideally represent a simple electrostatic attraction: $M^+ + S^- \rightleftharpoons MS$ (Nelson *et al.*, 1981). In reality, the chemistry of metal ion aqueous solutions is much more complicated. In aqueous solution, metal ions are usually hydrated. In natural water systems, metal ions can be attracted to a number of dissolved, colloidal or solid organic and inorganic substances. Only when the effects of pH, E_h interfacial nature, chemical attributes of the metal (heat of hydration, charge density, electronic shell, etc.) and presence of competing ions and other biological surfaces are taken into account, can we begin to grasp the true complexity of bacterial metal binding (McLean and Beveridge, 1991).

Tenneg and Verhoff (1973) reported that the electrophoretic mobility of activated sludge bacteria indicates an increase in surface charge negativity with increasing extracellular polymer concentration. Steiner *et al.*, (1976) demonstrated that the ratio of glucuronic acid

to carbohydrate in activated sludge has more or less constant value of 1 : 6. Cellulose treatment of activated sludge was found to cause a steady release of sugars. The same could be true for waste digested sludge, since both types of sludge consist of biomass. Initially, an increase in surface charge was monitored, but this began to decrease after four hours. The increase in charge was attributed to the production of hydroxyl groups by the cleavage of *B* 1,4-glucan linkages. The subsequent decrease was thought to be due to the release of 1,3 - attached hexuronic acid molecules.

Much of the research conducted thus far on the magnitude of surface charge on biological matter such as sludge, was restricted to its applications to sludge conditioning to increase particle size and facilitate solid/liquid separation; influence of charge density of cationic polyelectrolytes on sludge conditioning; and to determine the optimium coagulant dosage in relation to colloidal characteristics of the sludge (Tiravanti *et al.*, 1985). Previous research by Bux and Kasan (1994a) compared selected methods for the assessment of sludge surface charge. The pH/millivolt method proved to be appropriate for the relative assay. A relationship between sludge surfaces and biosorption has previously been confirmed (Bux and Kasan, 1996). During the present investigation, determination of sludge surface charge was conducted to assess differences in magnitude of surface charge among various waste digested sludges with the intention of substantiating their biosorptive potentials and thus using surface charge as an indicator of superior biosorbents.

2.5 LABORATORY SCALE BIOSORPTION AND DESORPTION

2.5.1 Biomass availability and biosorption

In order to present any possible industrial application, the magnitude of laboratory scale biosorption and desorption trials, with regards to volume, had to increase ie., treatment of large volumes of effluent as generated by industry. The industrial application of biosorption requires that sufficient quantities of the appropriate microbial biomass becomes available for use. This biomass can be produced by fermentation for specific use as biosorbent, or it can be the by-product of other biochemical operations, such as brewing, pharmaceuticals production or, as in the present application, biolgical wastewater treatment (Brierley *et al.*, 1986). The removal efficiency is the ability of the bacterial biosorbent to remove metals from solution to achieve the desired regulatory discharge standards. The problems with achieving high removal efficiencies are mostly related to removing metal ions when:

1) initial concentration of metal in solution is very low;
2) presence of other metal ions which compete for binding sites on the biosorbent material;
3) complexing or chelating agents are present that compete with the biosorbent; and
4) displacement of one metal with another occuring at biosorbent binding sites (Brierley, 1990).

The metal loading capacity is defined as the amount of metal that is loaded onto a biosorbent on a dry weight basis. Metal loading is important because it controls the size of the

contactor unit, dictates the frequency of regeneration or replacement of the biosorbent and influences the overall cost of waste treatment. The lower the metal loading, the larger and more capital intensive becomes the contactor unit. Replacement of the product or biosorbent regeneration becomes more frequent, increasing operating and, potentially, capital costs. Research by Bux *et al.*, (1994) showed waste sludges could be used in repeated biosorption cycles, but in order to achieve maximum desorption of sludge-bound metals, mineral acids were used as desorbents which irreversibly damaged the sludge surface thus compromising reusability of the biosorbent. The principal factors affecting metal loading are:

1) number and nature of exchange, chelation and nucleation sites on the biosorbent;
2) initial metal concentration in solution; and
3) presence of chelating or complexing agents (Brierley, 1990).

It should be noted that binding sites vary with the type of biomass used. The lower the initial metal concentration in solution, the lower will be the loading on the biosorbent. This is particularly noted when initial metal concentrations are less than 10 $mg.\ell^{-1}$. Longer contact time between the biosorbent and the metal containing solution diminishes this effect somewhat (Brierley, 1990).

2.5.2 Desorption of metal-bound sludge

Technical applications of metal and/or radionuclide accumulation by biomass may depend on the ease of element recovery either for subsequent reclamation or further containment of toxic and radioactive substances. Recovery may also be desirable in order to regenerate the

biomass for reuse in multiple adsorption-desorption cycles (Tsezos, 1984). For maximum benefit, desorption techniques should be highly efficient, economical and result in minimal damage to the biomass so that subsequent readsorption is not impaired. During the present application, the latter was not possible as discussed earlier. With industrial application of biosorption, the sequestered metal ions need to be recovered in a concentrated solution, simultaneously regenerating the biosorbent for additional use. Regeneration of the biosorbent also affords an opportunity for reclamation of the stripped metal into a form which is reusable by the waste generator, or conversion of the metal into a form that can be reintroduced to commerce through further processing and refining. The increased enforcement of environmental regulations will soon preclude landfill disposal of metal wastes and necessitate implementation of technologies that reclaim metals from wastes. To that end, biosorbent technologies must incorporate the capability for repeated regeneration and metal reclamation (Brierley, 1990).

Adsorption and desorption are usually coupled processes. Desorption is also known as elution, particularly in processes involving adsorbents in column configurations. 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 0.1M nitric acid, 0.1M disodium ethylene diaminetetraacetic acid (EDTA) and 0.1M ammonium carbonate for 16 hrs and obtained only 59.3, 72.3 and 83.5% removal, respectively. They also attempted desorption with two other agents viz., 0.1M sodium citrate and 1.0M potassium oxalate, and obtained 57 and 14% removal, respectively. They did, however, report increased adsorption in 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. Wong *et al.*, (1993) investigated copper removal and recovery from an industrial effluent using an immobilised *Pseudomonas putida* -II strain isolated from a metal plating effluent. They eluted biomass with a 0.1M HCl solution and were able to recover more than 90% of adsorbed copper. Research by Bux *et al.*, (1995) investigated a range of desorbents and showed 0.1M HCl to be the most efficient at removing metal ions from sludge surfaces. Results also showed desorption to be agent-dependent rather than sludge-dependent.

2.5.3 Simultaneous biosorption/desorption process

Over the last 15 years, biosorption of metals developed very rapidly from a laboratory curiosity to a full scale industrial process (McCready and Lakshmanan, 1986; Krambeer, 1987). The proper engineering design of process equipment requires a good understanding of the process kinetics in addition to the equilibrium conditions. Naidoo (1995) attempted to create a fully mixed biosorption and desorption process on a continuous basis. This was not possible due to biomass being damaged by desorbent, subsequently resulting in the process being halted to allow new biosorbent feed. Subsequently, a simultaneous process was designed that allowed biosorption and desorption to occur simultaneously thus reducing the process time and increasing industrial applicability. In general, there is an observed overall rate of biosorption and an intrinsic rate of biosorption. Overall biosorption rates are the result of intrinsic biosorption rate superimposed on the rate of transfer of the metal ion from the bulk solution to the actual biosorption sites (Tsezos, 1988). The use of a well-mixed batch reactor to observe the rate of biosorption usually allows a direct observation of the intrinsic biosorption rate. A well-stirred reactor provides sufficient mixing so that the

rate of transport of the metal ion in the bulk solution is not rate limiting.

2.6 BIOREACTORS AND SUBSTRATE IMMOBILISATION

2.6.1 Bioreactor configurations

Several bioreactor configurations can be utilised to interact metal ions with biosorbent. The solid-liquid contact is very similar to that which is employed in ion-exchange. Configurations used can range from batch, semi-continuous to continuous flow. These can be developed in any of the following process equipment:

a) Stirred tank contactors

As discussed earlier, the biosorbent is suspended in liquid containing metal and biosorbent laden with metal is recovered and metal eluted to regenerate the biosorbent for reuse.

b) Fixed packed-bed contactors

The metal-bearing liquid percolates through a bed of active biosorbent. Equilibrium is not atttained since the upper layers become saturated before the lower ones. Once all biomass is saturated, the bed becomes inactive and this is indicated by a sharp rise in metal concentration in the outlet, termed the "breakthrough point". The saturated column has to be taken out of operation and the flow has to be stopped or re-routed to an active column. The saturated column has to be regenerated by eluting the bound metal from the surface of

the biosorbent, usually by forcing low volumes of elutant through the column to keep the desorbed metal in a concentrated state (Bux *et al.*, 1994).

c) Packed-bed contactors

These can be modified to operate as pulsating beds which are operated with upward flow of metal solution. This allows periodic removal of biosorbent from the bottom and and withdrawn biosorbent can be regenerated and inserted in a continuous manner. Fluidised beds are another modification where there is also an upwared flow but at a higher rate to maintain the biosorbent in a fluidised state. Periodic or continuous removal of biosorbent along with metal solution allows the process to be operated continuously. The most common of such schemes are the upflow or downflow packed-bed reactors and the continuous fluidised-bed reactors. Pilot scale results, for both types of reactors applied to biosorption from industrial solutions, have been reported (Brierley *et al.*, 1986; Tsezos *et al.*, 1989).

2.6.2 Immobilisation of biomass

Various industrial applications of biosorption use a variety of forms of immobilised biomass (Krambeer, 1987). Freely suspended biomass has a number of disadvantages (Gadd, 1988). It has low density which entails seperation problems. It also has low mechanical strength and rigidity and therefore tends to easily clog delicate inflow and outflow mechanisms (Tsezos *et al.*, 1987). Alternatively, immobilised microbial biomass could be produced in the form of particles of desirable size, mechanical strength and rigidity while maintaining the natural properties of the biomass. The simultaneous achievement of all the above objectives is not

an easy task. The biosorptive equilibrium properties of the microbial biomass can be protected to a large extent during immobilisation.

Satisfactory immobilised biomass types, also called biosorbents, resemble a conventional exchange resin in physical form. The principal application of biosorbents is in the sequestering of metal values from complex, dilute process solutions and industrial waste solutions where the selectivity of biosorption provides a definite advantage over ion exchange. The kinetic characteristics have shown that when an immobilised biomass particle is suspended in a solution containing a solute, eventually four consecutive mass transport steps are associated with the biosorption of the solute from the solution:

a) transport of the solute in the bulk solution which is very rapid because of mixing and convective flow;
b) diffusion of the solute through the hydrodynamic boundary layer that surrounds the biosorbent particle;
c) subsequently, the diffusional transport of the solute across the layer of admixes; and
d) diffusion of the solute in the biomaterial core.

It should be noted that because the steps act in series, the slowest will be the rate-limiting step (Tsezos, 1990).

Immobilisation is applied routinely for various applications. A form of immobilisation is the use of pelleted biomass where filamentous fungi are grown in agitated broth to produce pellets (DeRome and Gadd, 1991). Because of the ability for fungal biomass to grow on

inert objects, it can be immobilised by growth on the surfaces of nylon cord, waste sponge and rotating-disc reactors (Wainwright, 1992). A study by Iqbal and Zafar (1994) showed that filamentous fungi were successfully immobilised by growth within the vegetable sponge *Luffa cylindrica*. Immobilisation of yeast by this technique was not achieved as the yeast cells dissociated from the sponge into the surrounding broth. Minimal growth of yeast cells occurred on the surface of the vegetable matrix. To achieve immobilisation, developers of biosorbent systems have attached bacteria to inert substrates such as reticulated foams, stainless steel wire and pan sources (Macaskie and Dean, 1987). Immobilisation has also been achieved by growth within packed beds of sand (Huang *et al.*, 1990) and entrapment within alginate, acrylamide and polysulfone (DeRome and Gadd, 1991; Jeffers *et al.*, 1991; Brady and Duncan, 1994). Entrapment using polysulfone has been particularly successful and has already had industrial application in the USA where the product is marketed as "Bio-Fix" beads.

As discussed above, there has been an abundance of research conducted on a variety of immobilising techniques and immobilisation of different biological matter. It should be noted that no literature was available on immobilisation of waste sludges for application as potential biosorbents, thus indicating a relatively unresearched area. Such investigations were within the scope of the present study.

2.6.3 Immobilised biomass in packed-bed processes

In a seperation process such as biosorption, the best use of the biosorptive properties of immobilised biomass particles is presented by using multistage, countercurrent packed-bed reactors for contacting the biosorbent with the solution of interest. Considerable experience has accumulated in their use by the metal- and pollution-control industries (Tsezos, 1990). Immobilised waste sludge biomass, in a packed-bed process, has many advantages. The biomass could be regenerated using appropriate desorbents. Immobilisation, using polysulfone, provides an overall rigid structure to the biomass particles. In addition, since there is no agitation, the packed-bed process provides a final effluent of good quality due to minimal release of solids.

It should be noted that although the scope of the present research focuses on waste digested sludge, which is a product of anaerobic digestion, as metal biosorbent, all investigations were conducted aerobically and comparisons using existing literature were applicable to waste activated sludge. Most of the research involving waste digested sludge and heavy metal uptake were conducted *in situ* during the anaerobic digestion process.

CHAPTER 3

3.0 MATERIALS AND METHODS

3.1 ACQUISITION AND PREPARATION OF ANAEROBIC SLUDGES

3.1.1 Sludge collection

Waste digested sludges were collected from drying beds in 20kg plastic containers from the following wastewater treatment plants in Natal, namely, Amanzimtoti, S1, New Germany, S2, Northern Works, S3, South African Breweries (SAB), S4 and Umbilo Works, S5. Sludge from SAB was in the form of upflow anaerobic sludge blanket (UASB) pellets.

3.1.2 Sludge preparation

Sludge was sun dried for 6 days, to increase solids content. Poor weather conditions resulted in sludge being dried in a drying oven at 105°C to achieve complete drying. Sludge was subsequently milled using a Reutsch crossbeater mill (SK1), and sieved using a hand sieve, resulting in a sludge particle size of 2 mm, the predetermined optimum size resulting in good biosorption and settling (unpublished data). Dried, milled sludge was stored at room temperature for further use. For experimental purposes, sludge was resuspended in deionised water at a concentration of 25 000 mg.ℓ^{-1}.

3.2 BATCH BIOSORPTION

3.2.1 Pretreatment of materials

Polypropylene tubes, vials and all glassware were soaked overnight, at ambient temperature, in 5% (v/v) Extran MA-01 alkaline (Lasec, South Africa). Vials and centrifuge tubes were then rinsed in triple deionised water and subsequently dried. Glassware, including pipettes, were subjected to a stringent acid wash procedure, ie., rinsing in 50% (v/v) nitric acid (HNO_3), tap water followed by 50% (v/v) hydrochloric acid (HCl), tap water and finally, rinsing in triple deionised water with subsequent drying (Smith and Vasiloudis, 1989).

3.2.2 Preparation of solutions

Heavy metal species used for batch experimentation included Cu^{2+}, Cd^{2+}, Cr^{3+}, Cr^{6+}, Ni^{2+} and Zn^{2+}. Analar-grade glassware was used throughout for preparation of metal solutions. Aqueous metal stock solutions of 1 000 mg.ℓ^{-1} were prepared in one litre volumes and stored at 4°C in volumetric flasks. Working solutions of each metal were prepared by allowing aliquots of stock solution to attain room temperature before preparing required concentrations. Chemicals, $K_2Cr_2O_7$ (BDH, England), $CrK(SO_4)_2.12H_2O$ (BDH, England), $Cu(NO_3)_2.3H_2O$ (BDH, England), $ZnSO_4.7H_2O$ (BDH, England), $NiCl_2.6H_2O$ (BDH, England) and $Cd(NO_3)_2.4H_2O$ (BDH, England), were analar grade.

3.2.3 Biosorption procedure

Heavy metal species used in the experiments were prepared individually from 1 000 mg.ℓ^{-1} stock solutions when required, at final concentrations of 30, 60, 90, 120 and 150 mg.ℓ^{-1}. Experiments were performed per single metal solution in triplicate. Aliquots of 8 mℓ metal solutions were dispensed into 15 mℓ screw-cap polypropylene centrifuge tubes. This was followed by addition of 2 mℓ of 25 000 mg.ℓ^{-1} sludge, resulting in a final concentration of 5 000 mg.ℓ^{-1} sludge in each tube. Controls of each concentration of metal solution were prepared by substituting 2 mℓ deionised water for digested sludge. Tubes were capped, agitated using a vortex mixer and incubated in a shaking incubator at 25°C at 150 rpm for 3 hrs, at a slant, to ensure efficient mixing between sludge and metal solution. Centrifugation followed at 4 000 x g, for 30 min., using a J6-MC Beckman centrifuge. Supernatants were decanted into 20 mℓ screw-cap polypropylene scintillation vials and stored at 4°C overnight, before being analysed. Free metal was measured in solution, using a Varian-1275 Atomic Adsorption Spectrophotometer, after preparation of appropriate standards (Appendix A).

3.2.4 Analysis of data

Data were converted to ratios of quantities metal biosorbed versus amount sludge (mg.g^{-1}), and plotted against corresponding metal ion concentrations (mg.ℓ^{-1}). In addition, percentage metal biosorbed was plotted against metal ion concentration (mg.ℓ^{-1}) (FIGS 4.1 - 4.12).

3.3 MECHANISMS OF BIOSORPTION

Free metals present in supernatants were quantified by atomic adsorption spectrophotometry. Sludge-bound and free metals were expressed as adsorption isotherms to determine adsorption mechanisms. First order regression coefficients, ($> 0,90$) were calculated for linear reciprocal transformations of adsorption isotherms to determine whether the model was applicable to sludge-metal interactions. Equations of these straight lines were determined from which sludge-metal bond strengths (k_a) and binding capacities (X_m) were calculated (TABLES 4.1 and 4.2). Sludges were ranked according to the latter two criteria.

3.4 DETERMINATION OF SLUDGE SURFACE CHARGE

Grab samples of waste digested sludge were obtained from the drying beds of waste water treatment plants, namely, S1, S2, S3, S5 and dried UASB pellets from S4, and stored in one litre glass collection vessels. Electronegativity of the sludge particles was determined within 24 hrs of obtaining samples. Previous research by Bux *et al.*, (1994), investigated various methods for sludge surface charge determination, and recommended the millivolt quantification method as being appropriate for such applications. The procedure involved using a Crison micropH 2000 combination pH/millivolt meter. The meter was standardised using standard buffer solutions of pH 7 (Beckman), since the solution produced no net charge. Samples were diluted to a final volume of 100 mℓ with deionised water in conical flasks at a concentration of 5 000 mg.ℓ^{-1}. The unit was operated in the mV/Rel mV mode. Sludge samples were read in triplicate and the combination electrode was rinsed with deionised water between each reading. This method is well suited for the determination and

comparison of surface charge of sludges under investigation (Bux *et al.*, 1994).

3.5 LABORATORY SCALE BIOSORPTION

3.5.1 Selection of superior sludge

Previous research by Bux *et al.*, (1994), presented a definite relationship between biosorptive capability and the degree of electronegativity of the sludge surface. For further investigation, sludges were selected on the basis of greatest biosorption during batch experimentation, their binding strengths (k_a) and metal binding capacities (X_m), as well as their electronegativities. Sludges selected for further investigation were New Germany (S2), Northern Works (S3) and SAB (S4).

3.5.2 Pretreatment of sludge

Samples were collected from drying beds and UASB digesters. Sludges were sun dried on porous cotton cloth to facilitate water drainage. Depending on the moisture content of the sludges, they were dried for approximately six to nine days. Dried sludge was milled using a Retsch cross beater mill (model SK-1), equipped with a 2 mm sieve and receptacle. Milled sludge was subjected to further sieving through a 2 mm sieve to remove very fine sludge particles and obtain an average particle size of 2 mm, which were stored dry at room temperature until required.

3.5.3 Design and construction of bioreactor

Bioreactors were designed in consultation with chemical engineers (Appendix B). Construction of bioreactors was by Maizey Plastics (Durban). Perspex was used as material of choice due to its relative inertness and clear visibility. Agitation rate had to be optimised such that no uneven settling (dead spots) occured in the bioreactor. Therefore, conditions had to be optimised to ensure maximum exposure of metals in solution to the sludge particles. Experiments were conducted on a batch basis, but bioreactors could be adapted for continuous operation.

3.5.4 Preparation of synthetic effluent

Synthetic effluent, composed of 50 $mg.\ell^{-1}$ Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+} and Cr^{6+}, was prepared in 50ℓ perspex containers (Appendix C). Synthetic effluent was prepared fresh for immediate use.

3.5.5 Acquisition of industrial effluent

In an attempt to assess the industrial applications of the process, an industrial effluent was obtained from Saayman Danks Electroplaters Pty (Ltd). Samples were collected from the post-galvanising rinse process (Appendix D). Samples were collected in 40ℓ aspirators and stored at room temperature. Since the company concerned had primarily high concentrations of Zn^{2+} in their effluent, and samples collected were from the post-galvanisisng rinse, Zn^{2+} would be the major component of the effluent. Effluents were tested for free metal ions

using AAS. Effluents were diluted with deionised water when necessary.

3.5.6 Biosorption procedure

Fifteen litres of synthetic effluent were decanted into 40ℓ perspex bioreactors. Subsequently, milled sludge samples of S1, S2 and S3 were individually dispensed into the bioreactors at a previously optimised concentration of 25 000 mg.ℓ^{-1} (Bux *et al.*, 1994b). Immediately upon addition, triplicate 20 mℓ samples were extracted and dispensed into polypropylene vials, representing the zero minute sample. Thereafter, triplicate 20 mℓ samples were taken every 15 min., for a period of 90 min. Agitation was optimised at approximately 450 rpm, $\pm$ 2% rpm. Upon termination of the experiment, treated effluent was tapped off from the bioreactor. Samples were analysed for remaining metal concentration using an atomic adsorption spectrophotometer. Total chromium was measured using AAS and hexavalent chromium determination was conducted using a modified SABS 206 and Merck method (Appendix E). Trivalent chromium concentrations were then determined by the difference between total chromium and hexavalent chromium concentrations.

3.6 LABORATORY SCALE DESORPTION

3.6.1 Selection of desorbent

Previous research (Bux *et al.*, 1995), investigated a range of desorbing agents to determine which was most suitable for application. Subsequently, optimum concentrations of desorbents selected for the present experiments included 0.2*N* H_2SO_4, 0.2*N* HCl and 0.4*N*

CH_3COOH. Required volumes of acids were prepared and stored in 20ℓ glass aspirators. Since H_2SO_4 was cheaper than HCl, the former mineral acid's efficiency for metal removal from sludge was to be compared with that of the latter, to determine whether it was more conducive to large scale application. Efficiency of desorption was calculated, using the following formula:

$$\text{Desorption efficiency} = \frac{\text{quantity desorbed (mg.}\ell^{-1}\text{)}}{\text{quantity adsorbed (mg.}\ell^{-1}\text{)}} \times 100\%$$

(Bux *et al.*, 1994)

3.6.2 Desorption procedure

Since S1 demonstrated greatest metal biosorptive potential during laboratory trials, desorption experiments were conducted using the specific metal saturated sludge. Metal-bound sludge was exposed to each of the selected desorbents in individual desorption trials in perspex bioreactors. On addition of the mineral acids to the sludge, a zero minute sample was taken. Agitation was commenced and maintained at 300 rpm and thereafter 20 mℓ samples were collected in triplicate, every five min., for 15 min. (Appendix E). In contrast to the biosorption procedure, desorbent volumes were five litres (approximately $^1/_3$ of effluent). Samples obtained from desorption experiments were analysed using AAS. The above parameters for desorption were previously determined (Bux *et al.*, 1994b).

3.7 CONTINUOUS BIOSORPTION AND DESORPTION PROCESSES

3.7.1 Design and construction of simultaneous process

In order to make the fully-mixed batch process applicable to remediate large volumes of effluent and to simultaneously be efficient, both biosorption and desorption should be combined in the form of a continuous process. However, a continuous process was not possible as it had to be periodically halted for movement of sludge, effluent and desorbent between bioreactors and desorbed sludge could not be reused due to destruction of metal binding sites by strong mineral acids. The process could however be referred to as a simultaneous process, since biosorption and desorption ocurred concurrently. Since waste digested sludge S3 presented comparatively superior biosorption during preceeding batch experiments, it was to be used for subsequent investigations. Figure 3.1 represents the simultaneous model schematically. Perspex 40ℓ bioreactors, along with agitators, were used (Appendix B). Silicone tubing was used to connect bioreactors to pumps (Appendix F).

3.7.2 Optimisation of process

The simultaneous process occurred in the following sequence (FIG. 3.1):

Biosorbent (S1) was exposed to the synthetic effluent according to previously optimised parameters (batch biosorption procedure). Upon completion of biosorption, treated effluent was tapped off into a collection vessel. The biosorption reactor was then fed with desorbent ($^1/_3$ volume 0.2N H_2SO_4). Metal-bound sludge was mobilised by both the acid and agitators,

and transported, using a pump, to the desorption vessel. Desorption with agitation continued for 15min. Once the suspension was completely transported out of the adsorption reactor, a second mass of sludge and untreated effluent were introduced and biosorption commenced. While biosorption occurred for 90 min., desorption occurred for only 15 min., and once complete, the acid was pumped back to the desorbent storage vessel using a peristaltic pump. Biomass was discarded into a collection vessel.

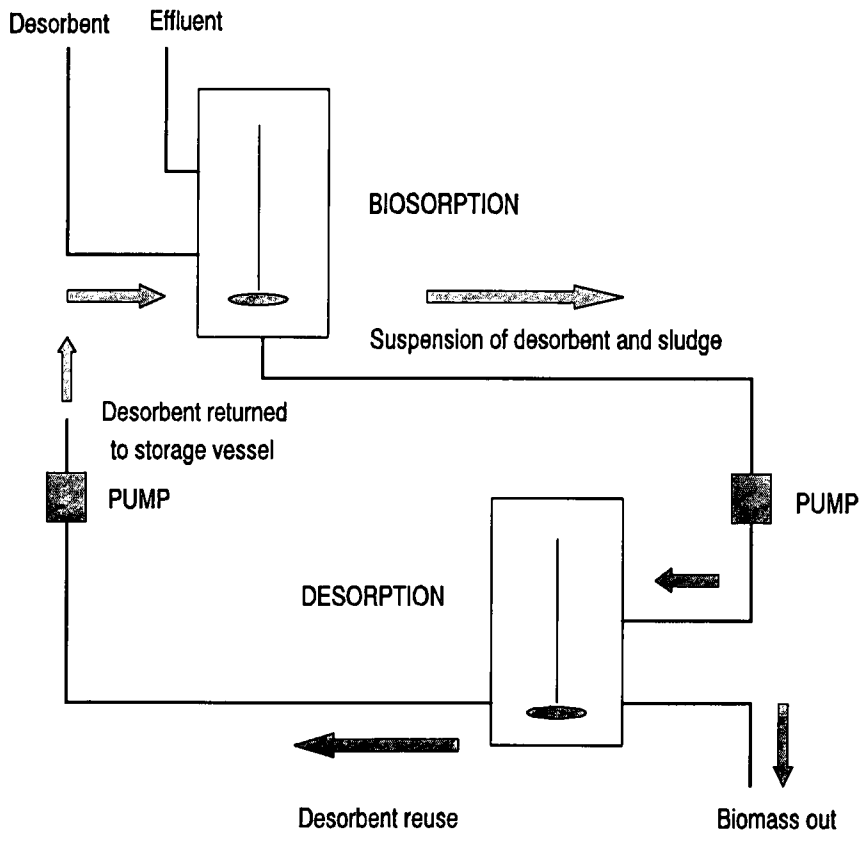

FIG. 3.1 Schematic representation of a simultaneous biosorption and desorption process.

3.8 IMMOBILISATION OF SLUDGE BIOMASS

3.8.1 Selection of immobilising agent

Previous research by McFarlane (1995), investigated a range of agents suitable for the immobilisation of biomass. Two immobilising agents were selected viz., calcium alginate beads and polysulfone resin (Acros, Belgium). Immobilisation of biomass was achieved by gel entrapment within the alginate beads (Kierstan and Coughlan, 1985). Problems were encountered, since the calcium alginate-biomass lacked consistency and the beads were easily ruptured. Polysulfone resin formed a more rigid complex with sludge biomass (S1), and was therefore selected as agent of choice for subsequent trials.

3.8.2 Immobilisation procedure

Biomass constituted dried, milled and sieved sludge solids (Appendix G). Polysulfone resin was dissolved in N,N - dimethylformamide (Appendix H). Sludge particles were added to the polysulfone solution in a ratio of 1 : 2. The mixture was stirred constantly on a magnetic stirrer for two hrs, after which it was allowed to stand without agitation for a further 30min., to allow any air bubbles to escape. The polysulfone-biomass solution was pumped via a peristaltic pump (Instrumentation Centre, Technikon Natal) through 5 mm internal diameter silicone tubing connected to an open 5 mℓ glass syringe (Sanitex). A 16 gauge needle was connected to the syringe via a luer lock system. The tip of the needle was maintained at a height of 10 cm above the surface of 500 mℓ triple deionised water in a one litre beaker. Using a slow flow rate, the biomass-polysulfone mixture was allowed to drip into the water,

instantly forming beads. Beads were left in the deionised water at 4°C overnight, to allow solidification (curing) and also for the organic solvent to diffuse out (Jeffers *et al.*,1990). Beads were subsequently rinsed and resuspended in deionised water and stored at 4°C until required.

3.9 LABORATORY SCALE PACKED-BED PROCESS

3.9.1 Design of bioreactor

Packed-bed experiments were conducted in glass columns (FIG. 3.2).

3.9.2 Optimisation of process

Experiments were conducted at room temperature. Beads were packed into the column, level with the first outlet port which represents the 94.14 mℓ bed volume (bed depth of approximately 11.3 cm). The bed was compacted using 200 mℓ deionised water which was dispensed into the reactor until the beads formed a consistent bed without large spaces between beads. The process was set up in such a way that effluent could be pumped freely up through the packed bed. Silicone tubing with an internal diameter of 5 mm connected the initial effluent resevoir, via a peristaltic pump, to the inflow port (10 mm internal diameter).

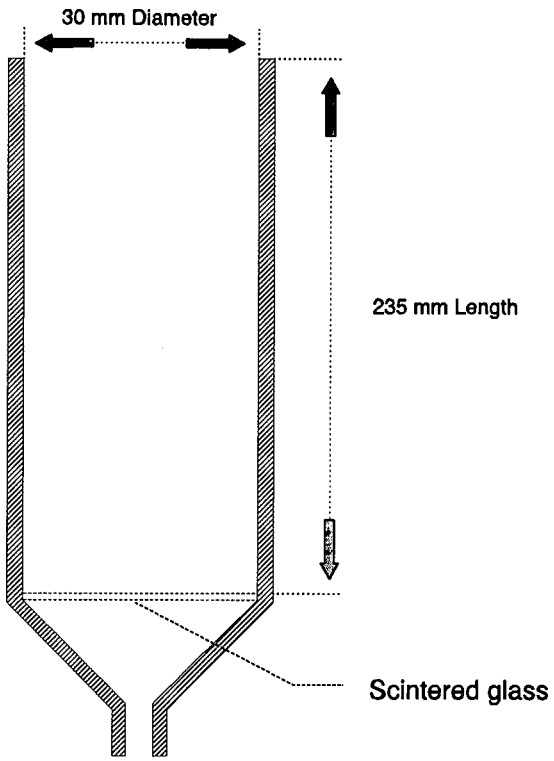

FIG. 3.2 Schematic representation of glass column bioreactor.

Silicone tubing of similar diameter was used to connect the outflow port to the final effluent reservoir. Synthetic effluent, comprising 50 mg.ℓ^{-1} of each of the following metals, Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+} and Cr^{6+} was used for experimentation. Effluent was pumped from the initial effluent reservoir, up through the packed-bed and into the final effluent reservoir. A set flow rate of 20.92 mℓ.min^{-1}, for a set period of time, determined the volume of effluent exposed to the biomass. A narrow tube, connected to a plastic 20 mℓ syringe (Promex), enabled 20 mℓ samples to be taken directly from the top of the packed-bed. Samples were taken in triplicate and stored in 20 mℓ polypropylene scintillation vials at 4°C. Analysis of metals was conducted using AAS. The process is shown in FIG. 3.3.

Desorption experiments were set up following the same procedure as for adsorption experiments, whereby desorbent was pumped up through the packed-bed. The flow rate used was the same as that used during adsorption. Immobilised biomass was desorbed using 0.2*N* H_2SO_4.

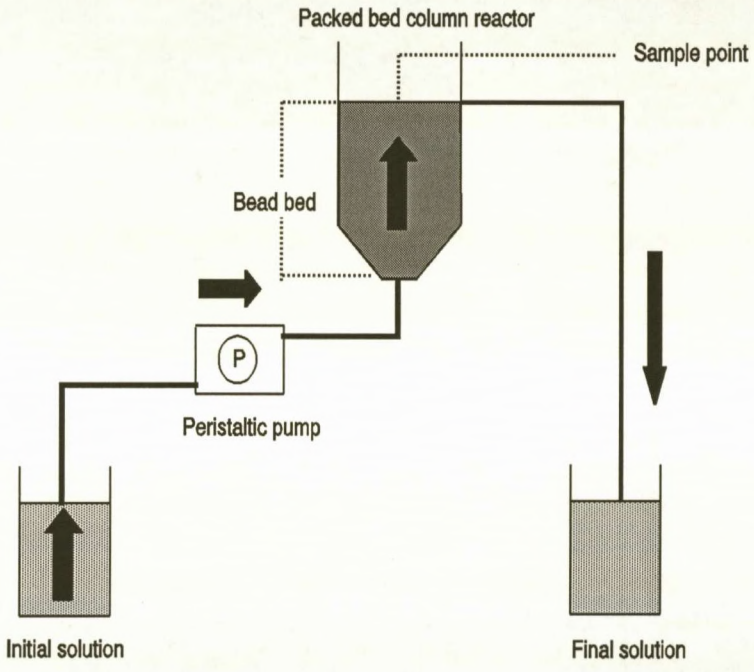

FIG. 3.3 Schematic representation of the packed-bed process.

CHAPTER 4

4.0 RESULTS

4.1 BIOSORPTION OF METAL IONS (BATCH)

4.1.1 Adsorption of metal ions from solution

Results of the present research showed that all five sludges investigated were capable of metal biosorption (FIGS 4.1 - 4.12). Quantities of Zn^{2+} adsorbed by the five sludges showed an increase as the concentration of Zn^{2+} in solution increased. Sludge S3 showed superior biosorption at higher concentrations ie., 120 and 150 mg.ℓ^{-1}. Sludges presented similar biosorptive capacities at 90 mg.ℓ^{-1} (FIG. 4.1). There was a marginal decrease in the percentage Zn^{2+} biosorbed with an increase in metal concentration in solution. This was evident with all sludges except S3 (FIG. 4.2).

Except for S5, all other sludges assessed showed an increase in biosorption as the concentration of Ni^{2+} in solution increased. Sludge S4 displayed superior Ni^{2+} biosorption when compared to other sludges (FIG. 4.3). The maximum percentage of Ni^{2+} biosorbed by the sludges was 50% by S3. Decrease in percentage Ni^{2+} biosorbed, with increase in metal concentration in solution, was not as evident as in the case of Zn^{2+} (FIG. 4.4).

Copper biosorption by sludges also exhibited the general trend of increase in the amount of metal biosorbed with increase in the concentration of metal in solution. Overall, superior

Cu^{2+} biosorption was demonstrated by S2. Sludge S1 showed decreases in Cu^{2+} biosorption at 150 mg.ℓ^{-1} (FIG. 4.5). With the exception of S3 and S4, a decrease in the percentage Cu^{2+} biosorbed by sludges was noted with an increase in metal concentration. Maximum biosorption was displayed by S2, at approximately 67%, at 30 mg.ℓ^{-1} (FIG. 4.6).

Biosorption of Cd^{2+} by sludges showed similar trends as other metals assessed, ie., there was a general increase in metal biosorbed with an increase in metal concentration in solution. Sludge S2 was the overall superior biosorbent. No significant differences in the amount of Cd^{2+} biosorbed were noted for S1, S4 and S5, at the higher concentrations (FIG. 4.7). There was an overall decrease in the percentage Cd^{2+} adsorbed by sludges, as the concentration of Cd^{2+} in solution increased. These findings were most evident at Cd^{2+} concentrations of 90 and 120 mg.ℓ^{-1} (FIG. 4.8).

Hexavalent chromium biosorption by sludges increased with increases in metal concentrations in solution. When compared to other sludges, S5 produced substantially lower biosorptive capacity. Comparatively, S4 showed greatest biosorption (FIG. 4.9). As compared with other metals, there was no decrease in percentage biosorbed by the sludges as concentrations of Cr^{6+} in solution increased. There was also minimal difference in percentage metal biosorbed by the sludges, at the different concentrations of metal in solution (FIG. 4.10).

Compared with other sludges, S3 was the only sludge that showed an increase in the quantities of Cr^{3+} biosorbed as metal concentration in solution increased. In addition, S3 was the best biosorbent with regard to the Cr^{3+} metal species. Some sludges showed no affinity for the metal at lower concentrations eg., S4, which showed no biosorption at 30 mg.ℓ^{-1}.

The capacity of S5 to biosorb Cr^{3+} was negligible, with minimal biosorption occuring only at 30 and 150 mg.ℓ^{-1} (FIG. 4.11). Sludges S2 and S3 were the only sludges that displayed the biosorption trend shown by sludge with other metals whereby percentage adsorption decreased as the concentration of the metal in solution increased. Maximum percentage removal by S3 was 60% at 30 mg.ℓ^{-1} (FIG. 4.12).

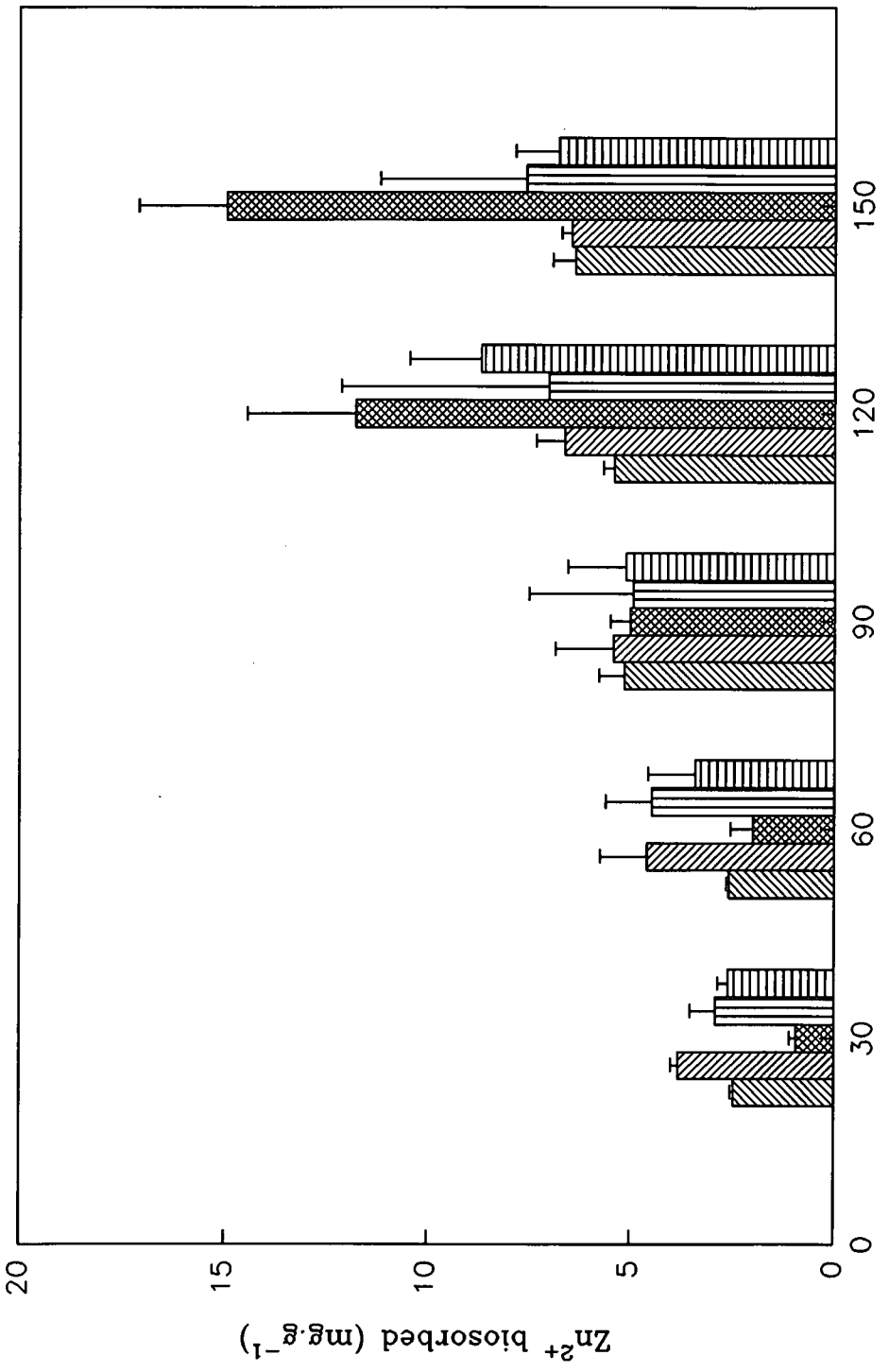

FIG. 4.1 Quantities Zn^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

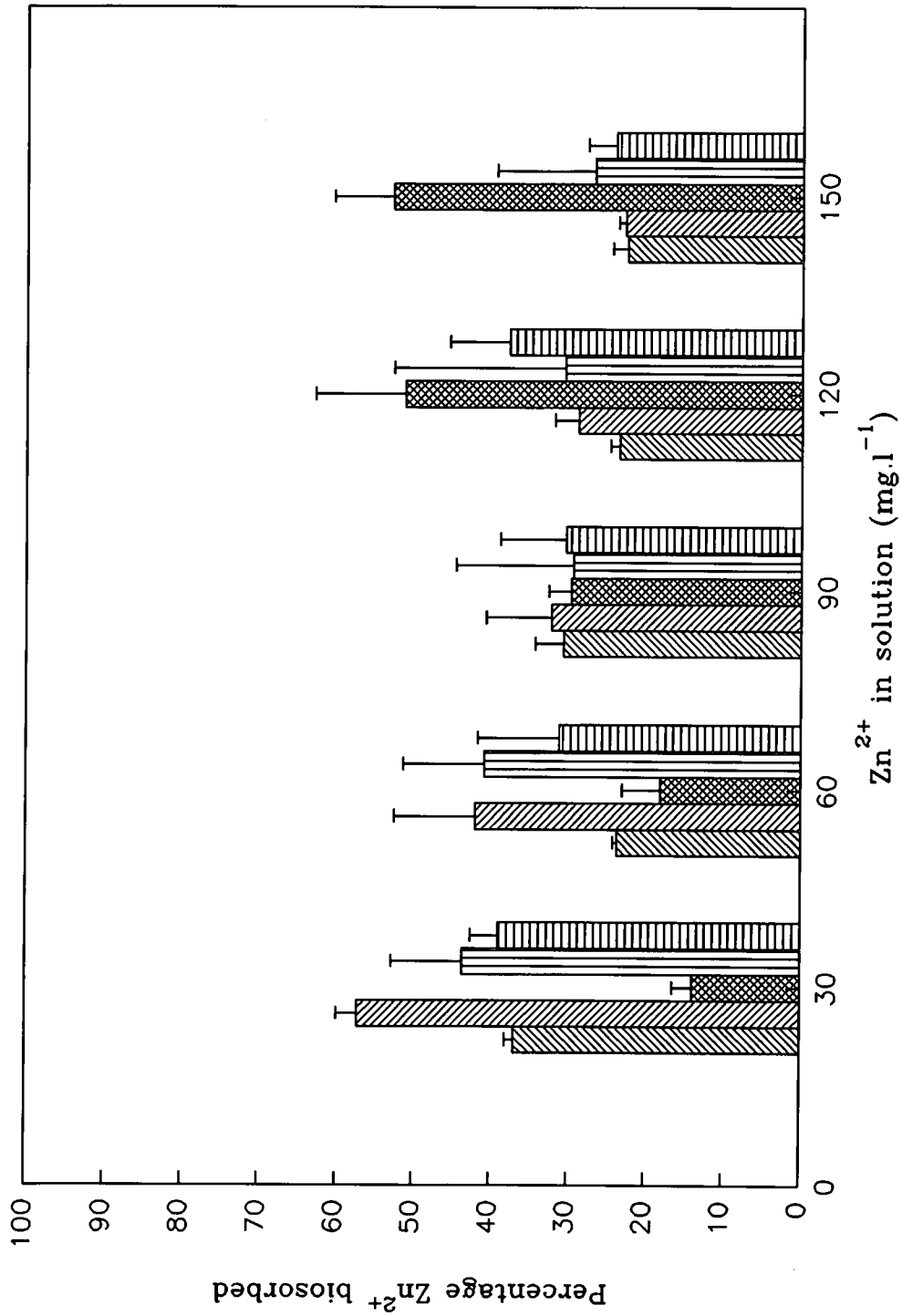

FIG. 4.2 Percentage Zn^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

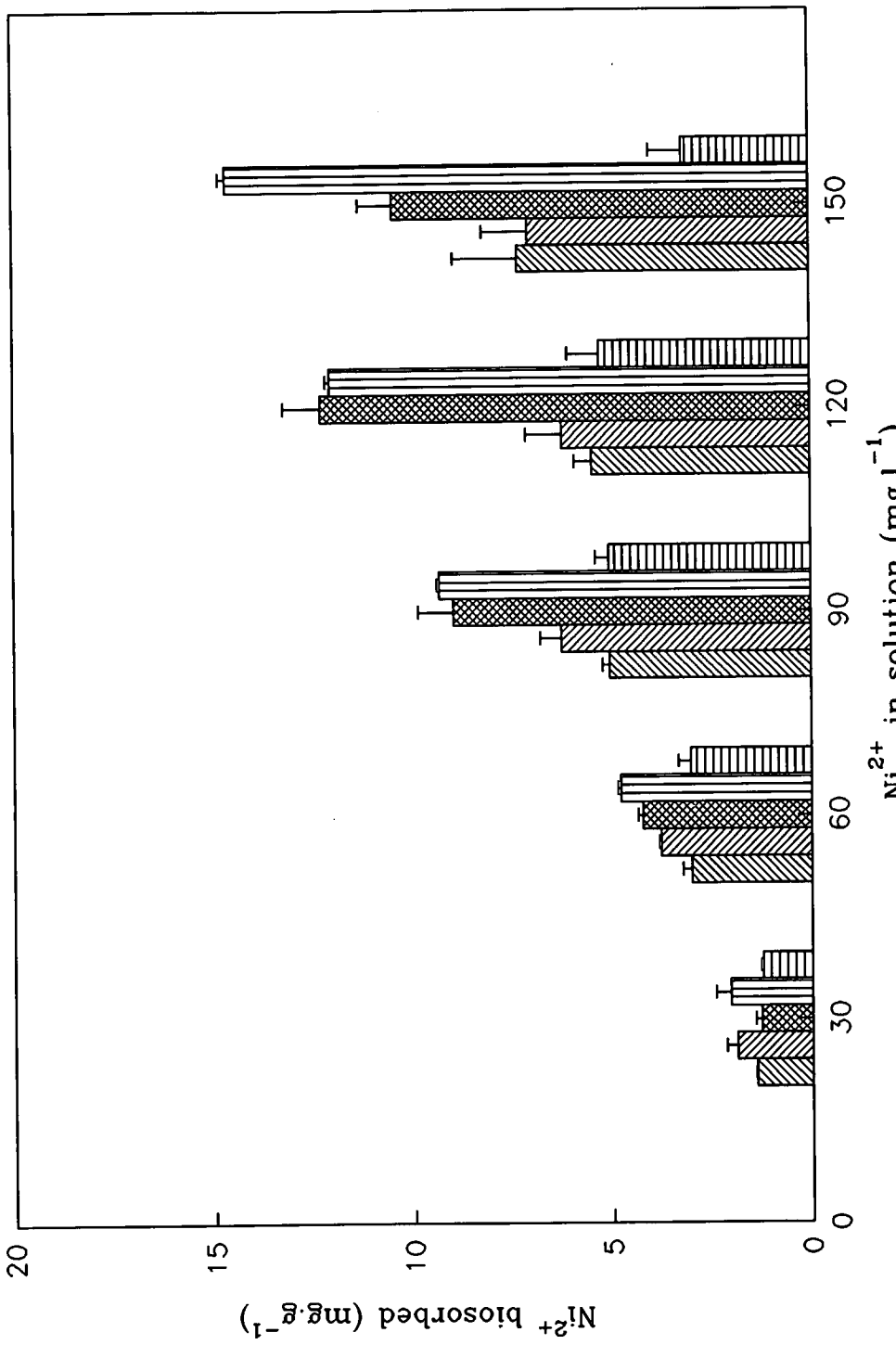

FIG. 4.3 Quantities Ni^{2+} biosorbed by S1 (▨), S2 (▨), S3 (▩), S4 (▥) and S5 (▤).

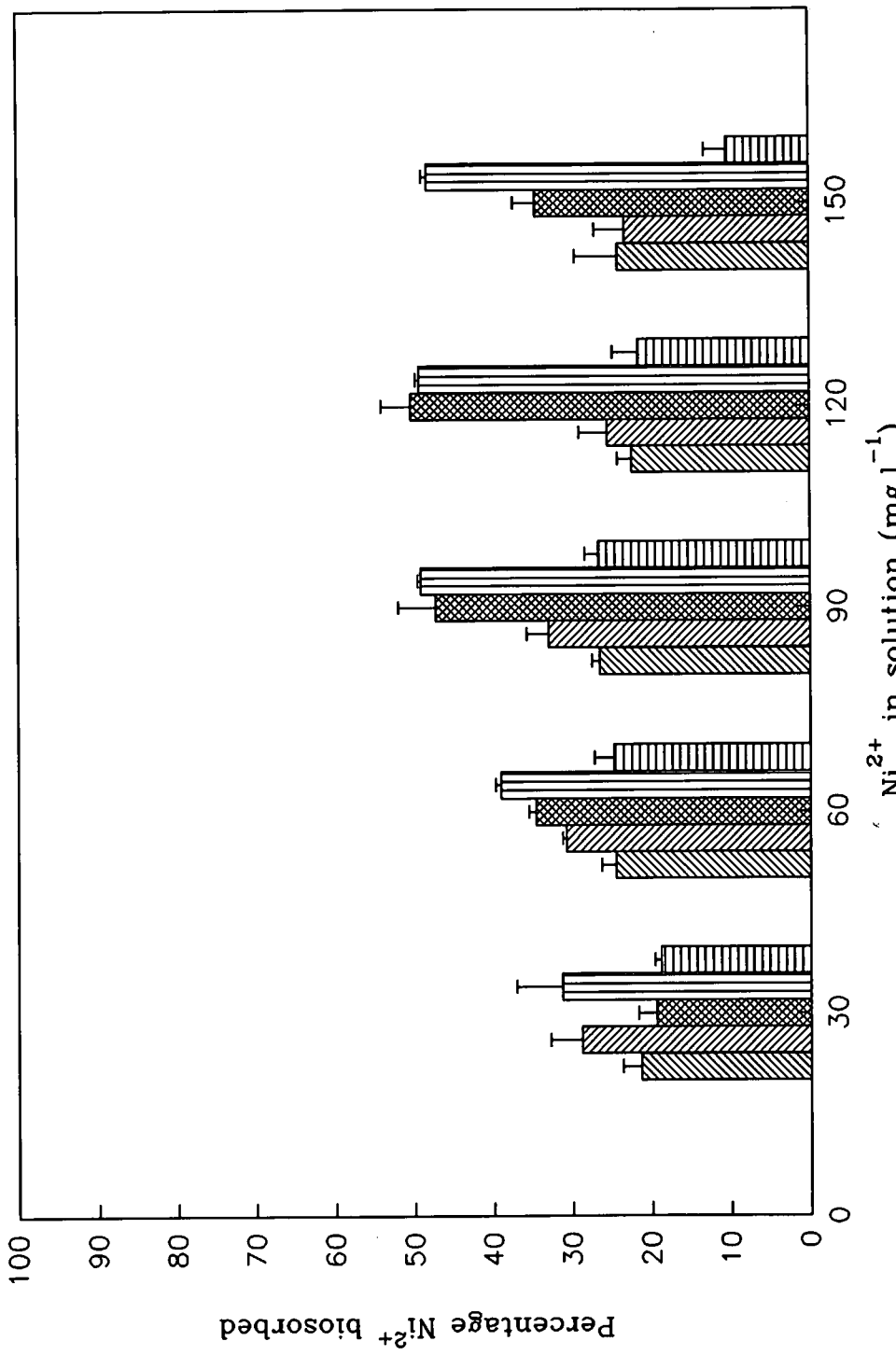

FIG. 4.4 Percentage Ni^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

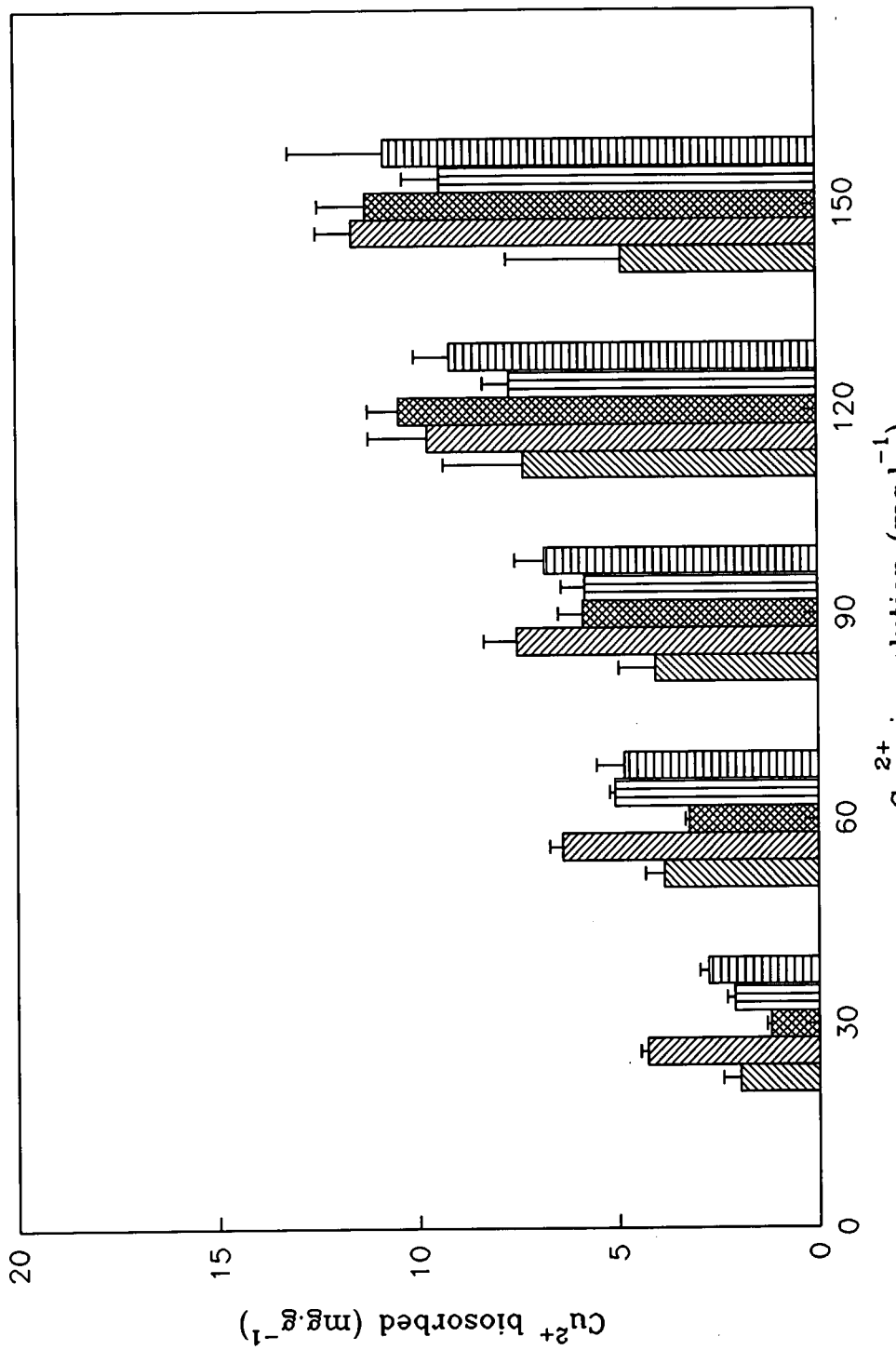

FIG. 4.5 Quantities Cu^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

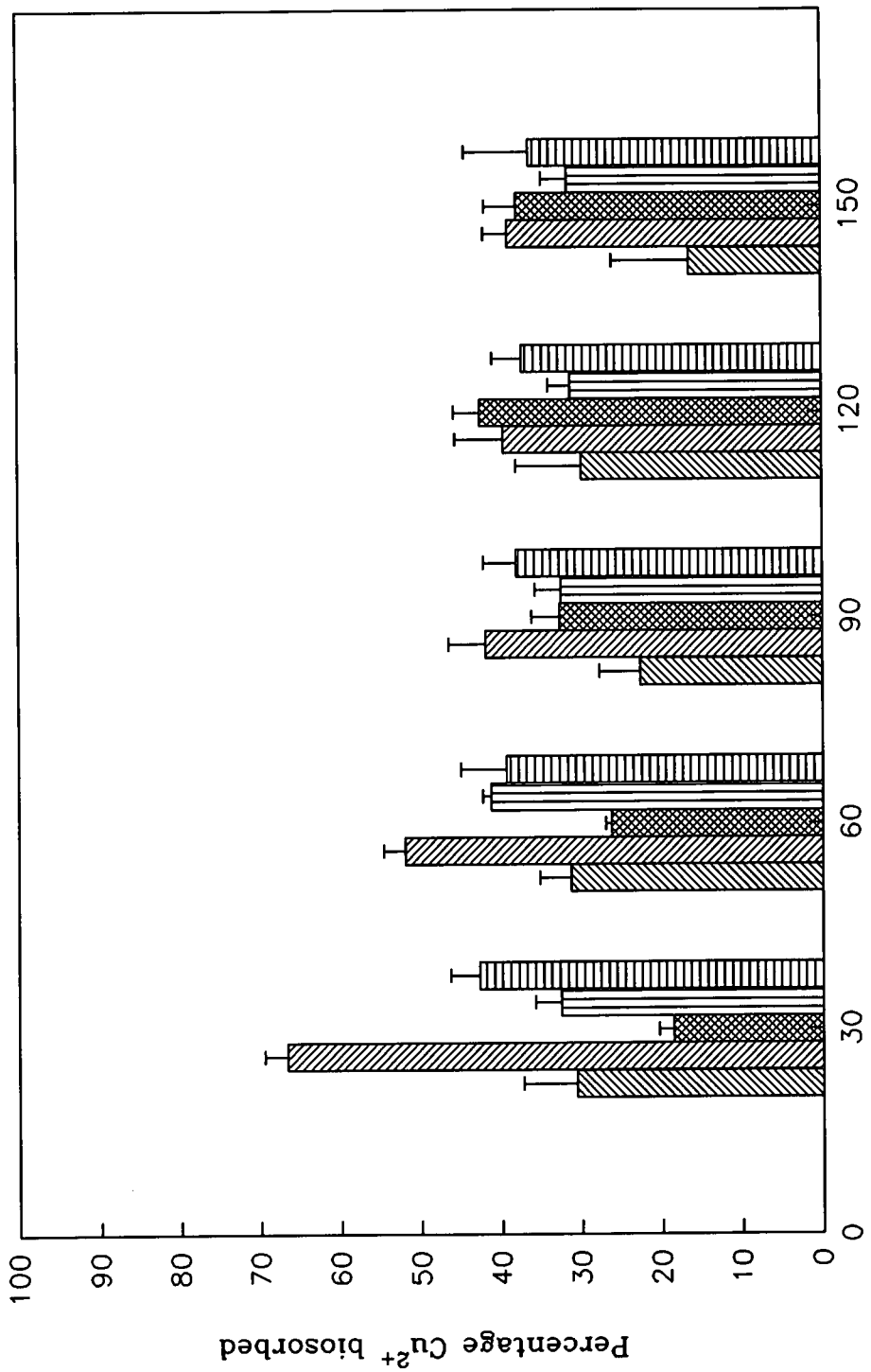

FIG. 4.6 Percentage Cu^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

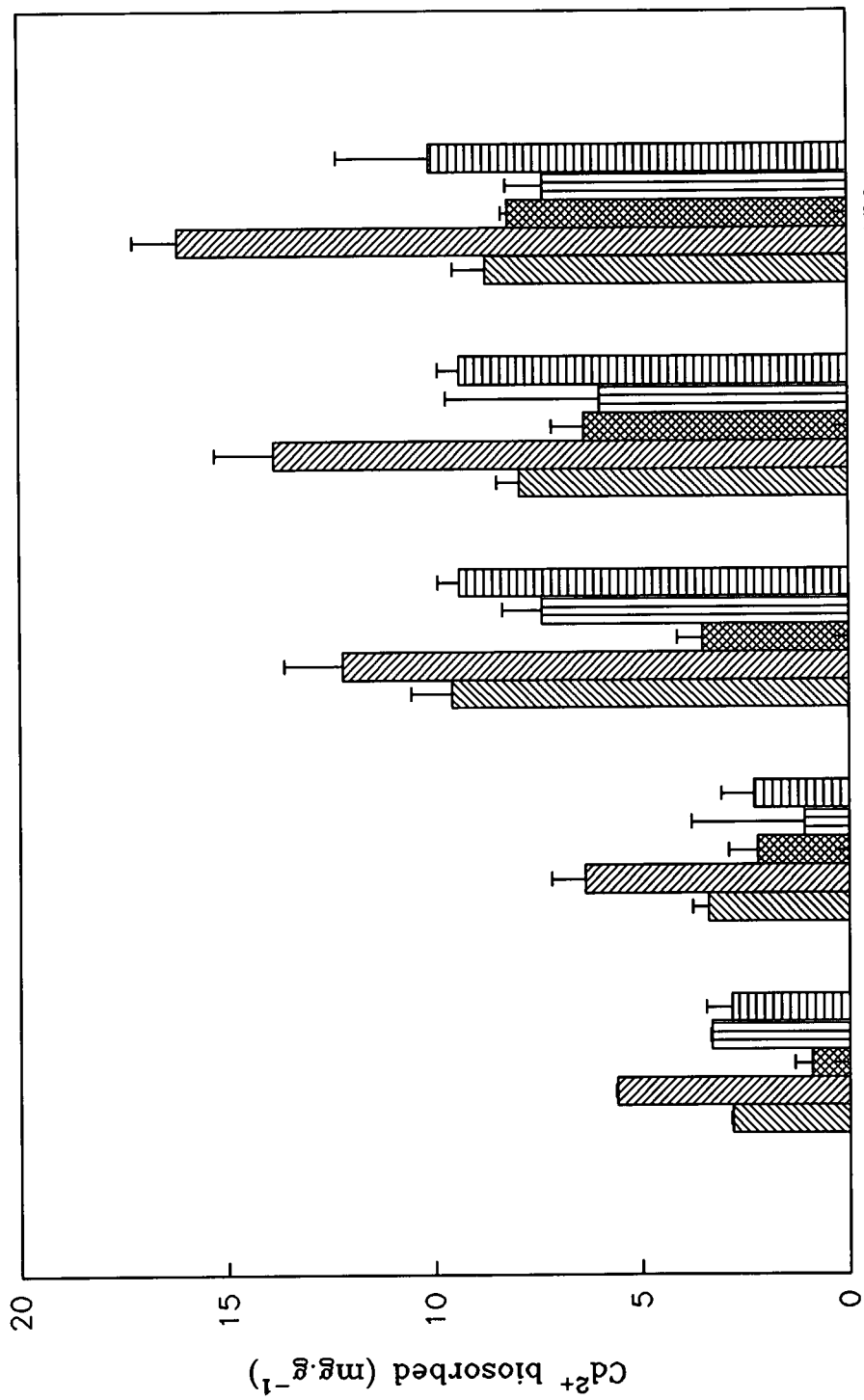

FIG. 4.7 Quantities Cd^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

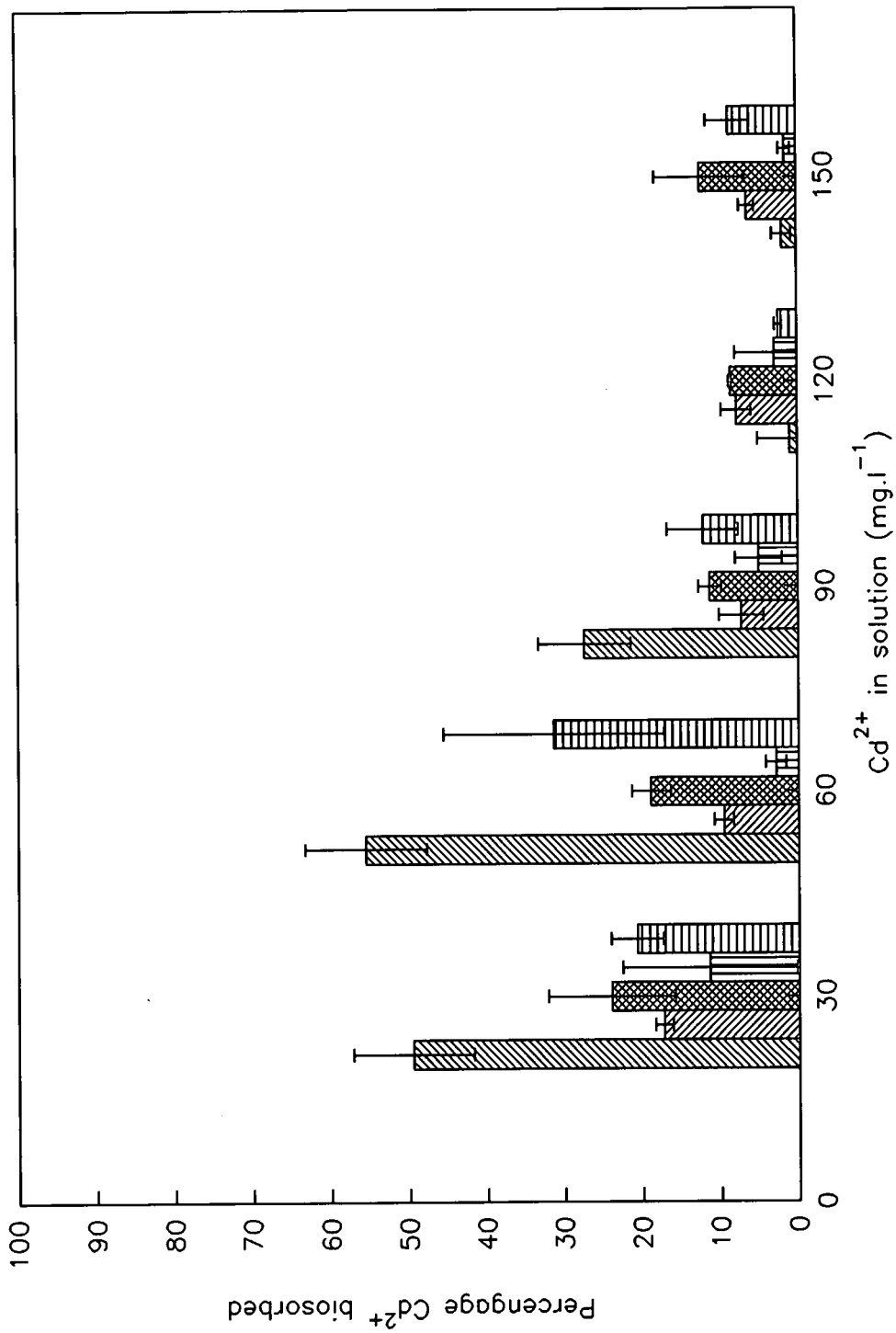

FIG. 4.8 Percentage Cd^{2+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

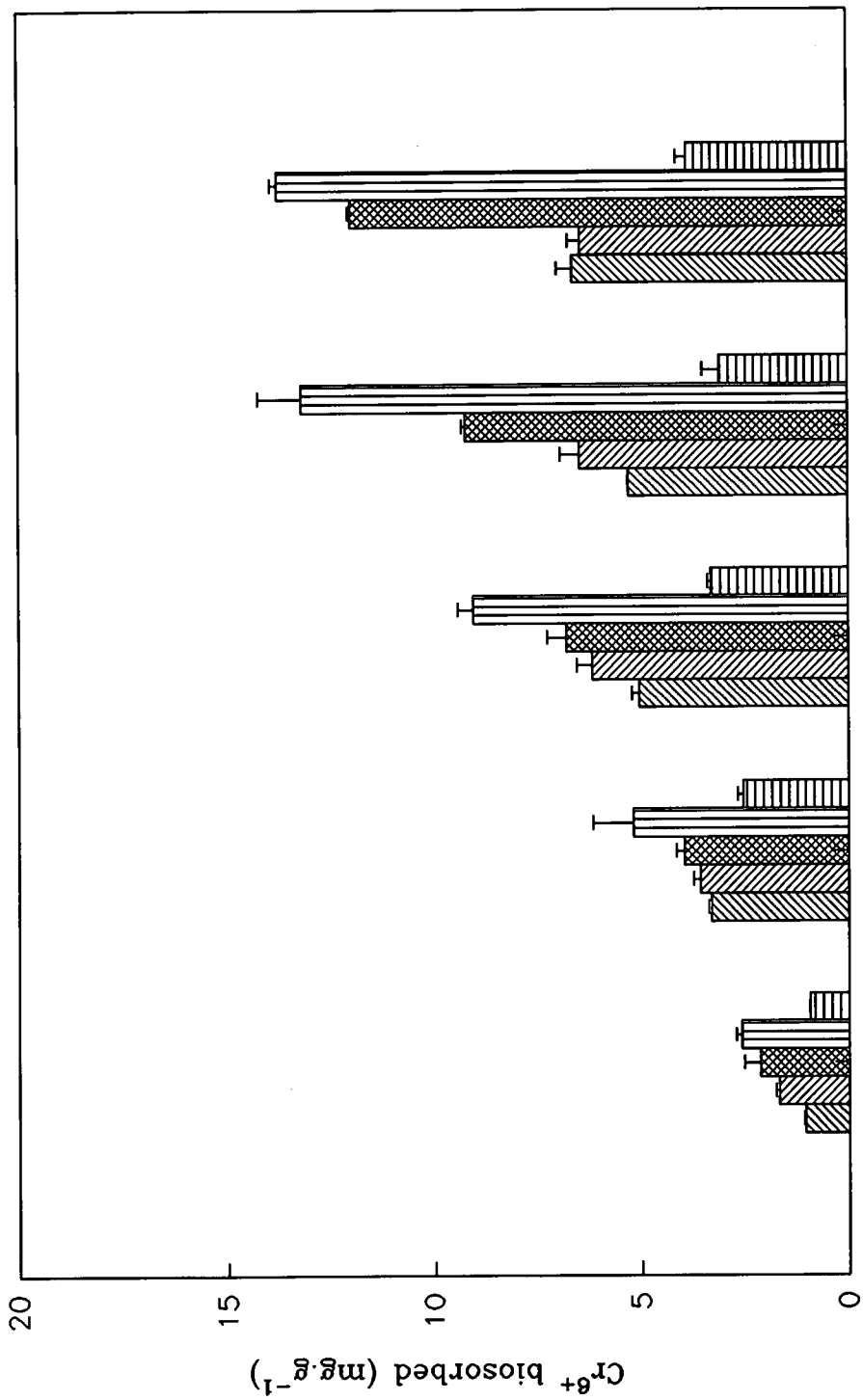

FIG. 4.9 Quantities Cr^{6+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

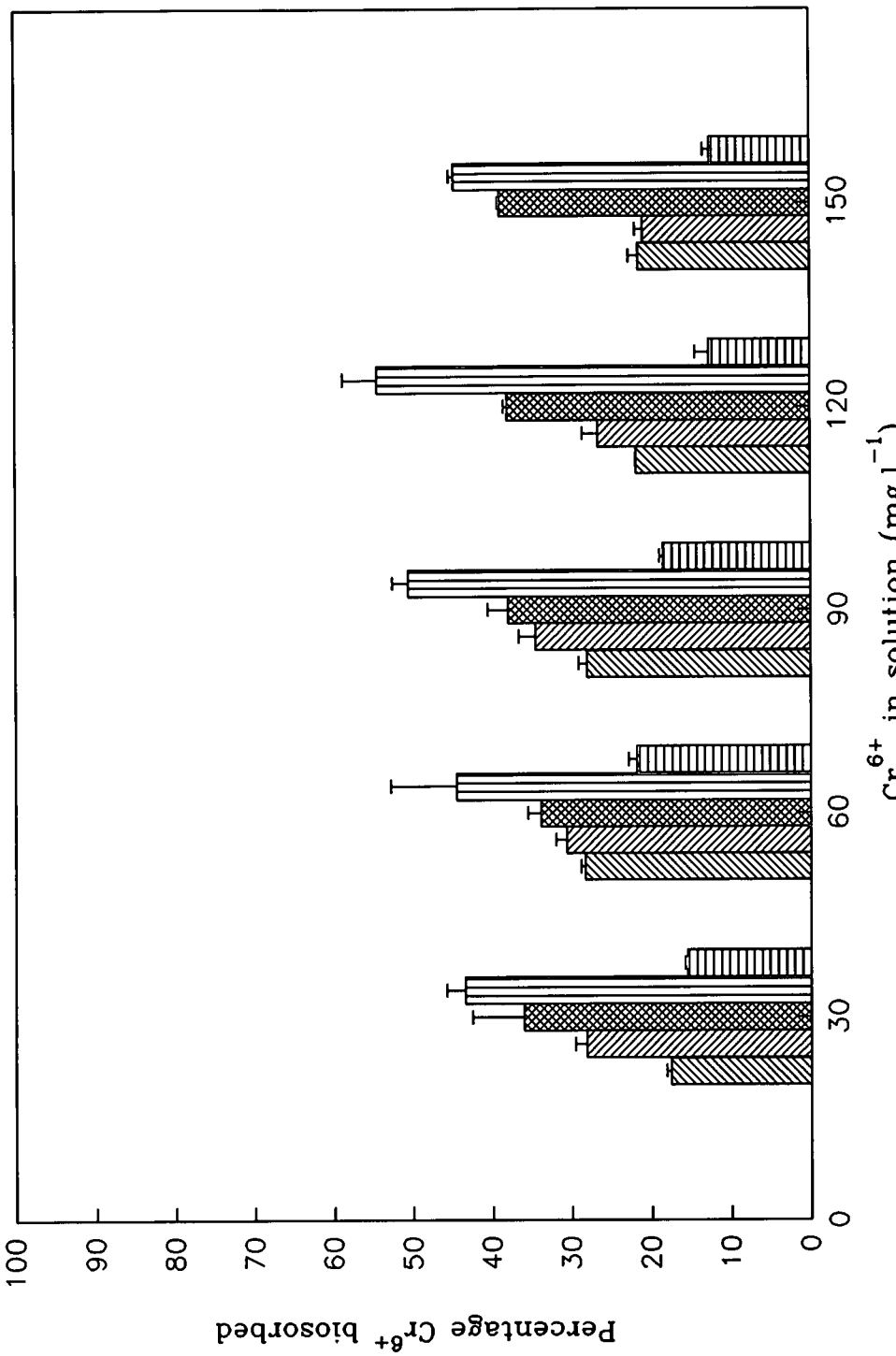

FIG. 4.10 Percentage Cr^{6+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

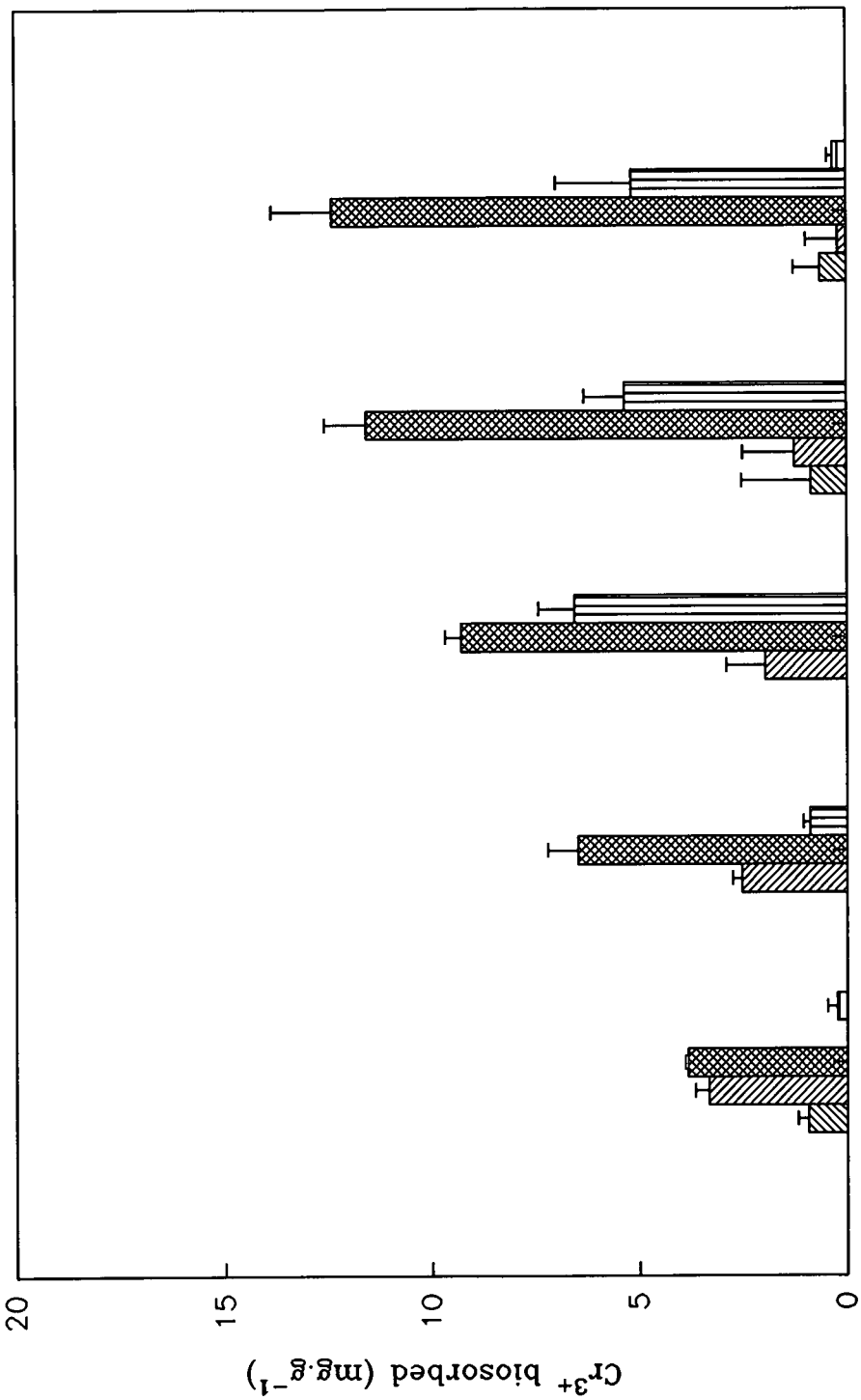

FIG. 4.11 Quantities Cr^{3+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

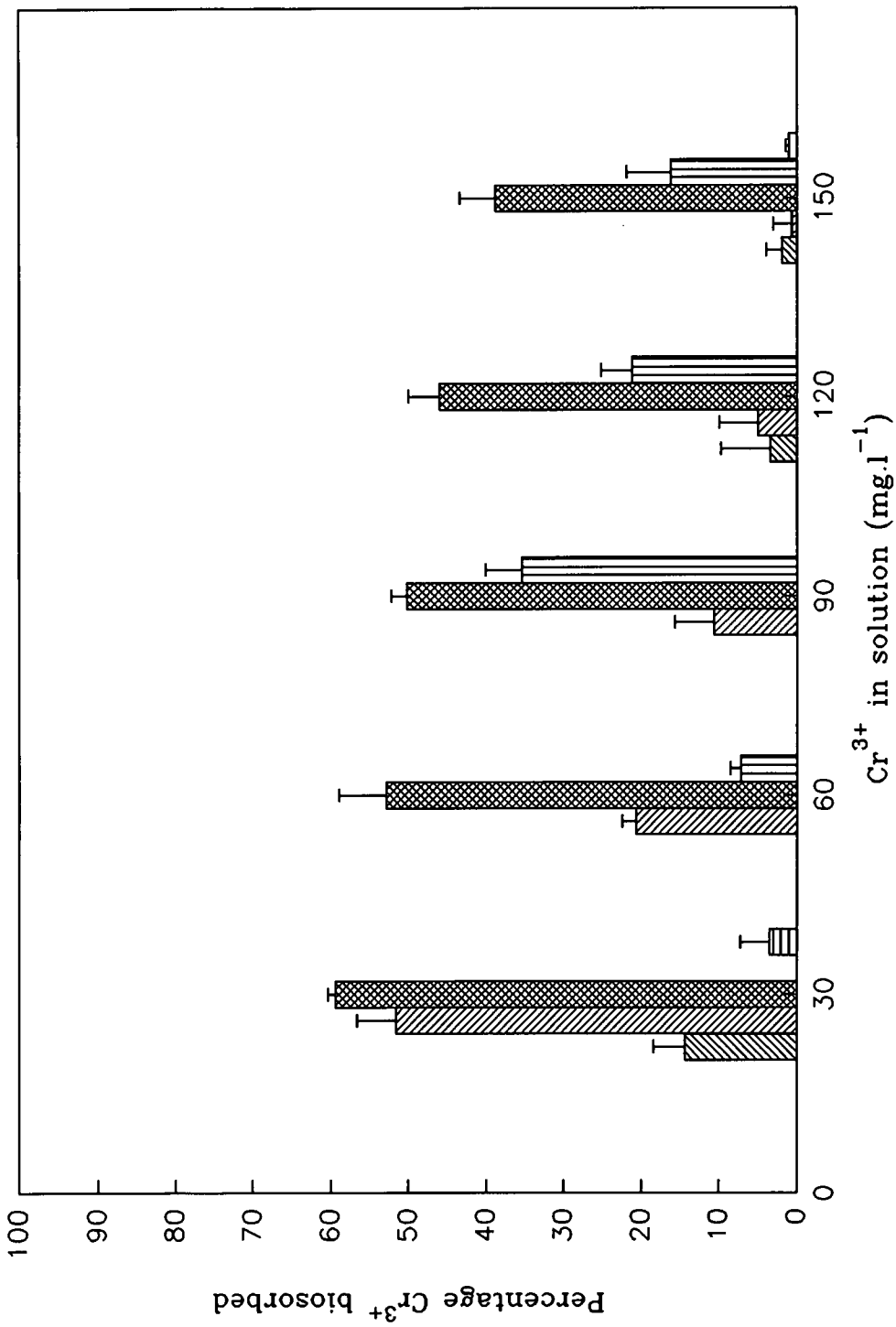

FIG. 4.12 Percentage Cr^{3+} biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

4.1.2 Comparison of adsorptive capabilities of sludges

Findings confirmed that when comparing the five sludges, some displayed increased metal biosorptive potential. Overall, sludges showing greatest metal biosorption were S3 > S2 > S4 (FIG. 4.13). It was also observed that certain sludges displayed preferential behaviour, ie., individual sludges showed an affinity for specific metal species, eg., S3 showed greater biosorption for Zn^{2+} and Cr^{3+} (FIG. 4.13). Efficiency of sludge biosorption of metal ions from pure solutions was found to follow the descending order of $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cr^{6+} > Cr^{3+}$. Excluding Cr^{3+}, there was no substantial difference in the concentrations biosorbed by the sludges of the various metal species (FIG. 4.14).

4.1.3 Mechanism of sludge-metal interaction

Adsorption isotherms, according to the Langmuir model, were plotted for all sludge-metal solution interactions (FIGS 4.15 - 4.44). Seven of the thirty isotherms displayed first order regression coefficients of values greater than or equal to 0.90, indicating their conformity with the model (FIGS 4.17; 4.21; 4.24; 4.31 - 4.33 and 4.42).

Cadmium biosorption by S3 demonstrated a bilayer or Brunauer Emmet and Teller (BET) type adsorption isotherm (FIG. 4.17). The rest of the sludges showed undefined shapes and presented linear regression coefficients of values not greater than 0.32, thus not conforming to the model (FIGS 4.15 - 4.16; 4.18 - 4.19).

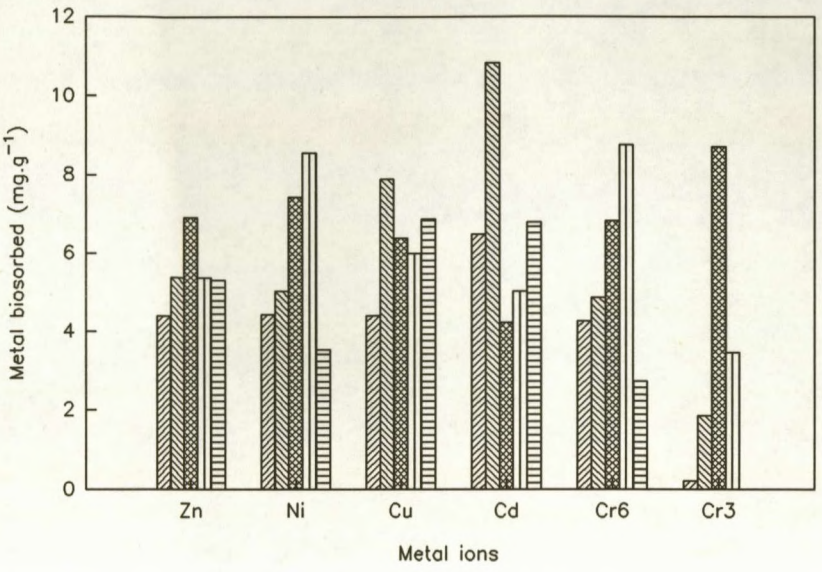

FIG. 4.13 Mean quantities of metal ions biosorbed by S1 (▨), S2 (▧), S3 (▩), S4 (▥) and S5 (▤).

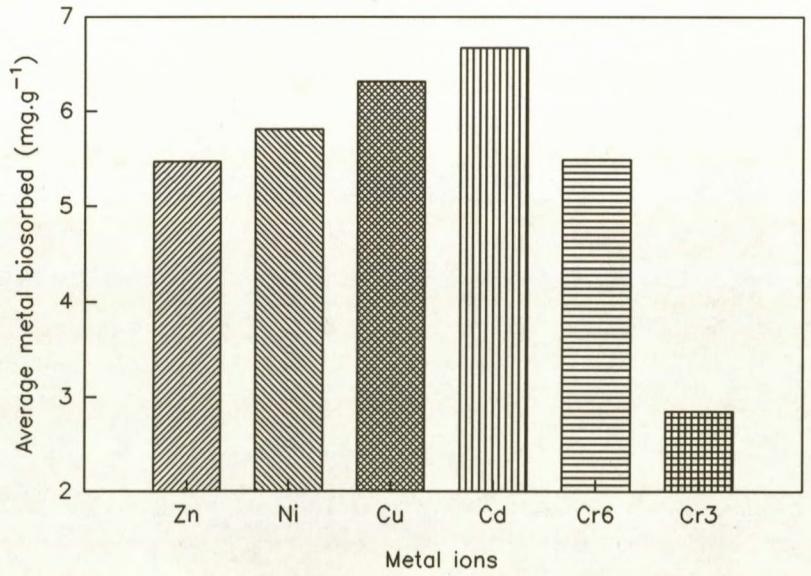

FIG. 4.14 Mean metal ion concentrations biosorbed by five digested sludges.

The results of Cu^{2+} with five waste sludges showed S2 and S5 displaying typical BET type isotherms (FIGS 4.21 and 4.24). Sludges S1 and S4 showed linear regression values of not greater than 0.55 and did not fit the model (FIGS 4.20 and 4.23). Sludge S3, equilibrated with Cu^{2+}, demonstrated a fairly close fit with a rectangular hyperbola, commonly referred to as an "L" shaped isotherm (FIG. 4.22).

Nickel adsorption by the sludges produced isotherms that did not conform well with the model. Although S2 produced low regression values (0.51 and 0.76), it appeared to fit the BET isotherm (Type 2), whilst S4 showed a closer fit to the Type 3 isotherm (FIGS 4.26 and 4.28). Other sludges interactions with Ni^{2+} showed very low regression values and isotherms of undefined shapes (FIGS 4.25; 4.27 and 4.29).

Zinc biosorption by the five digested sludges displayed results showing three of the sludges fitting the isotherm models. S2 equilibrated with Zn^{2+} ($R^2 = 0.99$) showed the typical Type 1 or "L" shaped isotherm (FIG. 4.31). S3 ($R^2 = 0.93$) adsorption conformed with a Type 3 adsorption isotherm (FIG. 4.32) and S4 ($R^2 = 0.90$) conformed most closely to that of a Type 4 adsorption isotherm. The exception to this trend was S1 and S5 which presented regression values of not greater than 0.52 (FIGS 4.30 and 4.34).

Hexavalent chromium biosorption presented very low regression coefficients of not greater than 0.57. Although the shapes of the graphs appear to fit into the typical "L" and "S" shaped isotherms, the low regression values do not facilitate interpretation in terms of the model (FIGS 4.35 - 4.39).

Trivalent chromium adsorption by the five waste sludges showed only S3 (R^2 = 0.96) to conform to the model, displaying a typical "L" shaped or Type 1 isotherm (FIG. 4.42). The balance of the sludges presented low regression coefficients and isotherms of undefined shapes (FIGS 4.40 - 4.41 and 4.43 - 4.44).

Sludge biosorption ranking, with respect to metal ions, was determined to be S3 > S2 > S4. This was determined by ascertaining the binding strength (k_a) of the metal ions and the metal binding capacities (X_m) of the waste sludges. Maximum binding capacities of sludges to metal ions did not correlate with the maximum bond strengths (TABLES 4.1 and 4.2).

TABLE 4.1 Binding strength (k_a, mg.ℓ^{-1}) of metal ions to anaerobic digested sludge.

	Ni^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}	Cr^{3+}	Cr^{6+}
S1	21.25367	10.50125	10.7478	12.64158	-78.6004	22.21062
S2	13.4232	5.803409	5.473245	4.620544	-80.1342	12.82892
S3	22.30148	27.31118	40.1393	42.27105	6.315088	13.65339
S4	15.30053	12.4053	26.54292	8.515797	22.56938	10.33404
S5	12.25579	10.46014	16.21837	10.85772	-90.1609	21.98813

TABLE 4.2 Metal binding capacities (X_m, $mg.g^{-1}$) of anaerobic digested sludge.

	Ni^{2+}	Cu^{2+}	Cd^{2+}	Zn^{2+}	Cr^{3+}	Cr^{6+}
S1	-0.01242	0.102117	0.033774	0.064944	1.611796	-0.0143
S2	0.04069	0.049301	0.022845	0.118146	1.826741	0.051402
S3	-0.09702	-0.13086	-0.17244	-0.29612	0.035124	-0.01312
S4	-0.05251	0.018048	-0.03297	0.070538	0.046887	-0.00898
S5	0.158549	0.0176	-0.01956	0.05045	2.314764	0.105962

TABLE 4.3 Mean values of metals biosorbed by five anaerobic sludges ($mg.g^{-1}$).

Metal	**Sludge 1**	**2**	**3**	**4**	**5**
Zn^{2+}	4.390667	5.374667	6.924	5.374667	5.309333
Ni^{2+}	4.44	5.03333	7.448	8.568	3.548
Cu^{2+}	4.412	7.89733	6.38933	6.004	6.868
Cd^{2+}	6.481333	10.836	4.22933	5.01333	6.790667
Cr^{3+}	0.213	1.853	8.702	3.465	0
Cr^{6+}	4.262667	4.868	6.82	8.756	2.742667
Mean	4.033277	5.977054	6.75211	6.19683	4.209777

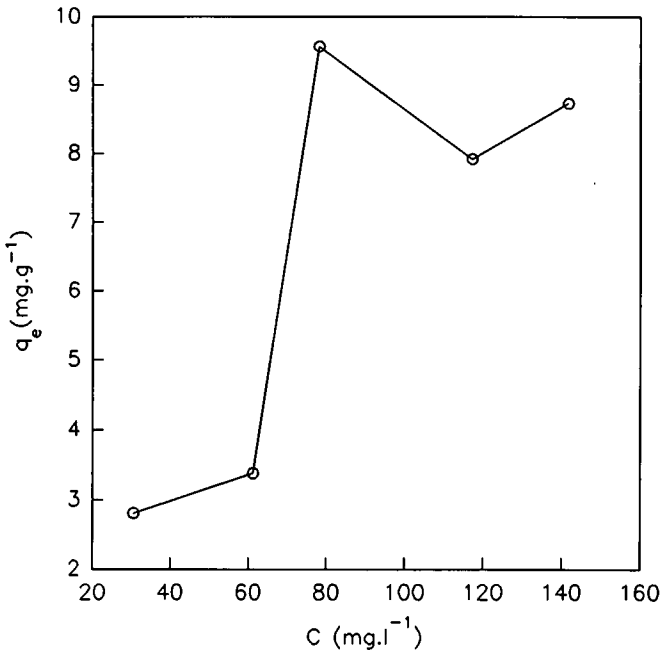

FIG. 4.15 Adsorption isotherm for Cd^{2+} uptake from solution by S1.

Square of correlation coefficient for linearisation of isotherm = 0.14.

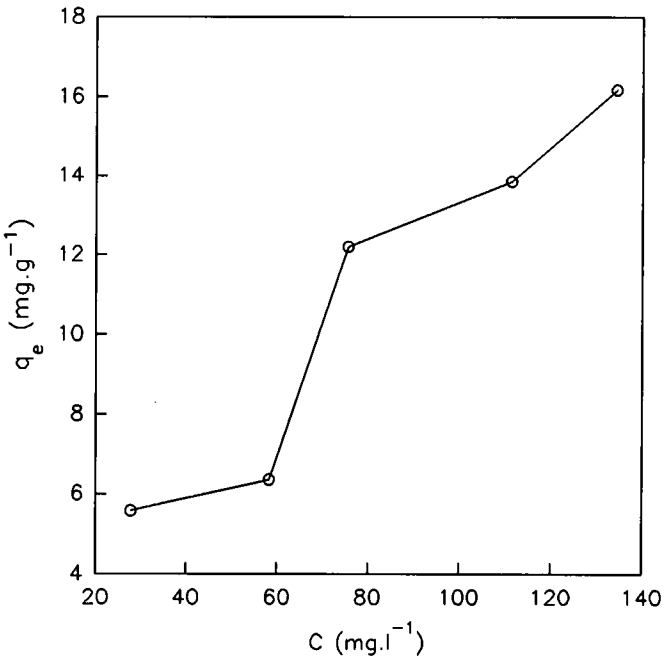

FIG. 4.16 Adsorption isotherm for Cd^{2+} uptake from solution by S2.

Square of correlation coefficient for linearisation of isotherm = 0.32.

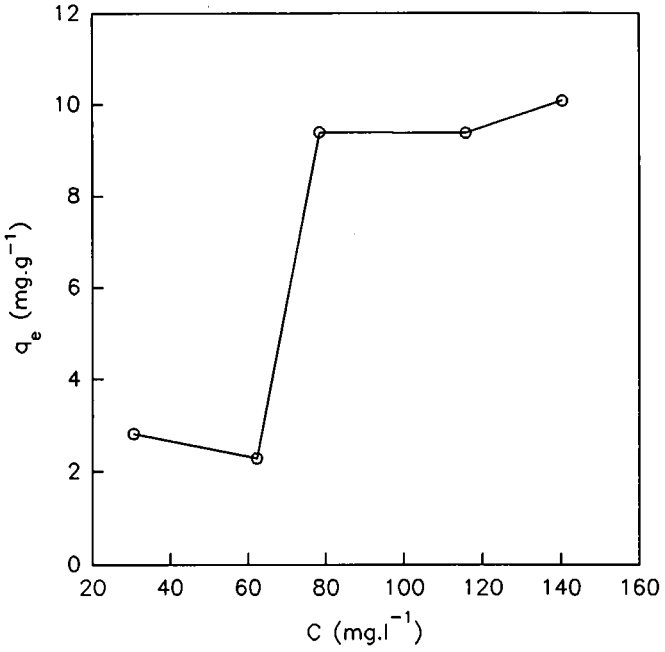

FIG. 4.17 Adsorption isotherm for Cd^{2+} uptake from solution by S3.

Square of correlation coefficient for linearisation of isotherm = 0.95.

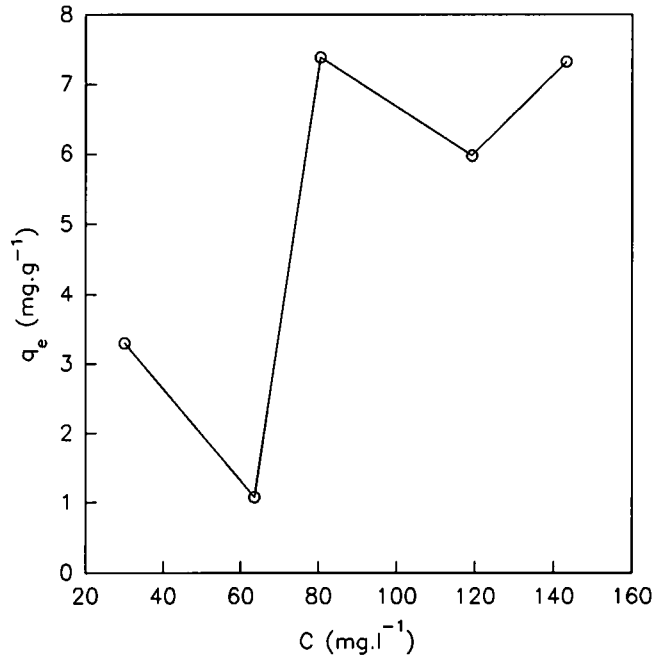

FIG. 4.18 Adsorption isotherm for Cd^{2+} uptake from solution by S4.

Square of correlation coefficient for linearisation of isotherm = 0.01.

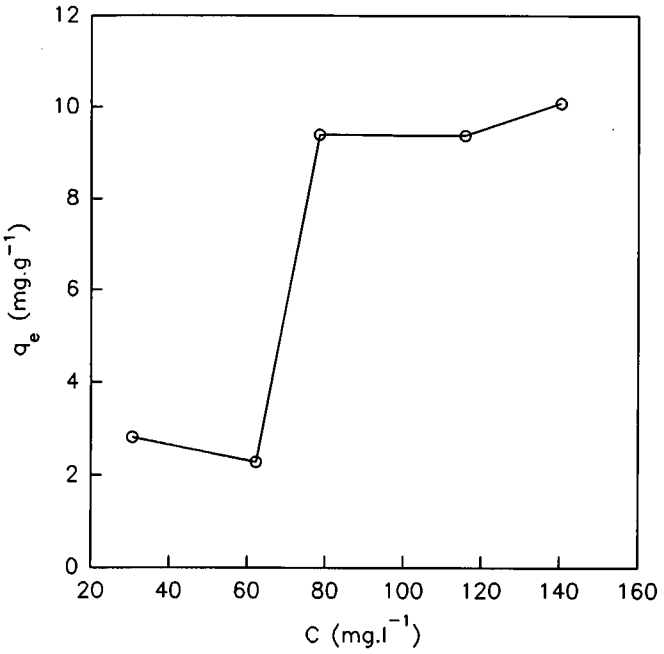

FIG. 4.19 Adsorption isotherm for Cd^{2+} uptake from solution by S5.

Square of correlation coefficient for linearisation of isotherm = 0.02.

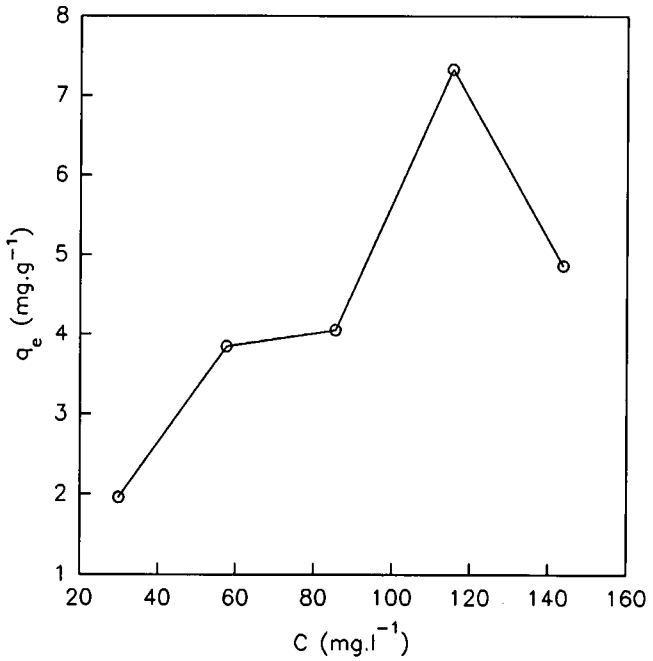

FIG. 4.20 Adsorption isotherm for Cu^{2+} uptake from solution by S1.

Square of correlation coefficient for linearisation of isotherm = 0.55.

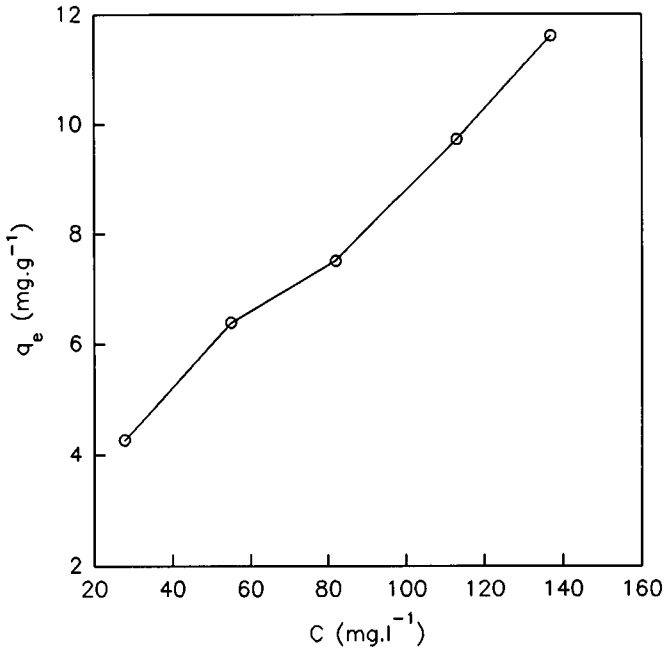

FIG. 4.21 Adsorption isotherm for Cu^{2+} uptake from solution by S2.

Square of correlation coefficient for linearisation of isotherm = 0.90.

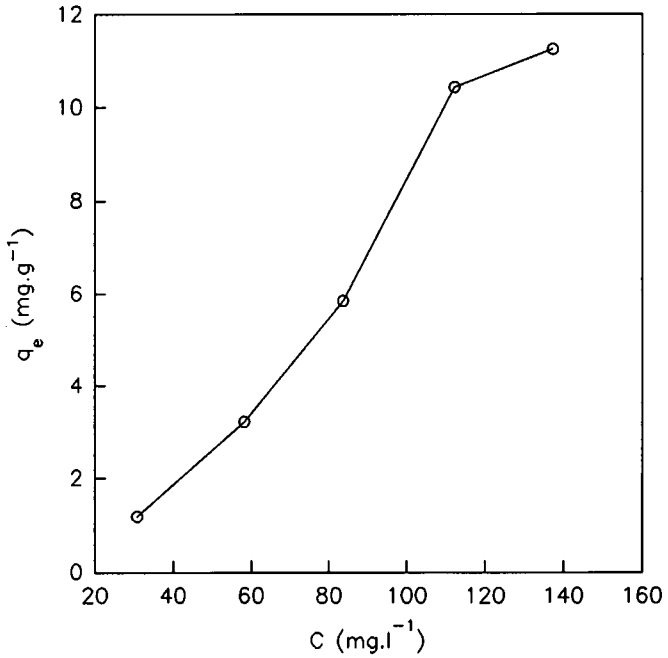

FIG. 4.22 Adsorption isotherm for Cu^{2+} uptake from solution by S3.

Square of correlation coefficient for linearisation of isotherm = 0.83.

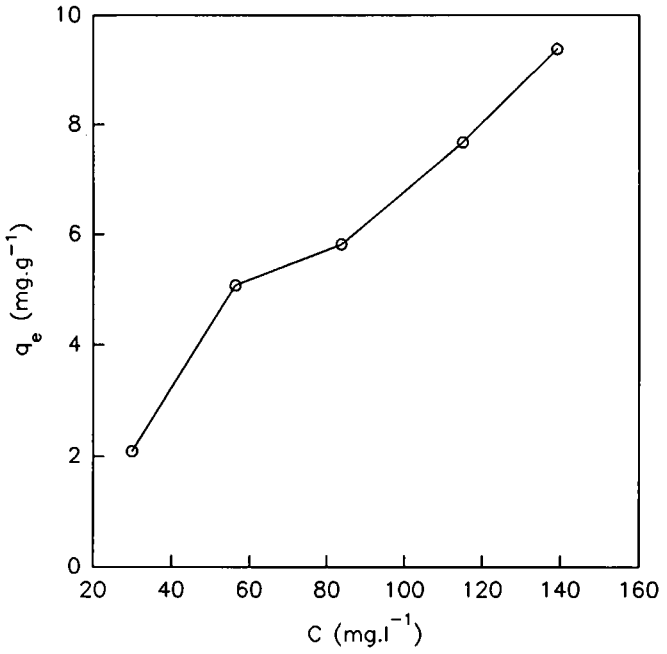

FIG. 4.23 Adsorption isotherm for Cu^{2+} uptake from solution by S4.

Square of correlation coefficient for linearisation of isotherm = 0.25.

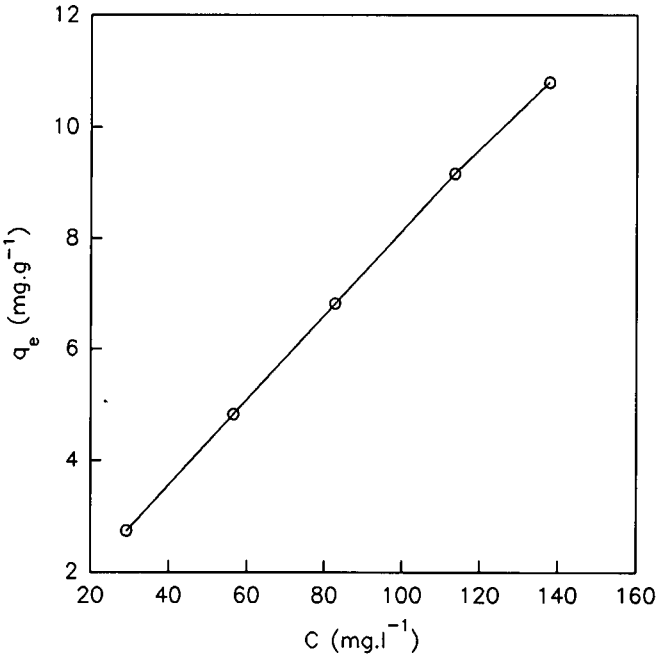

FIG. 4.24 Adsorption isotherm for Cu^{2+} uptake from solution by S5.

Square of correlation coefficient for linearisation of isotherm = 0.92.

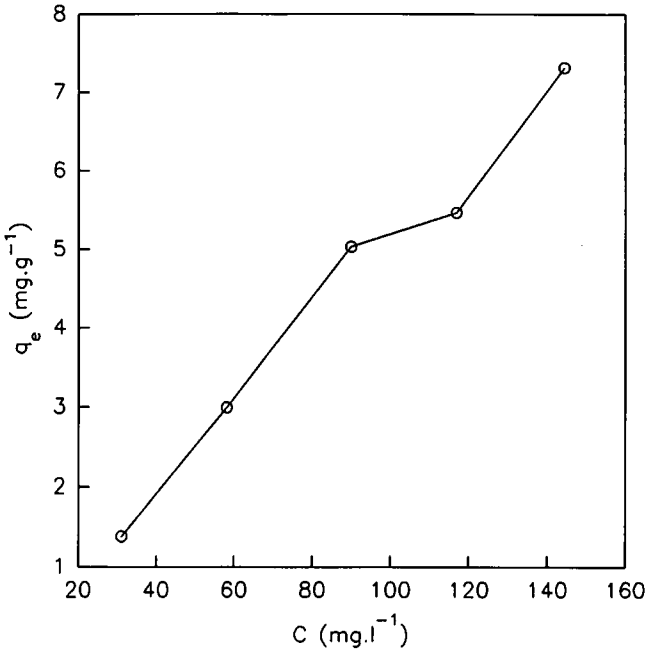

FIG. 4.25 Adsorption isotherm for Ni^{2+} uptake from solution by S1.

Square of correlation coefficient for linearisation of isotherm = 0.10.

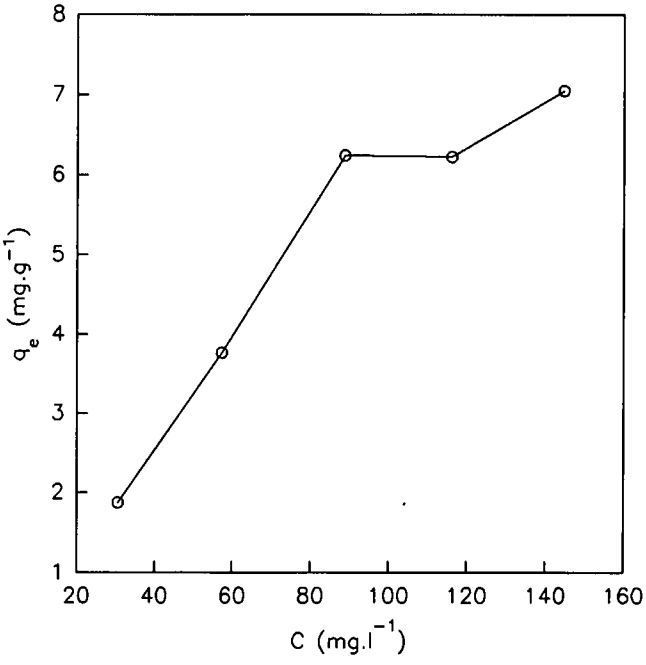

FIG. 4.26 Adsorption isotherm for Ni^{2+} uptake from solution by S2.

Square of correlation coefficient for linearisation of isotherm = 0.51.

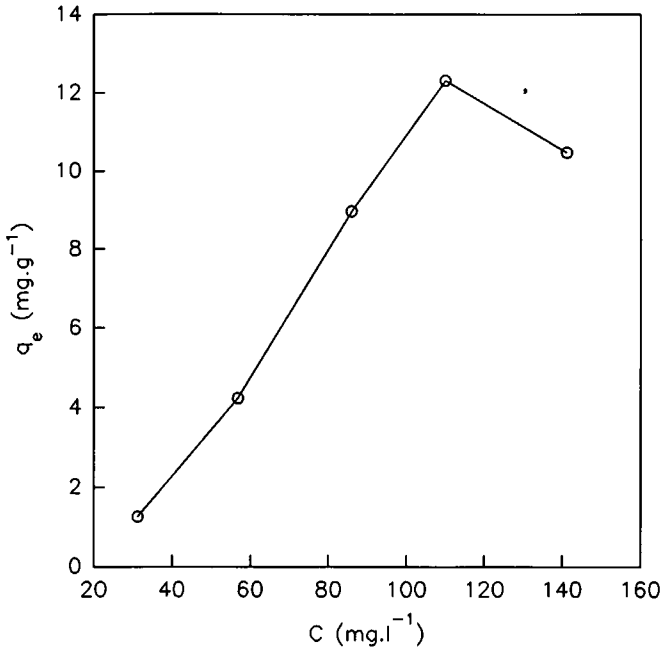

FIG. 4.27 Adsorption isotherm for Ni^{2+} uptake from solution by S3.

Square of correlation coefficient for linearisation of isotherm = 0.44.

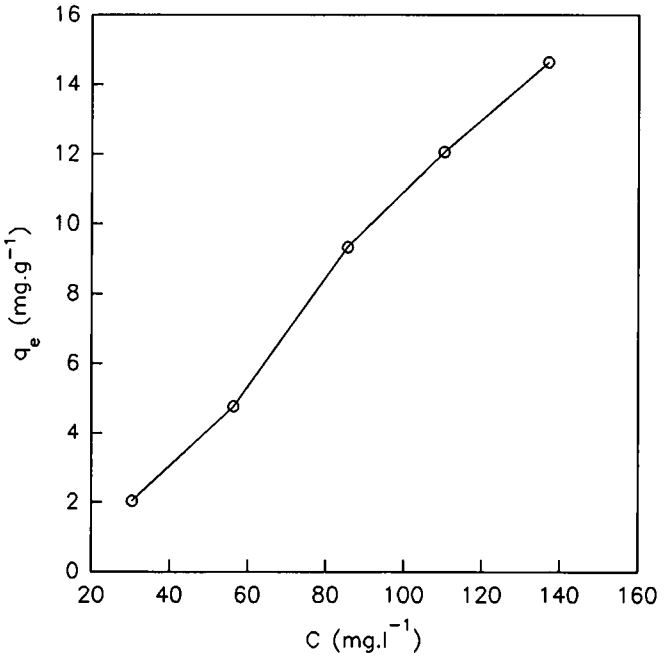

FIG. 4.28 Adsorption isotherm for Ni^{2+} uptake from solution by S4.

Square of correlation coefficient for linearisation of isotherm = 0.76.

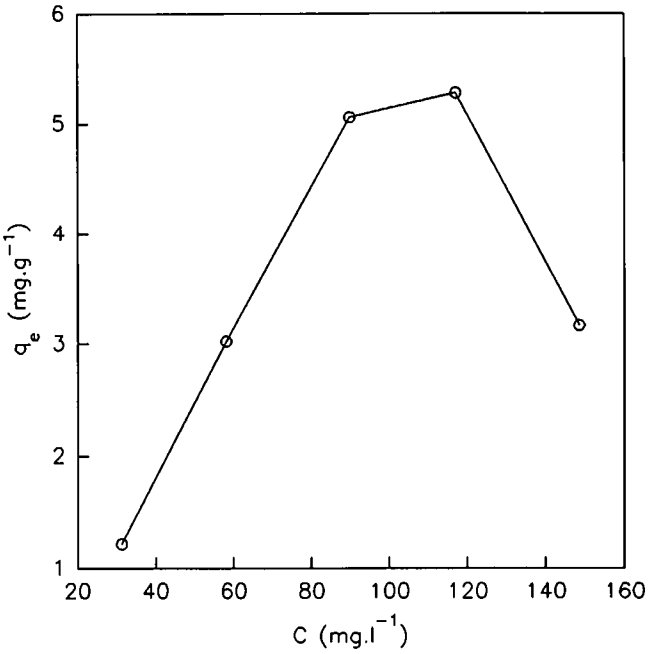

FIG. 4.29 Adsorption isotherm for Ni^{2+} uptake from solution by S5.

Square of correlation coefficient for linearisation of isotherm = 0.38.

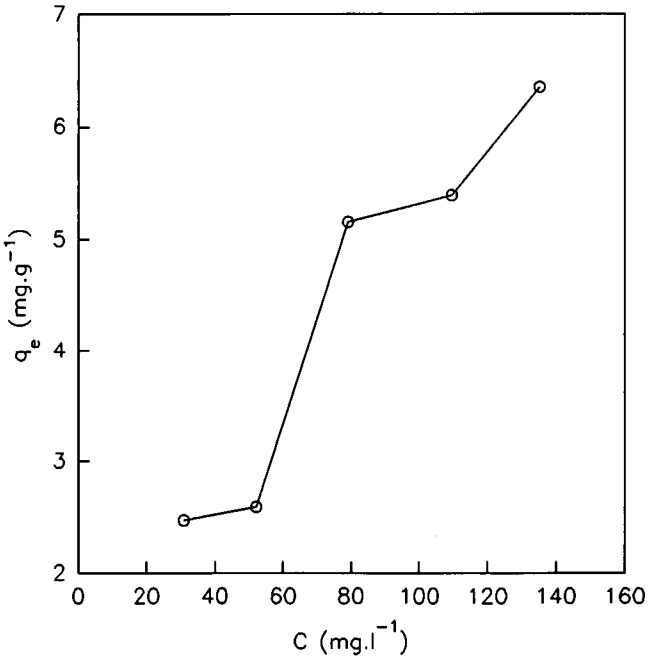

FIG. 4.30 Adsorption isotherm for Zn^{2+} uptake from solution by S1.

Square of correlation coefficient for linearisation of isotherm = 0.52.

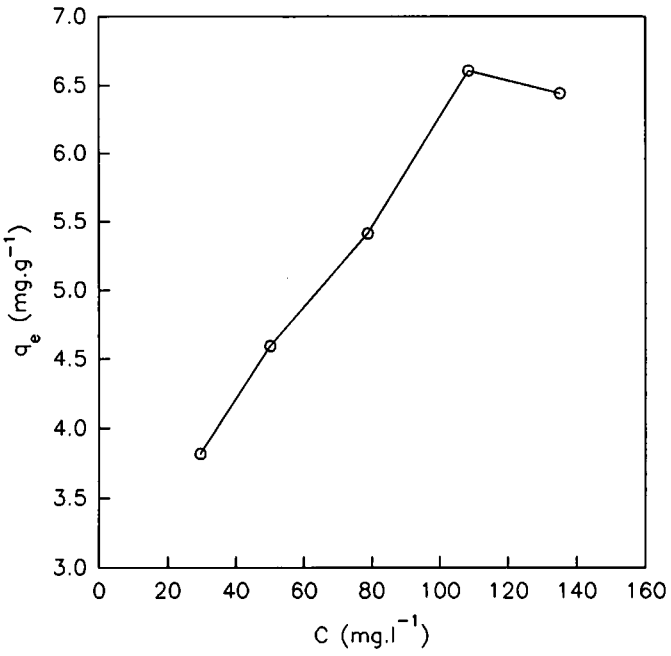

FIG. 4.31 Adsorption isotherm for Zn^{2+} uptake from solution by S2.

Square of correlation coefficient for linearisation of isotherm = 0.99.

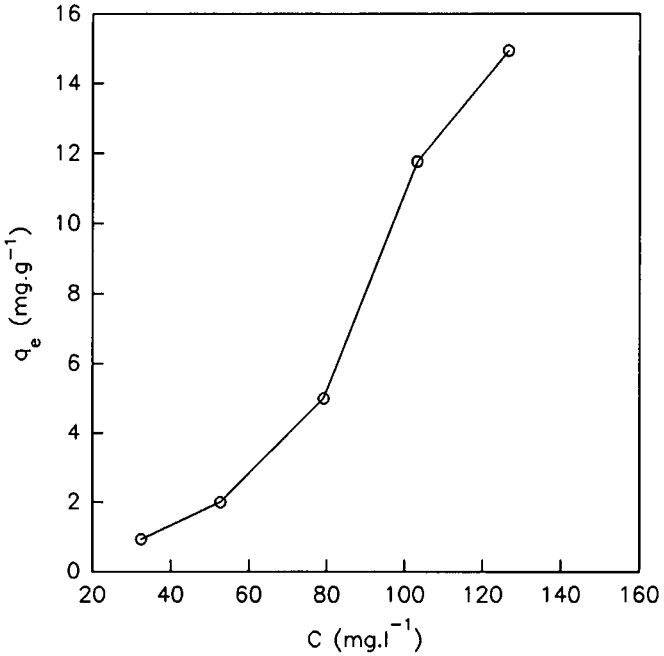

FIG. 4.32 Adsorption isotherm for Zn^{2+} uptake from solution by S3.

Square of correlation coefficient for linearisation of isotherm = 0.93.

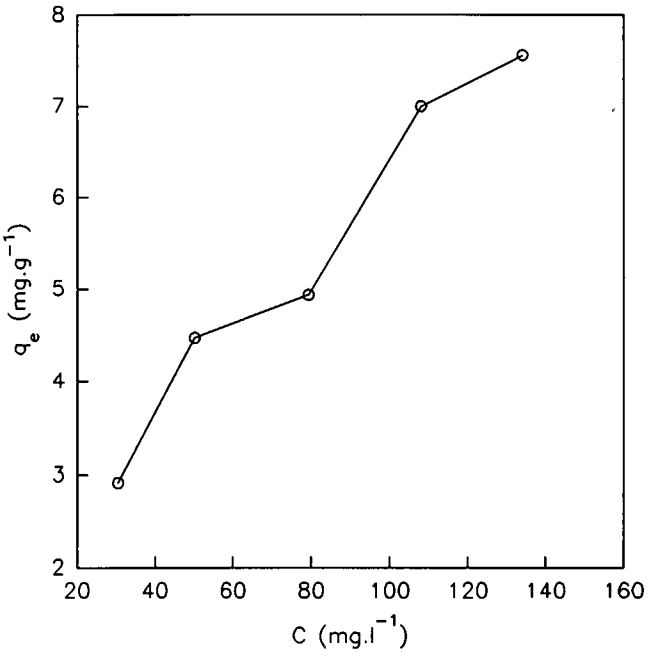

FIG. 4.33 Adsorption isotherm for Zn^{2+} uptake from solution by S4.

Square of correlation coefficient for linearisation of isotherm = 0.90.

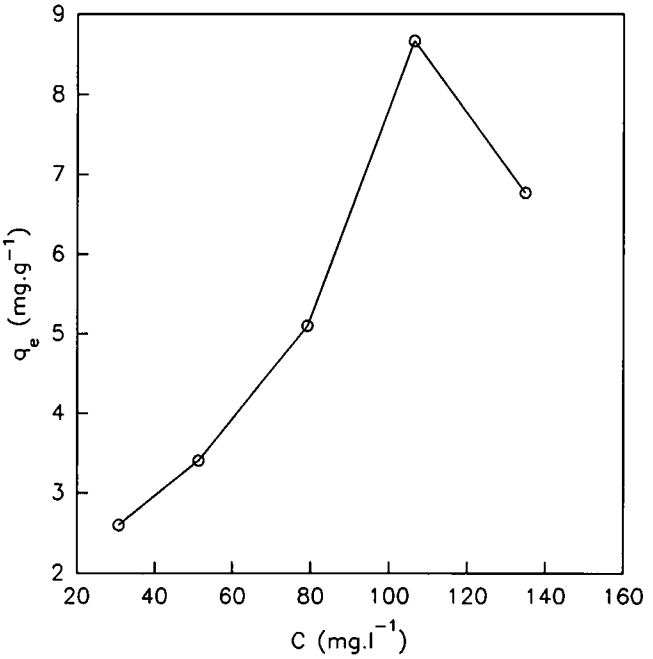

FIG. 4.34 Adsorption isotherm for Zn^{2+} uptake from solution by S5.

Square of correlation coefficient for linearisation of isotherm = 0.43.

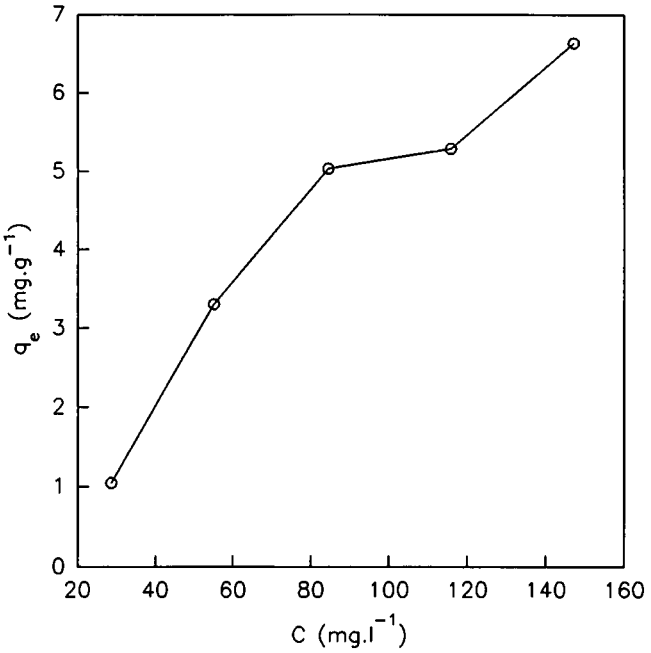

FIG. 4.35 Adsorption isotherm for Cr^{6+} uptake from solution by S1.

Square of correlation coefficient for linearisation of isotherm = 0.02.

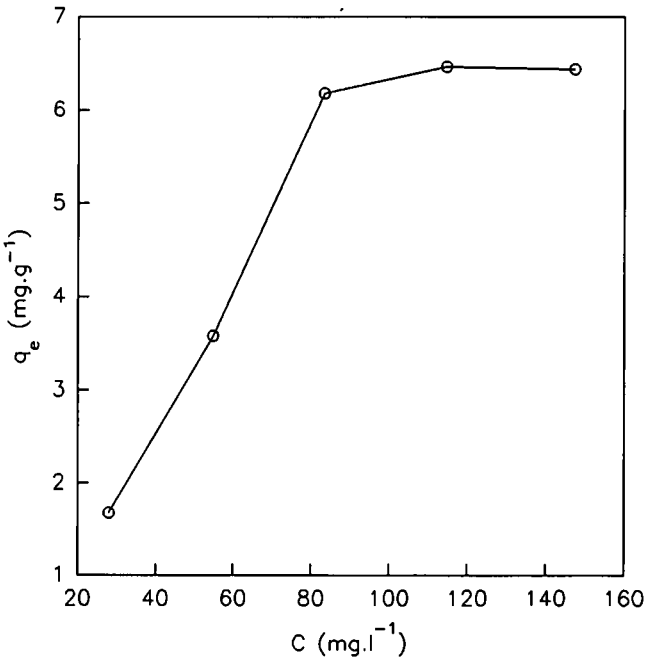

FIG. 4.36 Adsorption isotherm for Cr^{6+} uptake from solution by S2.

Square of correlation coefficient for linearisation of isotherm = 0.47.

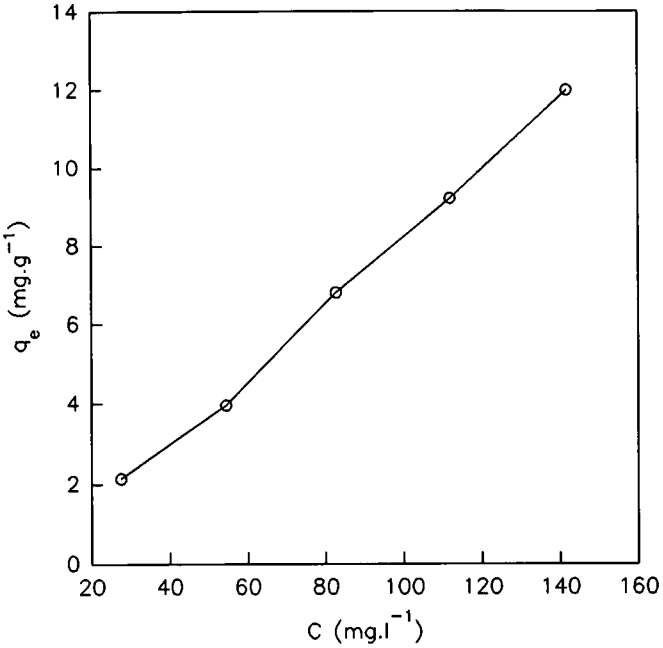

FIG. 4.37 Adsorption isotherm for Cr^{6+} uptake from solution by S3.

Square of correlation coefficient for linearisation of isotherm = 0.58.

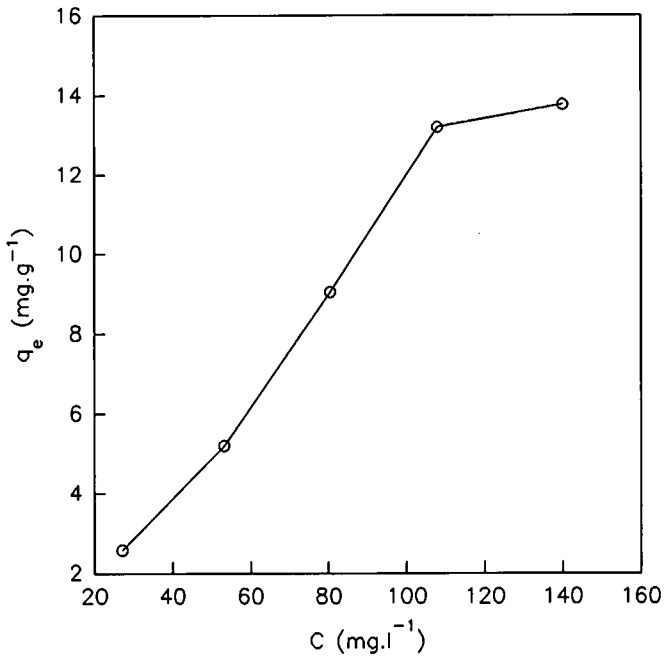

FIG. 4.38 Adsorption isotherm for Cr^{6+} uptake from solution by S4.

Square of correlation coefficient for linearisation of isotherm = 0.16.

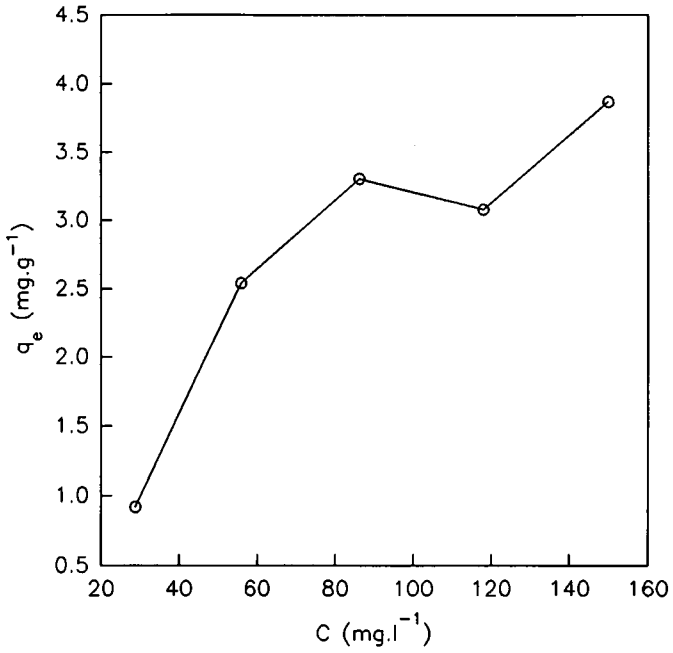

FIG. 4.39 Adsorption isotherm for Cr^{6+} uptake from solution by S5.

Square of correlation coefficient for linearisation of isotherm = 0.48.

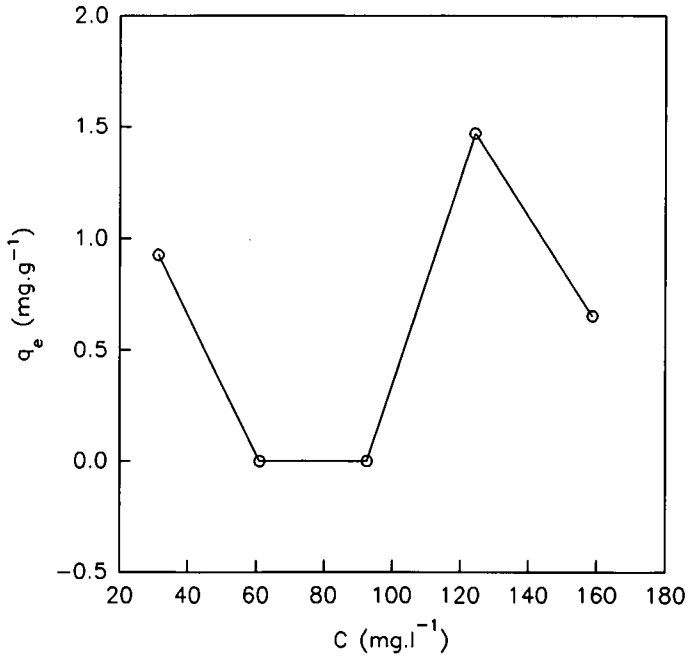

FIG. 4.40 Adsorption isotherm for Cr^{3+} uptake from solution by S1.

Square of correlation coefficient for linearisation of isotherm = 0.64.

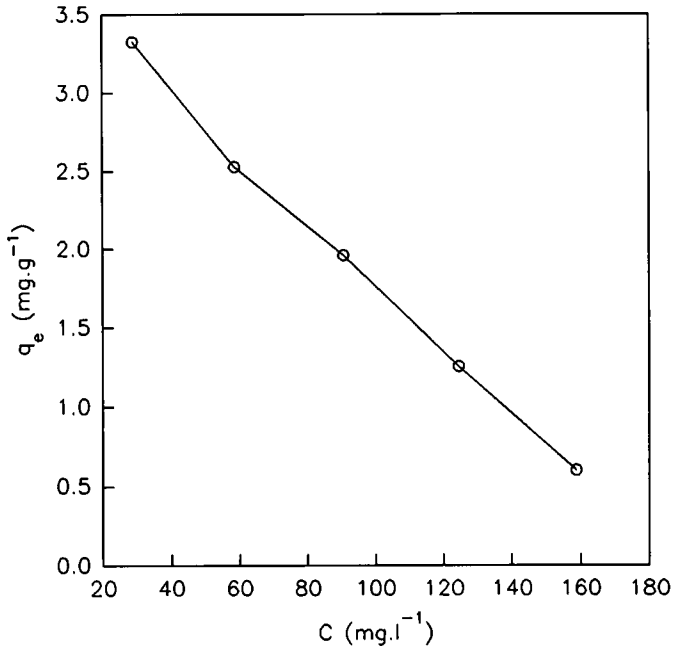

FIG. 4.41 Adsorption isotherm for Cr^{3+} uptake from solution by S2.

Square of correlation coefficient for linearisation of isotherm = 0.81.

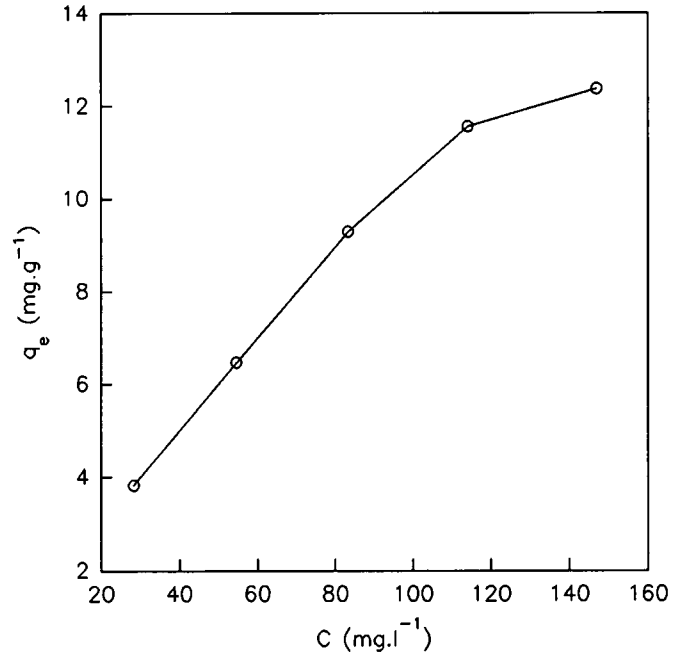

FIG. 4.42 Adsorption isotherm for Cr^{3+} uptake from solution by S3.

Square of correlation coefficient for linearisation of isotherm = 0.96.

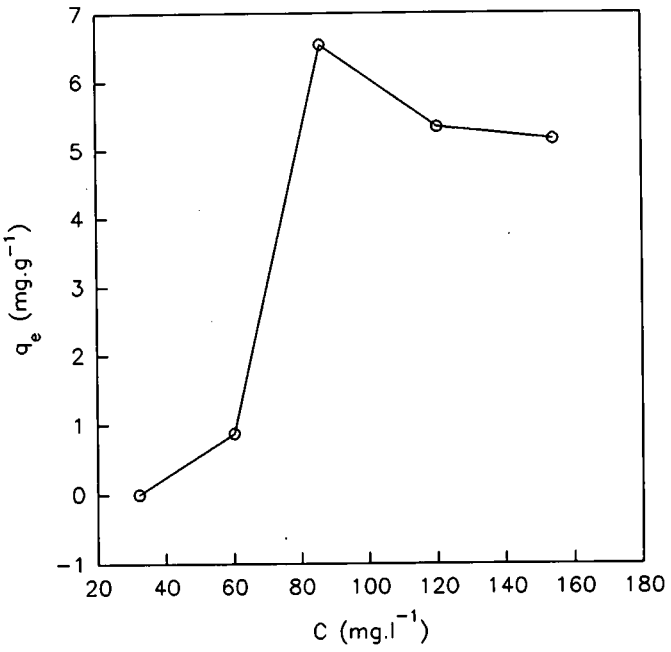

FIG. 4.43 Adsorption isotherm for Cr^{3+} uptake from solution by S4.

Square of correlation coefficient for linearisation of isotherm = 0.01.

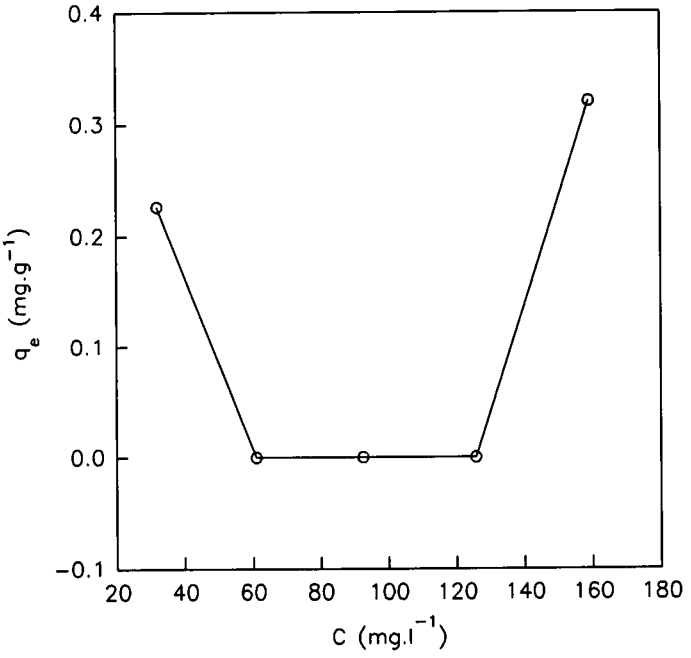

FIG. 4.44 Adsorption isotherm for Cr^{3+} uptake from solution by S5.

Square of correlation coefficient for linearisation of isotherm = 0.29.

4.2 SLUDGE SURFACE CHARGE

4.2.1 Millivolt quantification method

This method was adapted and determined to be appropriate for the present application (Bux *et al.*, 1994).

4.2.2 Comparison of surface charge between five anaerobic sludges

TABLE 4.4 Electronegativity of five anaerobic sludges using the pH/millivolt method.

SLUDGE	SURFACE CHARGE (mV)	% RSD
1	-1.75	0.957427
2	-68.25	2.753785
3	-97.50	1
4	-63.50	4.041452
5	-11.50	0.57735

Results showed S3 to be the most electronegative sludge. The other sludges followed in the descending order of S2 > S4 > S5 > S1. There was a substantial magnitude of difference in the electronegativity value of S3 and the second most electronegative sludge. S1 presented the least amount of electronegativity (TABLE 4.4).

4.3 CORRELATION BETWEEN SLUDGE SURFACE CHARGE AND SLUDGE-METAL BIOSORPTION

As determined by previous research (Bux and Kasan, 1994a), there was a definite relationship between the electronegativity of sludge surfaces and their metal biosorptive capacities. Metal biosorption by the sludges, with regard to adsorption capacities, displayed the following sequence viz., S3 > S2 > S4 > S5 > S1 (TABLE 4.3). Similarly, the charge on the sludge surfaces, occurred in a similar descending order ie., S3 > S2 > S4 > S5 > S1 (TABLE 4.3). The results showed that the most electronegative sludge ie., S3, also presented comparatively superior biosorptive capacity. Similarly, the least electronegative sludge also presented the least biosorption of metal. This trend was consistent with all the sludges investigated. Further investigations were restricted to the three sludges that presented superior biosorption ie., S3, S2 and S4.

4.4 LABORATORY SCALE BIOSORPTION (FULLY MIXED)

4.4.1 Adsorption of metal ions from synthetic effluent

The results of this phase of the study showed that all three waste digested sludges selected ie., S2, S3 and S4, were capable of metal biosorption from synthetic effluents (FIGS 4.45 - 4.50). Sludges S3 and S4 displayed similar biosorptive trends with regards to Zn^{2+} biosorption. Differences in their adsorptive capacities were marginal. Comparatively, S2 was not as good a biosorbent of Zn^{2+}. All three sludges showed maximum concentration of Zn^{2+} adsorbed after 45 min. (FIG. 4.45).

Sludge S4 presented slightly superior Ni^{2+} biosorption as compared to S3. The magnitude of difference in the biosorptive capacity of S2 and the superior biosorbents S3 and S4, for Ni^{2+}, were pronounced. There was little difference in the concentration of Ni^{2+} biosorbed after 15 min. (FIG. 4.46).

Superior biosorbents of Cu^{2+} were S3 and S4, as compared to S2, although the differences were marginal with an increase in time of exposure. S3 and S4 displayed similar biosorptive capacity for Cu^{2+}. Time zero, represented graphically, is a hypothetical value and actually represents a delay time (approximately 30 secs) for obtaining samples, thus indicating that removal of metal occurred instantly on exposure of the effluent to the biosorbent. Sludges S3 and S4 showed no increase in adsorption capacity of Cu^{2+} after 15 min. (FIG. 4.47).

Biosorption of Cd^{2+} by the three sludges followed similar trends as the other metals discussed ie., there was no marked increase in concentration adsorbed after 15 min. Sludges S3 and S4 once again presented superior biosorption of Cd^{2+} when compared to S2. Differences in biosorptive capacities of S3 and S4 were negligible (FIG. 4.48).

When compared to the other metals biosorbed, all three sludges presented relatively poor biosorption of Cr^{6+}. Unlike the poor adsorption capacity for other metals, S2 presented superior biosorption of Cr^{6+}, in comparison to S3 and S4. As seen with the other metals, there was no marked difference in the amount of Cr^{6+} adsorbed from the beginning of the experiment to 15 min. (FIG. 4.49).

At the beginning of the experiment, exact amounts of Cr^{3+} were biosorbed by all three sludges, although calculated standard deviations differed slightly. Sludges S3 and S4 showed similar superior biosorptive trends of Cr^{3+}, with increase in time, as compared to S2. There was a slight decrease in concentration biosorbed by the two sludges at 90 min. (FIG. 4.50).

Overall, S3 presented the best biosorptive capacity, followed by S4. Sludge S2 presented comparatively poor biosorption (FIGS 4.45 - 4.50). Further investigations were restricted to the use of a single sludge ie., S3. The overall results presented an affinity series by the sludge for specific metal ions, in descending order viz., $Zn^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+} > Cr^{6+}$ (FIGS 4.45 - 4.50).

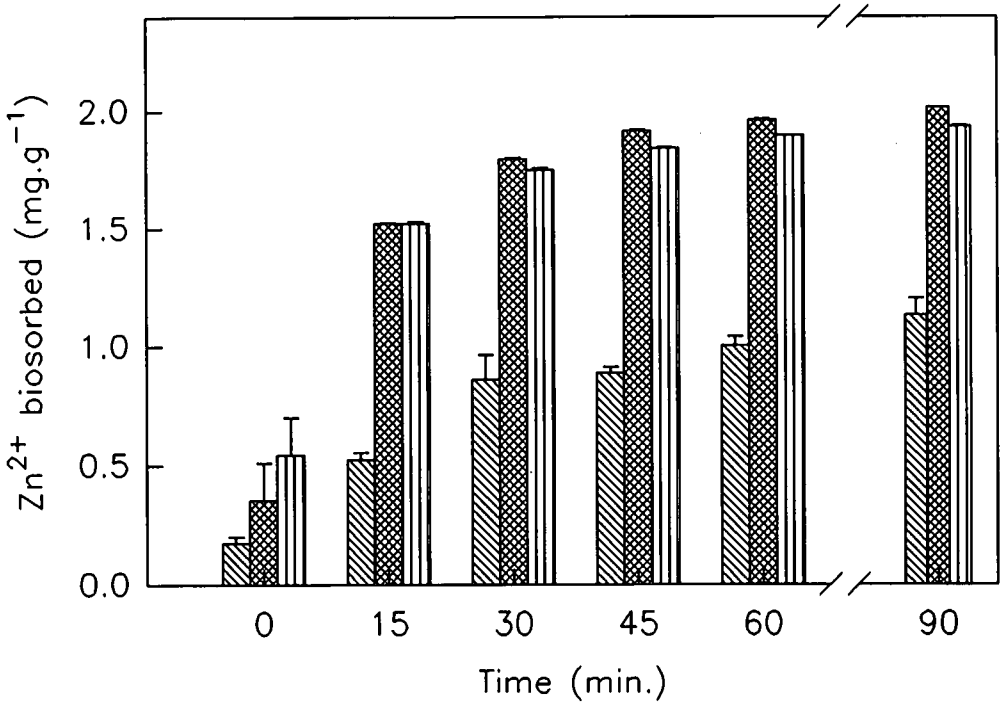

FIG. 4.45 Amount Zn^{2+} biosorbed ($mg.g^{-1}$) by S2 (▨), S3 (▩) and S4 (▥).

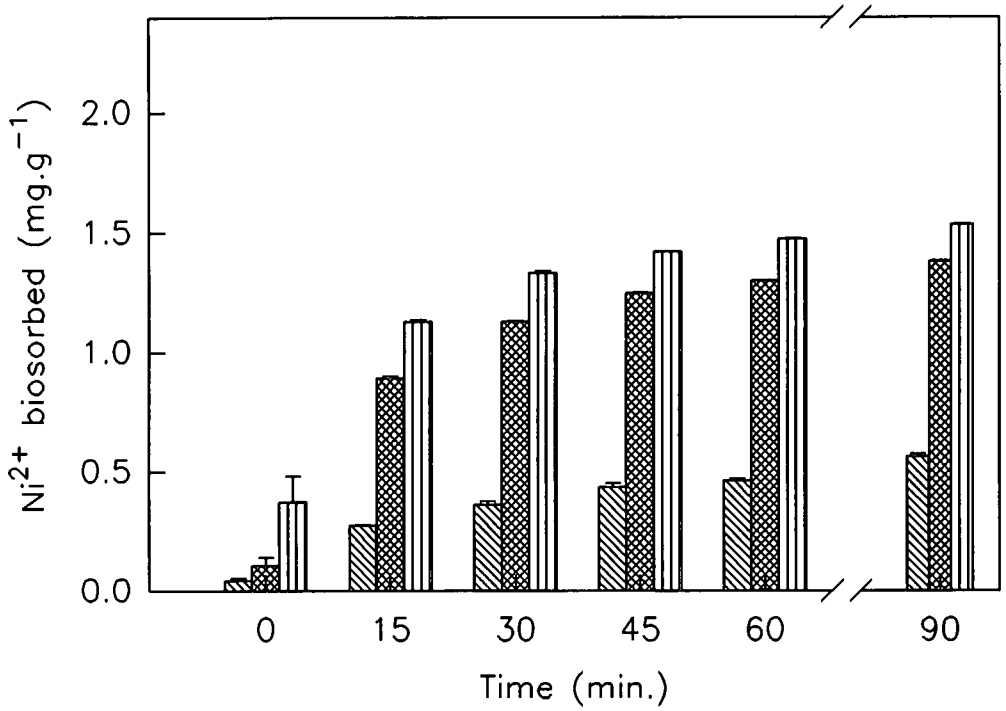

FIG. 4.46 Amount Ni^{2+} biosorbed ($mg.g^{-1}$) by S2 (▨), S3 (▩) and S4 (▥).

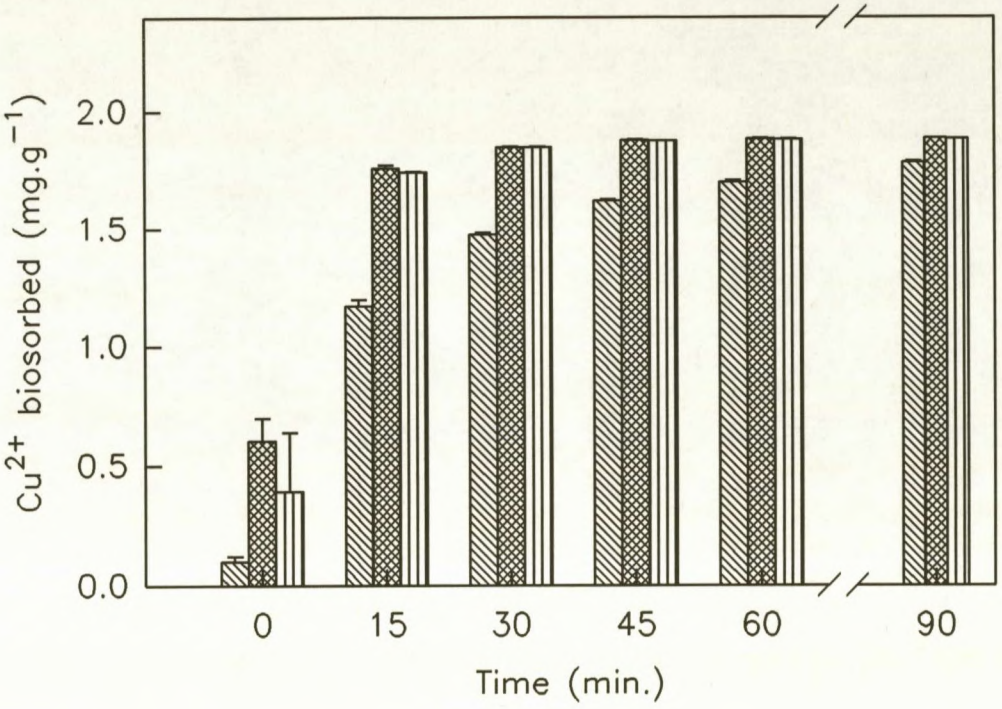

FIG. 4.47 Amount Cu^{2+} biosorbed ($mg.g^{-1}$) by S2 (▨), S3 (▩) and S4 (▥).

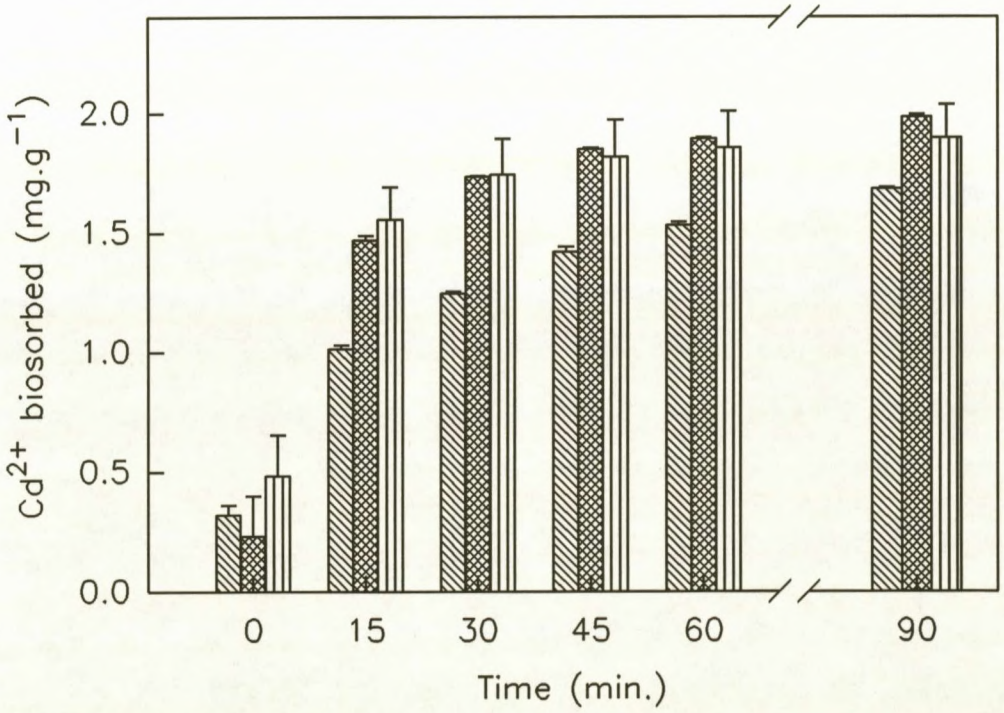

FIG. 4.48 Amount Cd^{2+} biosorbed ($mg.g^{-1}$) by S2 (▨), S3 (▩) and S4 (▥).

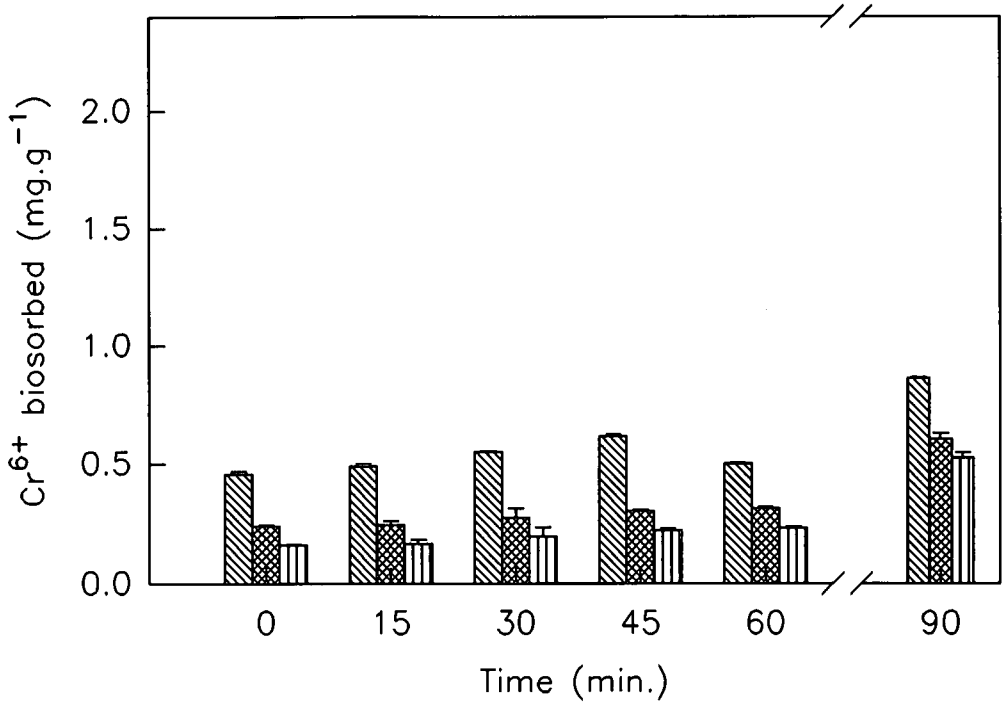

FIG. 4.49 Amount Cr^{6+} biosorbed ($mg.g^{-1}$) by S2 (▨), S3 (▩) and S4 (▥).

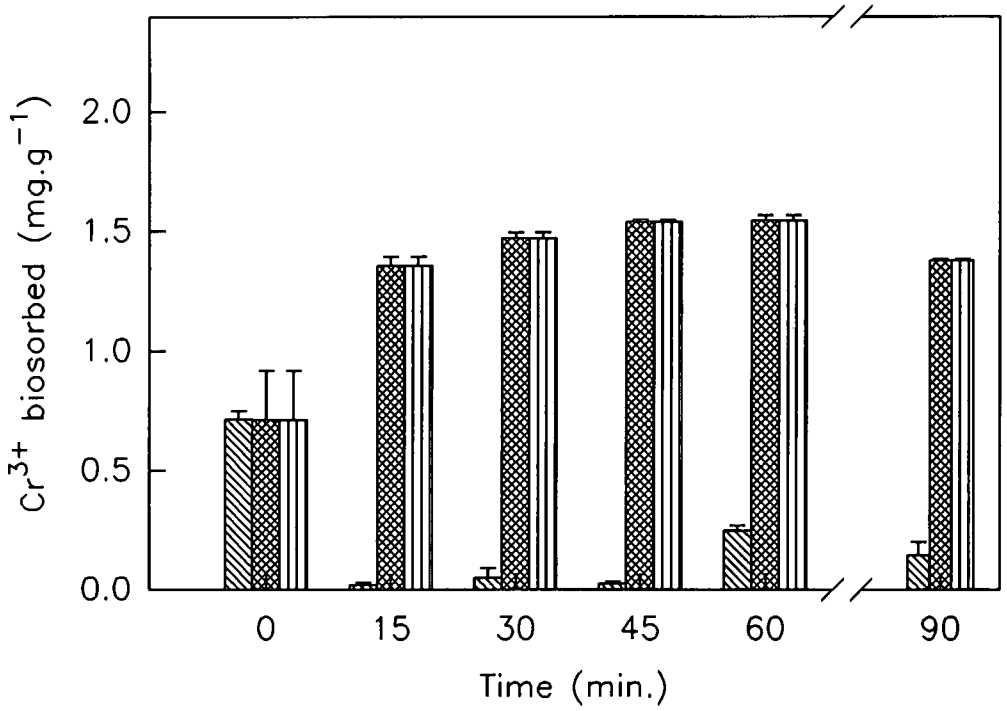

FIG. 4.50 Amount Cr^{3+} biosorbed ($mg.g^{-1}$) by S2 (▨), S3 (▩) and S4 (▥).

4.4.2 Adsorption of metal ions from industrial effluent

Post-galvanising rinse effluent was used from an electroplating company. Zinc was the predominant metal in the effluent. Initial Zn^{2+} concentration was found to be 119.4 mg.ℓ^{-1}. As shown in previous research (Bux *et al.*, 1994), the higher the concentration of metal in solution, the better the biosorption by sludge. Maximum Zn^{2+} biosorbed exceeded 4.0 mg.g^{-1} (FIG. 4.51).

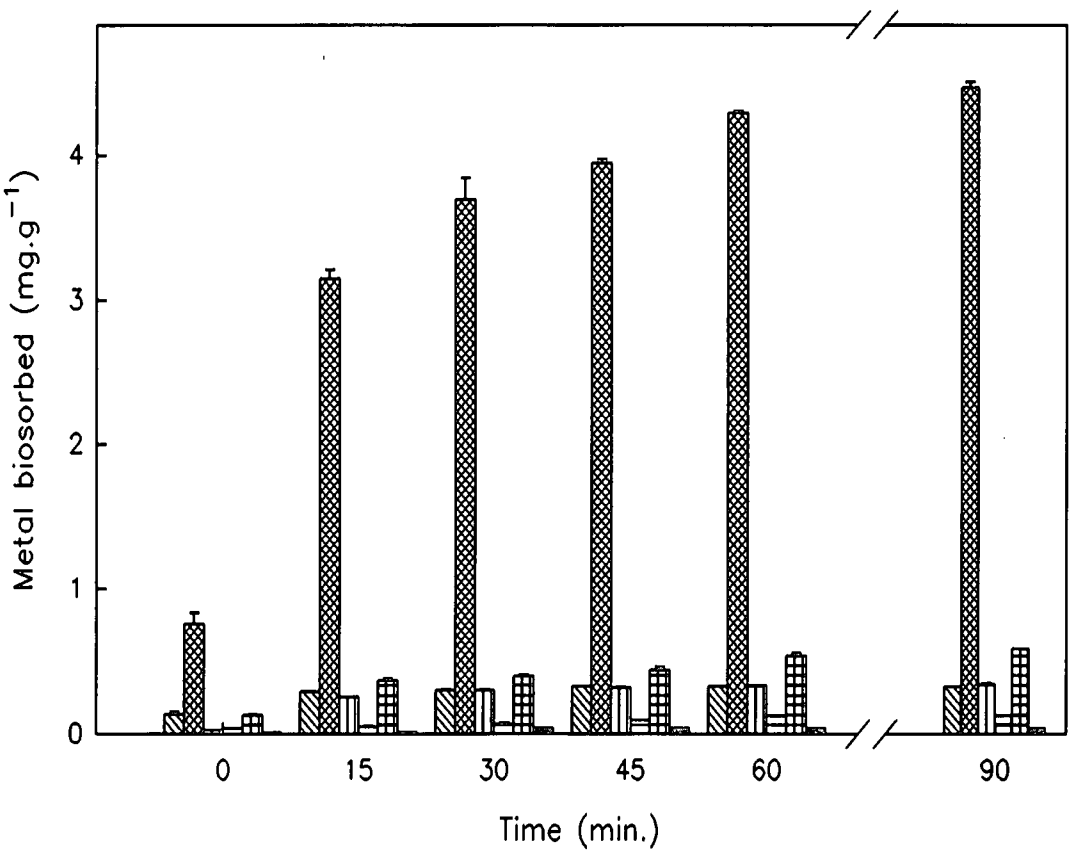

FIG. 4.51 Quantities Cu^{2+} (▨), Zn^{2+} (▩), Ni^{2+} (▥), Cd^{2+} (▤), Cr^{3+} (▦) and Cr^{6+} (■) biosorbed by S3 from industrial effluent.

4.5 LABORATORY SCALE DESORPTION (FULLY MIXED)

4.5.1 Desorption of metal from sludges by three mineral acids

The efficacies of 0.2*N* H_2SO_4, 0.4*N* CH_3COOH and 0.2*N* HCl, as desorbents, were tested against the metal bound sludge, S3, used in laboratory scale, synthetic effluent, adsorption experiments.

Most of the Zn^{2+} adsorbed, appeared to have been desorbed by 0.2*N* H_2SO_4, within 5 min. (FIG. 4.52). When comparing the three desorbents, H_2SO_4 appeared to be the superior desorbent with all metal ions tested (FIGS 4.52 - 4.57). Desorption was almost immediate, increasing initially and tailing off at approximately 10 min., for all metal ions. Nickel was not desorbed by HCl (FIG. 4.53). Hexavalent and trivalent chromium were least desorbed, probably due to their reduced amount biosorbed (FIGS 4.56 and 4.57).

4.5.2 Selection of superior desorbent

Sulphuric acid, at a concentration of 0.2*N*, presented superior desorption capacities when compared to other desorbents. The magnitude of difference in the desorptive capacity of H_2SO_4 was noticeable when compared to other desorbents. Acetic acid showed no or little increase in desorption within the time period allocated (FIGS 4.52 - 4.57). Further investigation was restricted to 0.2*N* H_2SO_4 as desorbent of choice.

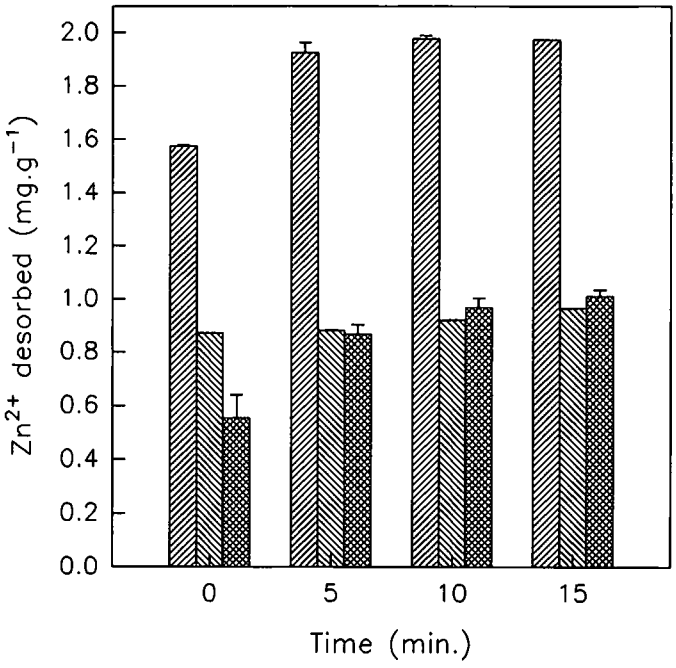

FIG. 4.52 Amount Zn^{2+} desorbed ($mg.g^{-1}$), from S3, using 0.2*N* H_2SO_4 (▨), 0.4*N* CH_3COOH (▧) and 0.2*N* HCl (▩).

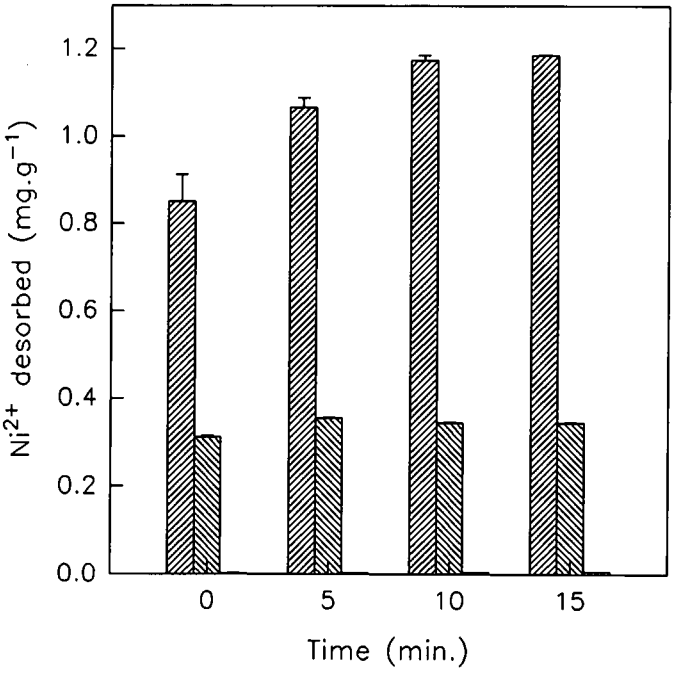

FIG. 4.53 Amount Ni^{2+} desorbed ($mg.g^{-1}$), from S3, using 0.2*N* H_2SO_4 (▨), 0.4*N* CH_3COOH (▧) and 0.2*N* HCl (▩).

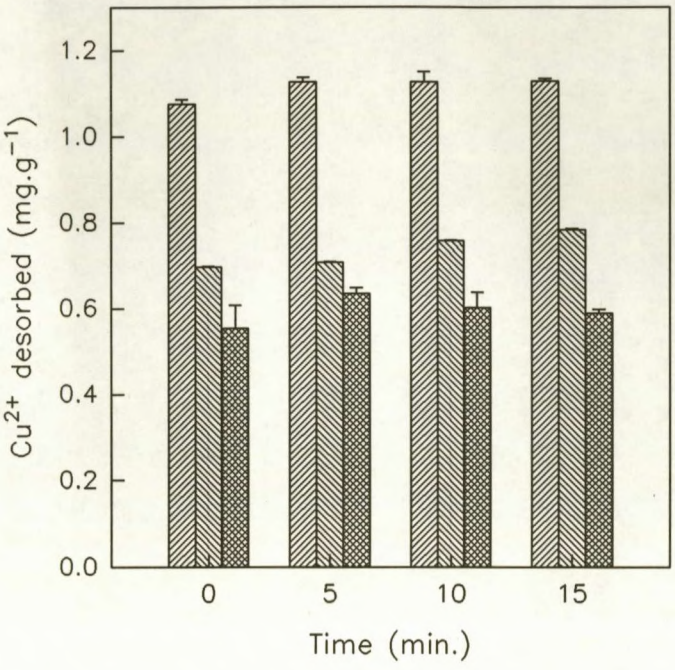

FIG. 4.54 Amount Cu^{2+} desorbed ($mg.g^{-1}$), from S3, using 0.2*N* H_2SO_4 (▨), 0.4*N* CH_3COOH (▧) and 0.2*N* HCl (▩).

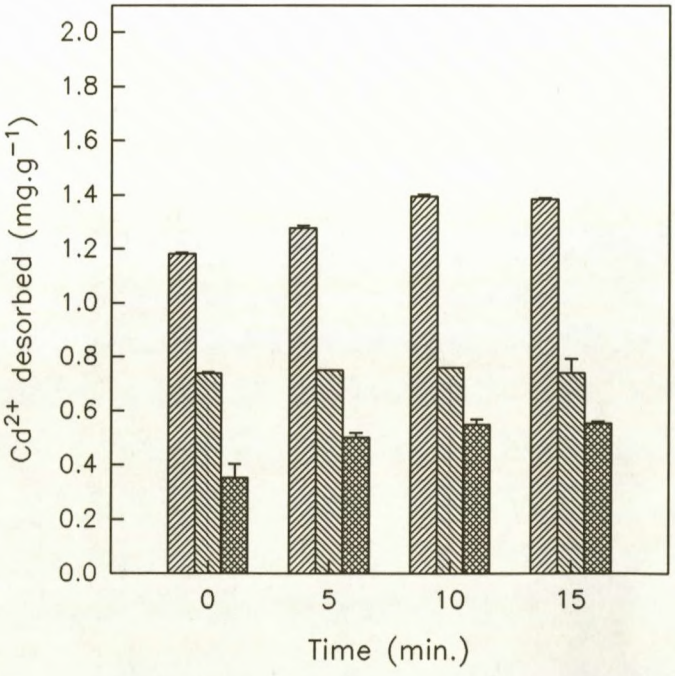

FIG. 4.55 Amount Cd^{2+} desorbed ($mg.g^{-1}$), from S3, using 0.2*N* H_2SO_4 (▨), 0.4*N* CH_3COOH (▧) and 0.2*N* HCl (▩).

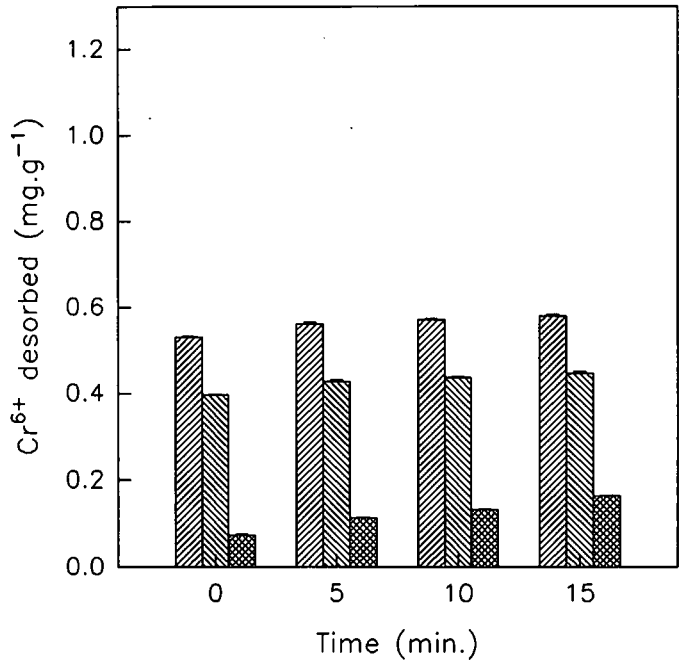

FIG. 4.56 Amount Cr^{6+} desorbed ($mg.g^{-1}$), from S3, using 0.2*N* H_2SO_4 (▨), 0.4*N* CH_3COOH (▧) and 0.2*N* HCl (▩).

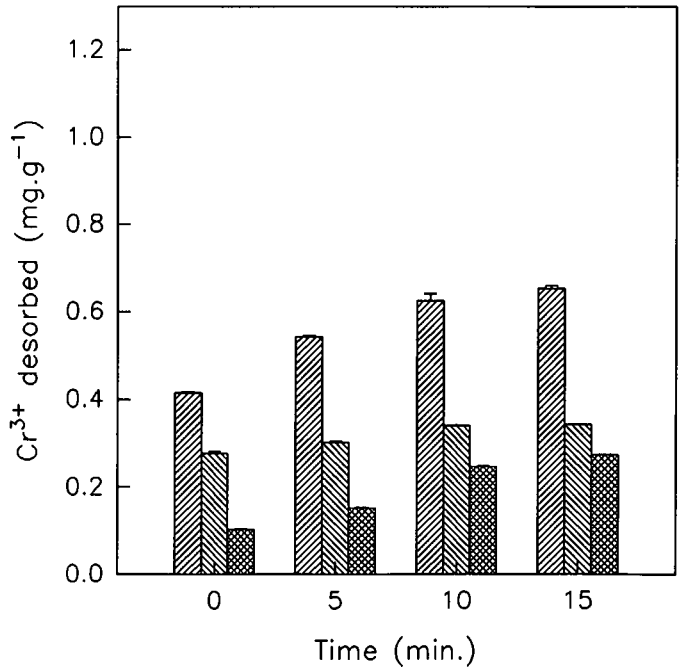

FIG. 4.57 Amount Cr^{3+} desorbed ($mg.g^{-1}$), from S3, using 0.2*N* H_2SO_4 (▨), 0.4*N* CH_3COOH (▧) and 0.2*N* HCl (▩).

4.6 SIMULTANEOUS BIOSORPTION AND DESORPTION PROCESS

4.6.1 Optimisation of process

The results indicated that the process had been optimised. However, a simultaneous rather than a continuous process was achieved since the process had to be halted to facilitate movement of metal bound sludge, which had to be mobilised by the desorbent and transported using a peristaltic pump, to another reactor, where desorption continued. In using the desorbent as a transport medium, desorption was effectively initiated on contact with the agent, thereby reducing time spent by the desorbent-sludge suspension in the desorption vessel (FIG. 3.1).

4.6.2 Adsorption of metal ions from synthetic effluent by a selected adsorbent

As shown in preceding biosorption experiments, S3 biosorbed metal ions from synthetic effluent. There was negligible difference in the concentration of metals adsorbed after 15min. Superior adsorbates were Zn^{2+}, Cu^{2+} and Cd^{2+}. As seen with previous adsorption, Cr^{6+} showed poor biosorption by S3. Maximum metal concentration adsorbed by the sludge was 2.0 $mg.g^{-1}$ (FIG. 4.58).

4.6.3 Desorption of metal ions from biosorbent

Most of the Zn^{2+} adsorbed by S3 was subsequently desorbed by the desorbent, $0.2N$ H_2SO_4. Desorption of metals occurred almost immediately upon exposure of sludge to desorbent.

Increases in desorption after 5 min., was negligible. Zinc was the predominant metal desorbed. Desorption efficiency of Cu^{2+} was comparatively unfavourable (FIGS 4.58 and 4.59).

The above results are similar to findings of the fully mixed separate biosorption/desorption trials. The significance of this aspect of the work was to synchronise the biosorption and desorption processes in order to make it applicable to industry. Although a continuous process was not possible, a simultaneous biosorption/desorption process was achieved.

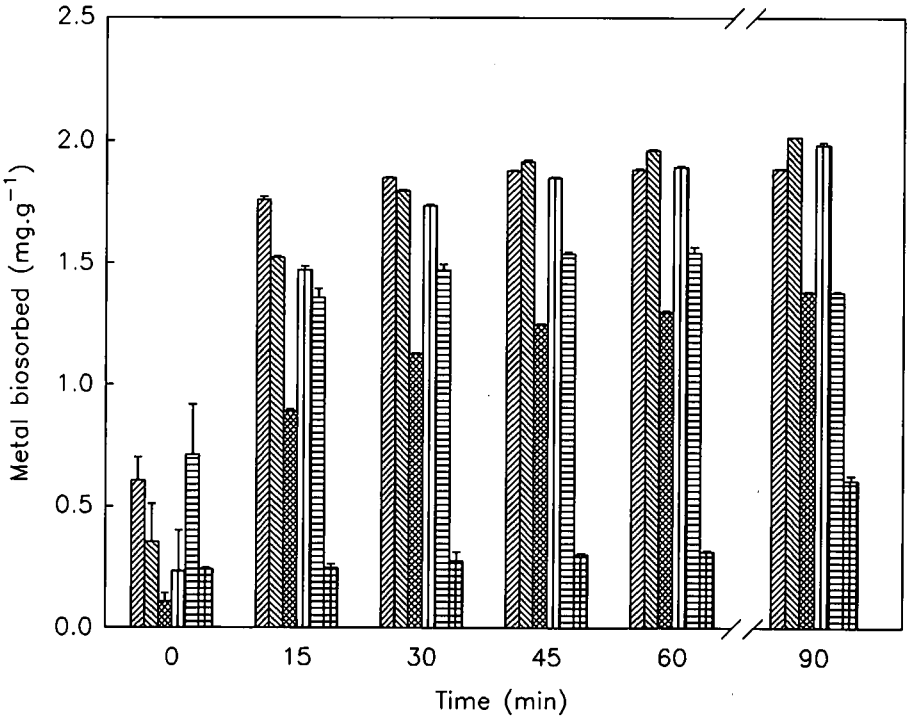

FIG. 4.58 Quantities Cu^{2+} (▨), Zn^{2+} (▧), Ni^{2+} (▩), Cd^{2+} (▥), Cr^{3+} (▤) and Cr^{6+} (▦) biosorbed by S3 using synthetic effluent in a simultaneous process.

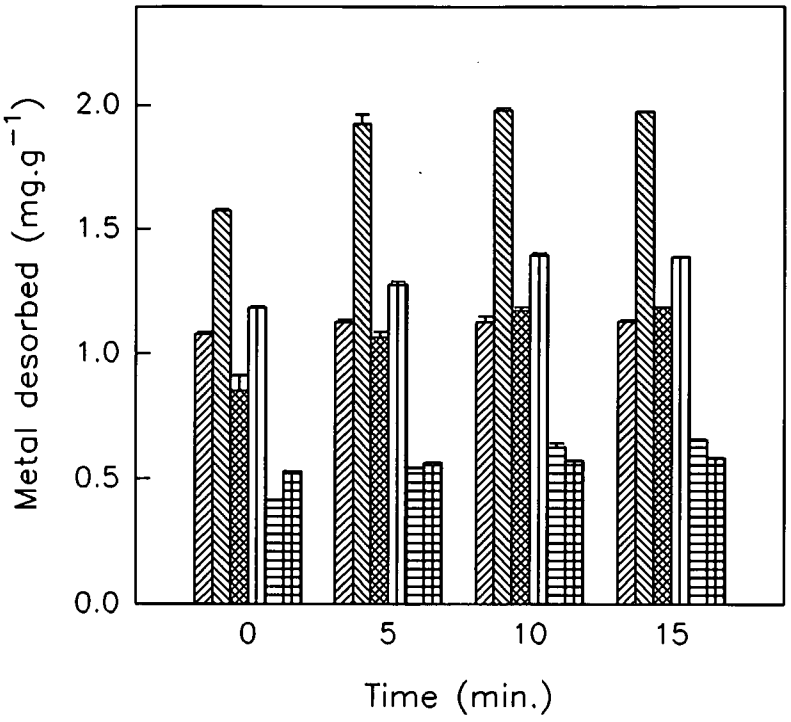

FIG. 4.59 Quantities Cu^{2+} (▨), Zn^{2+} (▧), Ni^{2+} (▩), Cd^{2+} (▥), Cr^{3+} (▤) and Cr^{6+} (▦) desorbed from S3 using synthetic effluent in a simultaneous process.

4.7 PACKED-BED BIOREACTOR PROCESS

4.7.1 Immobilisation of sludge and optimisation of process

After various trials, optimisation of immobilisation was achieved using polysulfone. The beads that were formed were of good consistency, with a "rubbery" texture and spherical in shape. Beads were stored at 4°C for a maximum of four days. Retention time of the effluent, as it passed through the column, was 4 minutes and 30 seconds. A volume of 1.883ℓ of effluent passed through the reactor during the 90 min., trial run.

4.7.2 Adsorption of metal ions from synthetic effluent

A control, using polysulfone only, was conducted. Results showed that the immobilised biosorbent, in a packed-bed configuration, exhibited the potential to remove metals from solution. All the metals tested showed decrease in biosorption by the immobilised biosorbent, with time. Rates of adsorption of all metals tested, decreased rapidly after 30 min. There was little difference in the concentrations of metals biosorbed after 40 min. Negligible amounts of Ni^{2+} were biosorbed after 60 min. The following affinity series was determined for the biosorption of metals from solution by the biosorbent viz., $Cr^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Cr^{6+} > Ni^{2+}$ (FIG. 4.60).

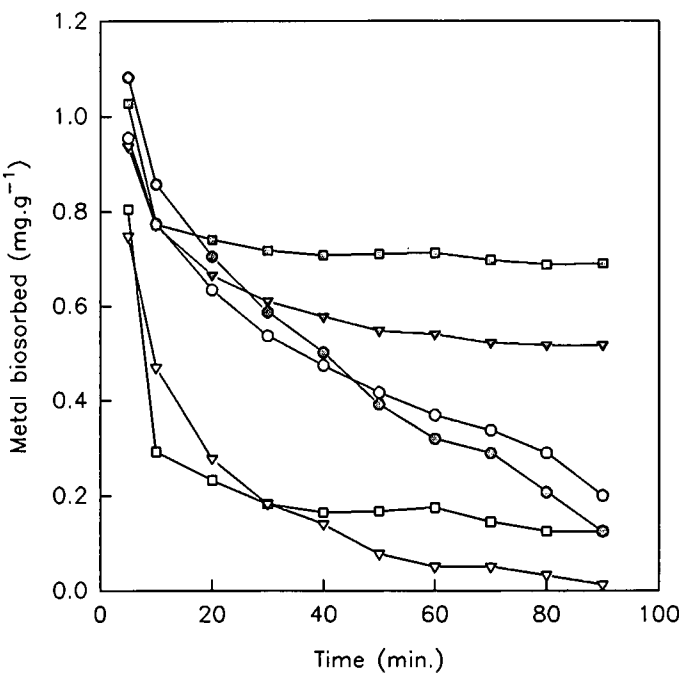

FIG. 4.60 Biosorption of Cr^{3+} (■), Cd^{2+} (▼), Zn^{2+} (○), Cu^{2+} (●), Cr^{6+} (□) and Ni^{2+} (▽) using S3 as biosorbent in a packed-bed column.

4.7.3 Desorption of metal ions from adsorbent

Most of the metals were desorbed within 10 min., by the desorbent. With the exception of Ni^{2+}, the desorbent exhibited high removal efficiencies. Trivalent chromium was the superior metal desorbed, possibly because it was biosorbed in large concentrations by the adsorbent. The results show 15 min., to be the optimum time for desorption since there was not much difference in the removal of the metal after 10 min., (FIG. 4.61).

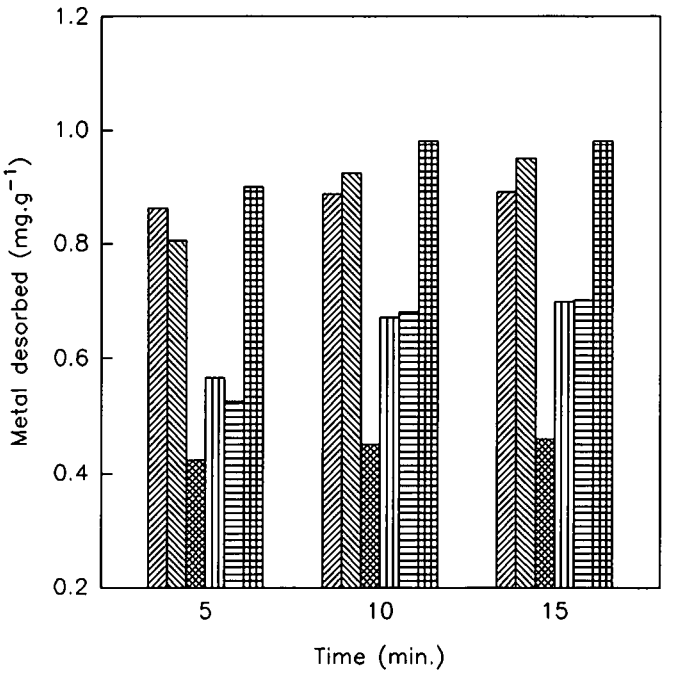

FIG. 4.61 Desorption of Zn^{2+} (▨), Cu^{2+} (▧), Ni^{2+} (▩), Cd^{2+} (▥), Cr^{6+} (▤) and Cr^{3+} (▦) from S3 in a packed-bed column.

CHAPTER 5

5.0 DISCUSSION

5.1 BIOSORPTION OF METAL IONS FROM SINGLE SOLUTIONS

5.1.1 Adsorption of metal ions from single solutions

Previous research in this field focused mainly on the biosorption of metals during the anaerobic digestion process and toxicity of these metals to the functioning of anaerobic digestion rather than exploring the potential of using waste digested sludge as metal biosorbent. Many workers have shown the ability of microorganisms to bioaccumulate metal ions (Beveridge and Murray, 1976; Sterritt and Lester, 1981; Kasan, 1988; Hughes and Poole, 1989). Bioaccumulation is essentially an active process and dependent on growth of the organism. However, certain types of microbial biomass can passively bind and accumulate metals even when metabolically inactive or dead (Petrasek and Kugelman, 1983). Waste digested sludges have shown potential for the removal of heavy metals from solution (Alibhai *et al.*, 1985; Fletcher and Beckett, 1987).

The findings of the present research demonstrated that all waste digested sludges which were investigated, presented the capacity to remove metals from solution (FIGS 4.1 - 4.12). With all metals investigated, it was evident that there was a general trend displaying increase in biosorption of metals by sludge with increases in metal quantities ($mg.g^{-1}$) in solution (FIGS 4.1; 4.3; 4.5; 4.7; 4.9; 4.11). These results support the findings of Forster (1983) and Bux

et al., (1994) and could be attributable to increasing pressure of the forward reaction of the equilibrium equation:

$$M + S \rightleftharpoons MS \qquad \text{(Nelson } et\ al.\text{, 1981)}$$

where: M = metal; S = sludge; MS = metal-sludge complex (Nelson *et al.*, 1981).

The increase in biosorption could also be attributable to various physio-chemical factors, eg., more binding sites were available on the sludge surface to facilitate free metal binding (Lawson *et al.*, 1984; Alibhai *et al.*, 1985). According to Mattuschka and Straube (1993), high rapid sorption rates are typical for adsorption of dissolved substances on solid material.

Except for Ni^{2+} and Cr^{6+} (FIGS 4.4 and 4.10), when metal adsorption was expressed as percentage adsorption ratios (FIGS 4.2; 4.4; 4.6; 4.8; 4.10; 4.12), there was a general trend of decrease in removal of metals with an increase in metal concentration in solution (FIGS 4.2; 4.6; 4.8; 4.12). This indicates that the equilibrium equation is not governed by a 1:1 ratio where adsorption is proportional to the quantity of metal in solution. These findings support the results of Swalaha (1993) and Bux *et al.*, (1994), who showed similar trends using waste activated sludge. However, these findings contradicted results of Brown *et al.*, (1973) who reported a proportional relationship between sludges and the metals Cr, Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+}, at a range of metal concentrations (< 2 mg.ℓ^{-1}). It could be possible that external factors limit the reaction of the metal with ligands on the sludge surfaces. There was a substantial difference in the biosorption of Zn^{2+} by S3 when compared to other sludges at higher concentrations ie., 120 and 150 mg.ℓ^{-1} (FIG. 4.1). This phenomenon could be attributed to more binding sites being available on the surface of S3 for the Zn^{2+} metal as compared to other sludges which could have these specific sites saturated (Alibhai *et al.*,

1985).

Quantities of Ni^{2+} biosorbed by all sludges increased as Ni^{2+} concentrations in solution increased between 30 and 120 mg.ℓ^{-1}. This indicates the positive pressure being applied by the solution concentration on Ni^{2+} biosorption from solution. However, at 150 mg.ℓ^{-1}, S3 and S5 showed decrease in biosorption. This could be attributed to saturation of surface sites, for Ni^{2+}, of these sludges. S4 displayed overall superior biosorptive capacity for Ni^{2+} when compared to other sludges, indicating large numbers of surface sites for this metal (FIG. 4.3). As with Zn^{2+}, the decrease in percentage biosorption with increase in metal concentration in solution was not evident but remained rather constant until 120 mg.ℓ^{-1}. At 150 mg.ℓ^{-1}, slight decreases were evident, thus indicating a possible fixed number of sites for Ni^{2+} biosorption. Maximum percentage Ni^{2+} biosorbed of 50% by S3 was much lower when compared to previous research using activated sludge where 85% removal was obtained (FIG. 4.4) (Bux *et al.*, 1994).

In keeping with the general trend shown by most metals, there was an increase in the amount of Cu^{2+} biosorbed with increase in the concentration of metal in solution. The physico-chemical properties which may be considered as being of significance to the binding of Cu^{2+} include pH, temperature, redox potential and presence of complexing agents (Alibhai *et al.*, 1985). Sludge S2 presented greatest affinity for Cu^{2+}, when compared to other sludges. This could be attributed to the sludge possessing greater number of surface sites for the metal. Decrease in quantities of Cu^{2+} biosorbed by S1 at 150 mg.ℓ^{-1} could be attributed to saturation of surface sites for Cu^{2+}. Maximum efficiency of biosorption was found for S2 at approximately 67% (FIG 4.6). When comparing the efficiencies of percentage Cu^{2+} bound

to waste activated sludge ie., 98%, the present results produced a much lower capacity (Bux *et al.*, 1994).

Similar to Cu^{2+} biosorption results, S2 showed superior biosorption capacity for Cd^{2+}. Sludges S1, S4 and S5 showed no increase in biosorption at higher concentrations, therefore indicating that there was no increase in presence of forward reaction in the equilibrium equation (Nelson *et al.*, 1981) (FIG. 4.7). Generally, sludges presented decreases in percentage Cd^{2+} biosorbed with increases of metal in solution (FIG. 4.8).

There was a near proportional increase in quantities of Cr^{6+} biosorbed by all sludges as concentrations of the metal in solution increased. Except for S3, there appeared to be no substantial increase in biosorption at Cr^{6+} concentrations of 150 mg.ℓ^{-1}, indicating possible saturation of sludge surface sites for the metal. Sludge S4 displayed overall superior biosorption for Cr^{6+}. Forster (1985) proposed that chromium biosorption occurs predominantly by hydroxyl groups on the sludge surface. Therefore, limited hydroxyl groups could be the limiting factor for S5 with regards to Cr^{6+} biosorption (FIG. 4.9). When comparing the efficacy of two types of inactive biomass, waste digested sludge showed maximum percentage removal of 45% Cr^{6+} at 30 mg.ℓ^{-1} (FIG. 4.10) as compared to 8% removal using waste activated sludge (Swalaha, 1993). Hexavalent chromium is toxic to most biological systems such as bacteria and other higher organisms, therefore limiting their capacity as biosorptive agents (Richard and Bourge, 1991). This toxicity does not effect the biosorptive capacity of inactive biomass such as waste sludges. It has been suggested that binding of chromium to digested sludge is a physico-chemical process, rather than biological, whereby sorption involves cation exchange (Alibhai *et al.*, 1985). Sharma and Forster

(1996), using granular activated carbon, showed biosorptive capacities of up to 145 $mg.g^{-1}$, when exposing the biosorbent to Cr^{6+}.

When compared to other sludges, superior biosorptive capacities of S3 for Cr^{3+} could be attributed to large numbers of hydroxyl groups on the sludge surface. Similarly, a lack of responsible hydroxyl groups, which play significant roles in Cr^{3+} biosorption to the surface of S5, could account for its negligible biosorptive capacity (Forster, 1985) (FIG. 4.11). Decreases in percentage Cr^{3+} biosorbed by S3, concomitant with increases in concentrations of metal in solution, was similar to trends displayed with other metals.

5.1.2 Comparison of sludge biosorptive capacity

The general affinity series established from the results follow the descending order of $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cr^{6+} > Cr^{3+}$ (FIG. 4.14). The affinity of the sludges for each of the metals closely emulated research conducted by Fletcher and Beckett (1987), the only difference being that of Cu^{2+} having greater affinity than Cd^{2+}. It should also be noted that there was not much difference in the concentration of average metals biosorbed between Cu^{2+} and Cd^{2+} (FIG. 4.14). The results confirm previous findings of the author, which showed similar affinity series using waste activated sludge (Bux *et al.*, 1994). One could conclude that production of waste biomass through different processes ie., digestion and activation, leads to inactive biological matter with similar physico-chemical properties. It should also be noted that except for Cr^{3+}, there was no substantial difference in the average concentration of metals biosorbed by test sludges. The most distinct difference between the biosorptive capacities of both waste sludges was $Cr^{6+} > Cr^{3+}$ affinities. These results contradicted

previous findings of Forster (1985), who postulated that because of Cr^{6+} possessing smaller ionic radii, the ion would be bound less frequently due to the availability of more binding sites for ions with larger radii.

The present findings confirmed that when comparing the five sludges, some displayed superior metal biosorptive potential (FIG. 4.13), although differences in amounts biosorbed ($mg.g^{-1}$) were not very pronounced (TABLE 4.3). The overall ranking of sludges according to their biosorptive potentials was S3 > S2 > S4 (FIG. 4.13). The superior biosorptive capacity of S3 could be attributed to the sludge being exposed to influent primarily of a domestic nature, therefore providing large numbers of unattached surface sites for adsorption of cations. Current research by the author using activated sludge, substantiated the above findings whereby sludge generated from the treatment of domestic waste showed greater capacity for biosorption than industrial sludge. Previous research by Swalaha (1993) showed that domestic sludge had adsorbed greater amounts of Zn^{2+}, Ni^{2+} and Cu^{2+}, when compared to industrial sludges. An important biological factor that could account for sludge biosorptive capacity is the difference in the concentration of bacterial extracellular polysaccharides (ECP), present in industrial sludge. Results showed individual sludges displaying affinity for certain metal species, eg., S3 displayed superior biosorption for Zn^{2+} and Cr^{3+} (FIG. 4.13 and TABLE 4.3). This could be attributed to differences in characteristics of sludge, which in turn, are a function of physical and chemical properties imposed by the particular sludge treatment process (Alibhai *et al.*, 1985). In addition, differences in chemical structure of binding sites on individual sludges, determine the metal uptake capacity of the particular sludge (Lester and Sterrit, 1985). Forster (1971) showed the principal ionogenic component of ECP to be glucuronic acid. Glucuronic acid is present in greater quantities in domestic

sludge ECP (Swalaha, 1993), which could be responsible for the increased adsorption of Zn^{2+} by domestic sludges, such as S3. Gould and Genetelli (1975) concluded that different metals may associate with different types of functional metal adsorbing groups, and the number of effective binding sites is dependent on the distribution of these groups.

Although the magnitude of difference in concentrations of metals biosorbed by the three superior biosorbents viz., S2, S3 and S4, was not substantial, S3 displayed overall superior biosorption.

5.1.3 Mechanisms of biosorption

Adsorption isotherms for each metal ion and the five sludges under investigation were plotted as amounts metal biosorbed per gram of sludge ($mg.g^{-1}$), represented as q_e, versus free metal in solution at equilibrium ($mg.\ell^{-1}$), C (FIGS 4.15 - 4.44). The square of correlation coefficients for linearisation of the isotherms was determined to indicate whether data generated conformed to the Langmuir model. First order regression lines were not expressed graphically since only seven of the thirty isotherms displayed first order regression coefficients greater than or equal to 0.90, indicating their conformity to the Langmuir model.

Cadmium biosorption by S3 demonstrated a typical type II isotherm (FIG. 4.17). Type II adsorption indicates a monolayer to multilayer adsorption and was first characterised by Brunauer, Emmet and Teller (BET isotherm) (Ruthven, 1984). The curve indicates a continuous progression with increasing load. As the load increases further, multilayer adsorption occurs. This can arise by two means ie., a wide range of pore sizes on the sludge

surface is available to accommodate metal ions whilst larger pores begin accumulating a second layer of ions or planar sludge surfaces adsorbing metal ions begin to accrue a second layer on the adsorbed surfaces (Ruthven, 1984).

Adsorption isotherms plotted according to the Langmuir model did not fit data for Cu^{2+} adsorption to S1 and S4, with unusual isotherms being observed (FIGS 4.20 and 4.23). In addition, linear regression values were not greater than 0.55 and did not fit the model. S2 and S5 demonstrated bilayer or BET type isotherms (FIGS 4.21 and 4.24). Sludge S3 equilibrated with Cu^{2+} displayed a fairly close fit with a rectangular hyperbolic or "L" shaped isotherm, also known as type I, being observed (FIG. 4.32). This is indicative that only one type of binding site on the sludge adsorbed Cu^{2+} from solution ie., charged carboxyl groups which may exist on amino acid or protein moieties of the sludge floc.

Adsorption of Ni^{2+} by the sludges produced isotherms that did not conform with the model. Sludge S4 showed a closer fit to the type III isotherm, thus indicating a continuous progression with increasing loading from monolayer to multilayer adsorption and then to capillary condensation (Gasser, 1985) (FIG. 4.28). Interaction of other sludges with Ni^{2+} resulted in very low regression values and isotherms of undefined shapes (FIGS 4.25, 4.27 and 4.29).

Results of the five sludges equilibrated with Zn^{2+} showed three fitting the isotherm models. Biosorption of Zn^{2+} by S2 showed a regression value of 0.99, therefore fitting the Langmuir isotherm model and demonstrating a typical type I or "L" shaped isotherm, thus indicating a fixed demand for the metal. The isotherm shows a characteristic increase and then

decrease as adsorbate pressure increases (FIG. 4.31). Previous research by Bux *et al.*, (1994) presented similar "L" shaped isotherms when equilibrated with Zn^{2+} using activated sludge. Sludge S3 conformed with a type III isotherm showing continuous progression with continuous loading (FIG. 4.32), whilst S4 conformed closely to a type IV adsorption isotherm (FIG. 4.33). Type IV isotherms are indicative of multilayer adsorption, in particular the formation of two surface layers, either on a plane surface or on the wall of a pore with a diameter much larger than the diameter of the sorbate. Sludges S1 and S5 did not conform to any of the models (FIGS 4.30 and 4.34).

The equilibration of Cr^{6+} with all the sludges presented low regression coefficients, therefore interpretation using any of the models was not possible (FIGS 4.35 - 4.39). Hexavalent chromium adsorption by sludges showed only S3 ($R^2=0.96$) displaying a "L" shaped or type I isotherm (FIG. 4.42). Sludge S3 showed a gradual increase with subsequential decrease as adsorbate pressure increased.

Computation of equilibrium constants k_a and X_m, representing strengths of sludge-metal bonds and capacities of sludge surfaces for metal adsorption respectively, were determined (TABLES 4.1 and 4.2). Data, with the square of correlation coefficient for linearisation of isotherm values greater than 0.90, are relevant with regard to the Langmuir model (R^2 value included in legends of graphs). All other data are considered empirical. Except for chromium, S3 presented overall superior k_a values for the other metals (TABLE 4.1). The present results showed that the maximum bond strengths of sludge to metal ions did not correlate with the maximum binding capacities of sludge to metal ion eg., S3 showed superior bond strength but overall poor binding capacity (TABLES 4.1 and 4.2). These

findings were in contrast to previous research by the author using waste activated sludge as an inactive biosorbent whereby a substantial degree of correlation between superior bond strength and metal binding capacity of the sludge was shown (Bux *et al.*, 1994). However, an ideal biosorbent should have a high metal binding capacity with a moderate to low bond strength to facilitate efficient removal of metals during desorption. Overall sludge biosorption ranking, with respect to metal ions, was determined to be S3 > S2 > S4 (TABLES 4.1 and 4.2).

Alibhai *et al.*, (1985), under anaerobic digester conditions, exposed metals to sludge and used the k_a values to determine the following affinity series viz., Cr > Zn > Fe > Pb. On the contrary, present research using k_a values showed an affinity series where Zn > Cr (TABLE 4.1). In addition, Farag *et al.*, (1981), using wool carbonising waste, produced an affinity series of Ni > Cr > Zn. Much of previous research, involving interactions of heavy metals with anaerobic sludges, occurs *in situ* using anaerobic digesters or are conducted from a toxicological perspective. In comparison, present work involves the use of waste digested sludges as biosorbent, under aerobic conditions. In addition, the former is viable biomass in comparison to inactive waste sludges. Therefore, it is difficult to draw comparisons on the mechanisms and affinities of both biomass types due to the vastly different environments.

Sludges showed preference in capacity and affinity for certain metal species, as determined by reciprocal linearisation of adsorption isotherms eg., S3 has shown superior affinity for Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} whilst S5 showed superior affinity for Cr^{6+}. Relationships could be drawn between superior bond strength and quantities metal biosorbed ($mg.g^{-1}$) eg., S3 had

a high k_a for Zn^{2+} and presented comparatively superior biosorption (TABLES 4.1 and 4.4). S3 produced superior overall biosorption. It should also be noted that reference to TABLES 4.1 and 4.4 will strongly show that sludges displaying high k_a and X_m values for specific metals do not always display superior biosorption ($mg.g^{-1}$). Sludges have been shown to adsorb metal ions from solution and these adsorptive capabilities were fitted to Langmuir models of adsorption which provide mathematical deductions to sludge-metal adsorption experiments, to facilitate selection of the most efficient sludge for the adsorption of metal ions.

5.2 SLUDGE SURFACE CHARGE

Previous research by Bux and Kasan (1994a) involved identifying an appropriate technique for the determination of sludge surface charge. Various techniques were investigated but, for the present application, the millivolt quantification method was deemed most suitable since the objective of this aspect of the research was to compare surface charge between the five sludges, rather than to determine the absolute charge on individual sludge surfaces. Previous research has shown that there is a relationship between superior electronegativity of sludge and its capacity to biosorb a variety of metal ions from solution (Bux and Kasan, 1994a). Charge present on sludge surfaces is a function of the physio-chemical properties of the surface. Alibhai *et al.*, (1985) attributed chemisorption through ion exchange as a function of ionic valency and ionic radius of the metal. Therefore, he suggested the charge, size and nature of the sludge surface will dictate the overall ionic exchange process.

The present research, investigating the surface charge of five sludges, showed S3 to be the most electronegative sludge, followed by S2 > S4 > S5 > S1. It should be noted that there was a substantial magnitude of difference in the electronegativity value of S3 and S2, yet little difference between S2 and S4. In addition, S1 showed the least electronegativity (TABLE 4.3). All sludges investigated produced an overall net negative charge. Several hypotheses have been postulated to explain this complex phenomenon (Forster, 1976; Morgan *et al.*, 1990). In the present context, differences in the electronegativity of S1, S2, S3 and S4 could be attributed to the chemical nature of the sludge surface influencing the magnitude of surface charge. The principal ionogenic component of sludge polysaccharide was shown to be glucuronic acid which, at neutral pH, contributes a strong negative charge, thus facilitating the polysaccharide to behave as a polyelectrolyte (Stumm and Morgan, 1962; Forster, 1971). Horan and Eccles (1986) showed that the nature and concentration of the ionogenic materials present on sludge surfaces will determine the magnitude of sludge surface charge. Therefore, there is sufficient evidence to support the present findings, showing large differences in magnitude of surface charge between S3 and other sludges which could be attributable to nature and concentration of ionogenic materials.

When comparing the electronegativity of ten waste activated sludges (Bux and Kasan, 1994a) against waste digested sludge using the pH/millivolt method, with regards to the most electronegative sludge, the latter showed a 30% greater negativity (-68.80 vs -97.50). In general, anaerobic sludges tend to have higher concentrations of proteins in the extracted polymers and a protein : carbohydrate ratio of approximately 3 : 1 for digested sludge extracellular polysaccharide (ECP) (Morgan *et al.*, 1990). This ratio showed a linear relationship with surface charge. Differences between the gross chemical nature of aerobic

and anaerobic biopolymers suggest that in the latter systems, different metabolic processes result in production of polymers which are not only released less readily but are also chemically different (Morgan *et al.*, 1990). There is a definite relationship between the concentration of surface biopolymers and sludge surface charge (Magera and Nambu, 1976). The five digested sludges investigated showed a large magnitude of difference in their relative electronegativities, with S3 displaying the greatest net negative charge.

5.3 CORRELATION BETWEEN MECHANISMS, SURFACE CHARGE AND SLUDGE METAL BIOSORPTION

Previous research by Bux *et al.*, (1994) had shown a definite relationship between the electronegativity of sludge surfaces and their metal biosorptive capacities. Present results substantiate previous research by the author whereby the affinity series between sludge-metal biosorption and sludge surface charge were identical ie., S3 > S2 > S4 > S5 > S1. Alibhai *et al.*, (1985) strongly supported surface charge as the major physico-chemical characteristic responsible for ionic exchange processes and, subsequently, biosorption of metal ions by sludge. Sludge S3 presented a superior net negative charge with related superior biosorption. Similarly, S1 being the least electronegative sludge, presented the least biosorption of metal. It should be noted that interpretation of the mechanisms of biosorption showed S3 having the highest k_a values for four of the five metals investigated, thus further substantiating reasons for its comparatively superior biosorption. Therefore, further investigation was restricted to using the three superior biosorbents ie., S2, S3 and S4.

5.4 LABORATORY SCALE BIOSORPTION (FULLY MIXED)

The present research substantiated findings by Mehrotra *et al.*, (1987) and Morgan *et al.*, (1990), and showed that the waste digested sludges S2, S3 and S4, in a large volume fully mixed configuration, were capable of metal biosorption from synthetic effluents (FIGS 4.45-4.50). S3 and S4 displayed similar biosorptive trends with regards to Zn^{2+} biosorption. This phenomenon could be attributed to similar nature and number of surface sites on the sludge. Maximum concentrations of Zn^{2+} biosorbed were approximately 2 $mg.g^{-1}$ after 45 min. Previous research by Bux *et al.*, (1994), using activated sludge under similar experimental conditions, showed maximum Zn^{2+} concentrations biosorbed of approximately 2 $mg.g^{-1}$. It could be argued that although both biomass types are generated from different treatment processes, both are metabolically inactive and their capacities to biosorb Zn^{2+} under aerobic, laboratory conditions, are similar. Maximum concentrations of Zn^{2+} adsorbed, for S3 and S4, occurred after 45 min., (FIG. 4.45). It is possible that there is some factor which limits the reaction of the metal with ligands present on sludge surfaces. This could be the ligands themselves, which, due to their limited numbers, can be limiting to the reaction.

Sludge S4 presented slightly superior biosorption when compared to S3 for Ni^{2+}. There was a marked difference in the concentration of Ni^{2+} biosorbed between S3, S4 and S2 (FIG. 4.46). This difference in binding capacity between sludges could be attributed to differences in ionogenic components on the sludge surface. When comparing the present process with functional anaerobic digesters, Ni^{2+}, present at low levels of 10 $mg.\ell^{-1}$, is actually toxic to the process. Therefore, regarding the distribution of heavy metals in digested sludge, it has been shown that only negligible quantities of metals are found in solution. Almost 90% of

the metals were found in the particulate fraction of the sludge (Katsiri *et al.*, 1988). Maximum concentration of Ni^{2+} biosorbed was approximately 1.5 $mg.g^{-1}$ (FIG. 4.46). Previous research using activated sludge presented similar results (Bux *et al.*, 1994). There was little difference in the concentration of Ni^{2+} biosorbed after 15 min., thus indicating early saturation of surface sites for Ni^{2+}. These findings were consistent for all three sludges investigated. Lawson *et al.*, (1984), upon addition of Ni^{2+} at concentrations ranging from 0.005 - 0.25 $mg.\ell^{-1}$ to both viable and inactive sludges, obtained 100% removal by the viable biomass. They also found Ni^{2+} removal to be an active process at low Ni^{2+} concentrations. Therefore, it is obvious that high concentrations of the metal are toxic to viable biomass, thus effecting uptake rates. Comparatively, since digested sludge is metabolically inactive, uptake is not active and exposure to even 50 $mg.\ell^{-1}$ Ni^{2+} facilitates biosorption.

All three sludges displayed similar biosorptive capacities for Cu^{2+} after 15 min., exposure time. As reaction time increased, differences in concentrations biosorbed by S2 and the superior Cu^{2+} biosorbents S3 and S4 were proportional (FIG. 4.47). This could be attributed to the surface chemistry of the sludges for specific metal ions. Forster (1985) proposed that binding sites for Cu^{2+} were predominantly hydroxyl groups at low Cu^{2+} concentrations and carboxyl groups at high concentrations. Bux *et al.*, (1994), using waste activated sludge under identical experimental conditions, produced overall Cu^{2+} biosorption of 1.65 $mg.g^{-1}$, which was slightly less than the 1.95 $mg.g^{-1}$ effected by digested sludge (FIG. 4.47).

Biosorption of Cd^{2+} by all sludges investigated presented very similar trends to that of Cu^{2+}, ie., there was no marked increase in biosorption concentrations after 15 min. Since initial concentrations of Cd^{2+} in solution remained constant at 50 $mg.\ell^{-1}$, it is possible that after 15

min., there was no increasing pressure of forward reaction in the equilibrium equation. S3 and S4 were once again superior biosorbents with regards to Cd^{2+} (FIG. 4.48). When compared with waste activated sludge, present results showed a 0.2 $mg.g^{-1}$ increase in biosorption (Bux *et al.*, 1994).

The biosorption capacity of Cr^{6+} by investigated sludges was low compared to that of other sludges. S2 showed maximum biosorption at 90 min., (approximately 0.9 $mg.g^{-1}$). These results could be compared favourably with previous research, by Bux *et al.*, (1994) and Kasan and Baecker (1989), which produced 0.6 $mg.g^{-1}$ and 0.04 $mg.g^{-1}$, respectively. Hexavalent chromium is considered toxic to microbial biomass (Smith and Vasiloudis, 1989) but since the present experimental biomass is inactive, effects of toxicity on biosorption can be negated. Forster (1985) proposed that chromium biosorption occurs predominantly by hydroxyl groups on the sludge surface. Contrary to poor biosorption results when compared to the other metals discussed, S2 showed overall superior biosorption of Cr^{6+} (FIG. 4.49). It should be noted that time zero is a hypothetical value since the synthetic effluent was already exposed to the sludge during sampling and biosorption occurs immediately.

For Cr^{3+} biosorption, results were unexpected whereby all three sludges adsorbed equal amounts of metal. The sudden reduction in Cr^{3+} biosorption between 15 and 45 min., could possibly be attributed to experimental error. A notable feature of Cr^{3+} biosorption is the identical biosorption capacity of S3 and S4 between 15 and 90 min., (FIG. 4.50). Interpreting this phenomenon, one could conclude that biosorption appears to be dependent more upon the physico-chemical characteristics of the metal rather than the sludge type. Comparison with waste activated sludge, with maximum biosorption of 0.6 $mg.g^{-1}$ (Bux *et*

al., 1994), present findings display superior biosorptive capacities of 1.5 $mg.g^{-1}$. Slight decreases in biosorption occurred consistently with all three sludges. This could be indicative of possible saturation of surface sites (FIG. 4.50).

Most of the other research conducted thus far, using digested sludges, focused on metal uptake and toxicity during the anaerobic digestion process rather than investigating the capacity of processed waste digested sludges to biosorb metals under aerobic conditions. The theme of previous investigations by Bux *et al.*, (1994) focused on heavy metal biosorption using waste activated sludge. Present research concentrated on determining the biosorptive capacity of waste digested sludges for metal ions. Therefore, comparisons of the metal uptake efficiencies of waste activated and digested sludges were more favourable since experimental conditions were the same and both occurred aerobically. It should be noted that, with the exception of chromium, concentrations of metals biosorbed during the present investigation were similar to previous findings using waste activated sludge (Bux *et al.*, 1994).

This aspect of the research involved the use of a "mixed cocktail" synthetic effluent, comprised of six metals, as opposed to pure metal solutions. It should therefore be noted that there was substantial speciation occurring between metal salts in the effluent, dictating biosorption of the three sludges compared. Competition between metal species for surface sites on the sludge also plays an important role in biosorption. Therefore, when comparing the biosorptive capacities of sludges exposed to mixed metal effluents and pure solutions, adsorption is largely reduced (FIGS 4.13 and 4.14).

The affinity series determined for laboratory scale biosorption, using synthetic mixed effluent, was, in descending order of preference, $Zn^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+} > Cr^{6+}$. As expected, pronounced differences were noted when comparing the present affinity series to that of single solutions. These findings indicate that metal adsorption is dependent on the actual metal ion species rather than sludge biomass. The order of adsorption efficiency of previous research by Swalaha (1993) using domestic and industrial waste activated sludge was $Cu^{2+} > Zn^{2+} > Ni^{2+} > Cr^{total}$. This trend contradicted present findings particularly with regard to the reverse order of Cu^{2+} and Zn^{2+}. However, Alibhai *et al.*, (1985), using anaerobically digested sludge to biosorb metal ions, determined a sludge ranking of $Zn^{2+} > Cr^{total} > Pb^{2+} > Fe^{2+}$ which ranks the metals Zn^{2+} and Cr^{total} in proper sequence. The chromium species was not specified as either hexavalent or trivalent. Although comparison with present research involves only two common metals, namely Zn^{2+} and Cr^{total}, it is valid since anaerobic sludge was equilibrated aerobically with metal ions. Foster (1983) postulated that ionic radius determined the binding efficiency of metal ions to extracellular polysaccharides present on sludge surfaces and stated that metal ions, with larger ionic radii, are capable of forming complexes with both carboxyl and hydroxyl groups whereas metals with smaller radii cannot form carboxyl based complexes. This would result in lower biosorption rates for these particular metal ions. Tobin *et al.*, (1984) determined the relationship between ionic radii of trivalent chromium, lanthanum, manganese, copper, cadmium, barium, mercury, lead, uranium and silver and biosorption of these metals by *Rhizopus arrizhus*. He reported that increasing ionic radii of these metals was accompanied by increasing uptake, with the exception of trivalent chromium. The ionic radii of Zn^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+} and Cr^{6+} are 0.83, 0.74, 0.80, 0.64 and 0.35, respectively (Forster, 1985). In terms of comparison between decreasing ionic size and the present affinity series, the only

anomaly recorded was the higher biosorption of Cu^{2+} than Ni^{2+} with Ni^{2+} having a slightly larger ionic radius than Cu^{2+}. Overall superior biosorption when comparing sludges was presented by S3, followed by S4 (FIGS 4.45 - 4.50). Further experimentation was restricted to the use of S3 only.

In order to make the fully mixed laboratory scale process more applicable to industry, trials were conducted using post-galvanising rinse effluent from an electroplating company. Since the effluent was generated from the rinse, Zn^{2+} was the predominant metal present, occurring at concentrations of up to 119.4 $mg.\ell^{-1}$. Comparatively, other metals were present at much lower concentrations. The results presented Zn^{2+} adsorption, by S3, to be as high as 4.5 $mg.g^{-1}$ (FIG. 4.51). Biosorption of Zn^{2+} from industrial effluent far exceeded the biosorptive capacity of the same sludge (S3) when exposed to synthetic effluent, comprised of equal metal concentrations (50 $mg.\ell^{-1}$) therefore creating equal interspecies competition for sludge surface sites, as opposed to industrial effluent which had far more Zn^{2+} than other metals present. Previous research by Bux *et al.*, (1994) confirmed that the higher the concentration of any metal in a mixed cocktail effluent, the better the biosorption of that particular metal by sludge. Waste activated sludge, under similar experimental conditions, was exposed to a mixed metal effluent containing 121.67 $mg.\ell^{-1}$ Zn^{2+} (present in the highest concentration) and removed approximately 4.0 $mg.g^{-1}$. Present findings further confirmed the similarity in the biosorptive capacities of both sludge types, given the same experimental parameters and high concentrations of any metal, facilitates comparative biosorption by the sludges. In addition, waste digested sludges could serve as metal biosorbents for industrial effluents.

5.5 LABORATORY SCALE DESORPTION (FULLY MIXED)

Research by Bux *et al.*, (1994) involved investigating a range of desorbents to identify suitable agents which could effectively desorb metal bound sludge. Mineral acids viz., 0.2*N* H_2SO_4, 0.4*N* CH_3COOH and 0.2*N* HCl, were identified as most appropriate for present applications. Although mineral acids were found to be highly effective desorbents, they were also known to destroy sludge surfaces thus preventing reusability of the biomass (Tsezos, 1984). This aspect of the research involved comparing the desorptive capacities of the three acids against the superior metal bound biosorbent, S3.

With all metals tested, a large magnitude of desorption occurred almost immediately or within 5 min., and maximum desorption occurred within 10 min., possibly due to the hydrolysis of sludge surfaces and subsequent release of bound metals (FIGS 4.52 - 4.57). Present results followed the exact trend of desorption of metal bound waste activated sludges using acids, with regards to maximum desorption occurring within 10 min., of exposure (Bux *et al.*, 1994). Both biomass types could be compared because previous research has shown that desorption is desorbent-dependent rather than sludge dependent (Bux *et al.*, 1994).

Comparison of the three acids showed 0.2*N* H_2SO_4 presenting overall superior desorptive efficacy for all metals investigated. Differences in the desorption capacity of H_2SO_4 and HCl were noticeable, but mainly between H_2SO_4 and CH_3COOH although the latter was present in greater concentrations, c.f., 0.2*N* to 0.4*N*. This is probably due to the fact that HCl and H_2SO_4 are regarded as strong acids and therefore liberate more protons, as opposed to CH_3COOH, to exchange with metal ions bound to the surface of the sludge.

Desorption of Zn^{2+} by H_2SO_4 occurred within a 5 min., contact time indicating that removal of ions was rapid. Maximum desorption efficiencies of approximately 1.9 $mg.g^{-1}$ Zn^{2+} removal were achieved by H_2SO_4 as compared to 1.1 and 1.0 $mg.g^{-1}$ by HCl and CH_3COOH respectively (FIG. 4.52). Desorption by H_2SO_4 indicated that 95% of the Zn^{2+} was removed by the acid. Results indicate that the mineral acid is a highly effective desorbing agent. These findings confirm previous work by other researchers (Khovrychev, 1973; Tsezos, 1984; De Rome and Gadd, 1987). Maximum desorption concentrations of Ni^{2+} were 1.2 $mg.g^{-1}$ at 10 min., by H_2SO_4 and 0.35 $mg.g^{-1}$ by CH_3COOH. Contrary to expectations, the present results showed HCl did not desorb any Ni^{2+}. This anomaly could possibly be attributed to experimental error since previous research has shown that HCl effectively desorbed Ni^{2+} bound to activated sludge (Bux *et al.*, 1994). It should also be noted that CH_3COOH previously showed superior desorption over HCl (Bux *et al.*, 1994). This could possibly be due to metal cations being more amenable to form metal acetate salts than metal chloride salts. Therefore, since more metal ions form acetate salts, more exchange of metal ions will occur between the bound metal on sludge and hydrogen cations liberated by acetic acid. Although no desorption of Ni^{2+} occurred by HCl, the formation of nickel acetate would be favoured and this is possibly why CH_3COOH is more efficient at desorbing Ni^{2+} ions from sludge surfaces. It should be noted that metals bound to sludge are not inert and can be displaced by cations which are able to form stronger complexes ie., acidification, where protonation of carboxylic acid and phenolic groupings will occur and displace the heavy metal from organic matter (McAdams, 1985). Sulphuric acid possibly formed stronger complexes and therefore produced comparatively superior desorption results.

Desorption of Cu^{2+} was almost double when comparing H_2SO_4 to other acids investigated and occurred almost immediately with all three acids. Similar to Ni^{2+} desorption, Cu^{2+} was more effectively desorbed by CH_3COOH than HCl, possibly due to Cu^{2+} cations being more amenable to form acetate salts than chlorides salts. Maximum levels of Cu^{2+} desorbed were 1.1 $mg.g^{-1}$ (FIG. 4.54), thus achieving high removal efficiencies, similar to previous research by the author (Bux *et al.*, 1994). In contrast, Lawson *et al.*, (1984) showed poor desorption of Cu^{2+} from sludge, using EDTA as compared to acids. Cd^{2+} desorption followed a similar trend with regard to comparative desorption affinities of acids viz., H_2SO_4 > CH_3COOH > HCl. In addition, desorption was immediate with little change in concentrations with increases in time, indicating immediate displacement of Cd^{2+} by acid from the sludge surface. Maximum concentrations of Cd^{2+} desorbed were 1.4 $mg.g^{-1}$, obtaining removal efficiencies of up to 70% (FIG. 4.55) with regards to Cd^{2+} adsorbed (FIG. 4.48). In contrast, previous research using mineral acids on waste activated sludge, obtained removal efficiencies of between 94 - 98% (Bux *et al.*, 1994).

The maximum concentration of Cr^{3+} desorbed by H_2SO_4 was 0.65 $mg.g^{-1}$ (FIG. 4.57). The efficiency of desorption, when compared to amounts adsorbed, was 43.3% (FIG. 4.50). There was a two-fold difference when comparing present findings to desorption of waste activated sludge (Bux *et al.*, 1994). Firstly, CH_3COOH showed superior desorption when compared to HCl. Maximum efficiency of removal using CH_3COOH was in the region of 85%. Hexavalent chromium desorption was low when compared to the other metals (FIG. 4.56). This could be attributed to low initial Cr^{6+} concentrations present on the sludge, thus resulting in poor desorption (FIG. 4.49). Maximum concentrations desorbed by H_2SO_4 were 0.6 $mg.g^{-1}$, followed by CH_3COOH and comparatively negligible amounts desorbed by HCl

(FIG. 4.56). Chromium adsorption is thought to occur due to continuous progression with increasing loading from monolayer to multilayer onto the sludge surface. Thus, as more layers are adsorbed, it becomes easier to desorb these surface layers (Lawson, 1984). With the present research, since initial concentrations biosorbed were low, lack of easily detachable surface layers resulted in poor desorption.

Therefore, desorption of metal bound waste digested sludges by the three mineral acids mentioned, has shown H_2SO_4 to be the superior desorbent with all metals tested, followed by CH_3COOH and HCl. Contrary to previous findings and present expectations, HCl showed inferior desorptive capacity as compared to the weaker CH_3COOH. Therefore, further investigation was restricted to the use of H_2SO_4 as the desorbent of choice.

5.6 SIMULTANEOUS BIOSORPTION AND DESORPTION PROCESS

5.6.1 Process optimisation

The emphasis of this aspect focused on optimising the biosorption/desorption simultaneous process in a fully mixed configuration. Thus far, results have confirmed the capacity of waste digested sludge to biosorb heavy metals from single solutions and mixed effluents. Comparative biosorptive capacities of sludges were evaluated and a single superior adsorbent was chosen for further investigation. In addition, desorption trials resulted in the selection of a superior desorbent. The applicability of such related, although isolated, processes ie., biosorption/desorption, would be enhanced if they could be combined into a continuous process.

The implementation of a continuous biosorption-desorption process was halted in view of the fact that the mineral acid used ie., H_2SO_4, destroyed metal binding sites of the biomass thus preventing its reuse. These findings substantiated previous research by Tsezos (1984) using other mineral acids. In contrast, previous research using 5mM calcium chloride and 1M sodium carbonate, did not produce efficient desorption as acids yet facilitated subsequent reuse of biomass. Since superior desorption was paramount to such a process and the easy accessibility of biomass negated the need for its reuse, a simultaneous process was developed whereby new biomass had to be introduced during adsorption cycles. A schematic representation describing the process is shown in FIG. 3.1 and occurs in the following sequence. The selected superior adsorbent (S3) was exposed to synthetic effluent as described earlier. After treatment, effluent was transferred into a vessel. The biosorption reactor was then fed with desorbent ($0.2N$ H_2SO_4), metal-bound sludge was mobilised by the acid and transported, via a pump, to another reactor, where desorption continued. In using desorbent as transport medium, transfer of the sludge between reactors and desorption occurred concurrently thereby reducing the time required for desorption in the reactor. Once this suspension was completely transported out of the adsorption reactor, a second mass of fresh sludge was introduced to a second batch of untreated effluent and biosorption commenced. While sludge and effluent were interacting, desorption was completed and the acid pumped back to the desorbent storage vessel for reuse in the next desorption cycle until the acid became saturated (FIG. 5.1). Experimental parameters such as adsorbent concentrations and agitation rates were the same as determined previously for fully mixed laboratory trials. The advantage of such a process was the fact that biosorption and desorption occurred simultaneously, thus effectively reducing processing time and, subsequently, bringing the technology one step closer to industrial application.

Regarding the biosorptive capacity of S3, maximum concentrations of metal biosorbed ie., Zn^{2+}, were 2.0 $mg.g^{-1}$ (FIG. 4.58). As expected, results were very similar to previous biosorption findings in connection with adsorption capacities of S3 in batch fully-mixed configurations. The affinity series obtained for the simultaneous process ie., $Zn^{2+} > Cd^{2+} > Cu^{2+}$ was the same as previous laboratory experiments using synthetic effluent and therefore substantiates the validity of the data. It is also important to note that, similar to previous findings, there was not much difference in concentrations of metals biosorbed after 15 min., (FIG. 4.58). This finding would particularly suit the process since it would make it more economically feasible and not as time intensive when applied to industry.

Similar to previous findings, most of the desorption occurred within 5 min., of exposure of sludge to desorbent. Once again, this would ideally suit large scale industrial application. Most of the Zn^{2+} adsorbed was subsequently desorbed (FIGS 4.58 and 4.59). The only anomaly with desorption findings was the poor removal of Cu^{2+} bound to sludge by the desorbent. There appeared to be no difference in the desorption of Cu^{2+} after immediate exposure, making further removal highly unlikely (FIG. 4.59).

Simultaneous biosorption/desorption trials provided sufficient evidence to conclude that a reduction in process time to 15 min., adsorption and 5 min., desorption, without affecting adsorptive and desorptive capacities, would be ideally suited to industrial application.

FIG. 5.1 Photograph showing biosorption/desorption simultaneous process.

5.7 PACKED-BED BIOREACTOR PROCESS

5.7.1 Immobilisation and process optimisation

The success of this aspect of the research depended on immobilisation of the biomass. Trials were conducted to achieve the ideal immobilising agent. A method of immobilisation, detailed by Jeffers *et al.*, (1991), proved to be ideal for the immobilisation of dried waste sludge. They showed that the advantages of using polysulfone to immobilise biomass were high mechanical strength and the resistant nature of the beads to a wide range of environmental conditions. The porous nature of the beads allowed maximum contact of biomass with metal ions in solution. Difficulties were encountered when attempting to use calcium alginate due to lack of consistency with regard to bead formation. The immobilised biomass was loosely packed in glass columns to facilitate easy percolation of synthetic effluent which had to be pumped up through the column (FIG. 3.3). Rivera (1983) developed an energy-conserving wastewater treatment system based on an anaerobic, upflow (Anflow) bioreactor which utilised films of bacteria fixed to inert, stationary packing material. Similar to the present packed-bed design, except occurring under anaerobic conditions, wastewater flows upward through the bioreactor for continuous treatment. Release of solids using the packed-bed treatment process was minimal. Research by Tsezos *et al.*, (1988) indicated that a packed-bed column could be used successfully with upflow contact of the effluent solution with the biomass. The direction of flow was important as downflow may have the effect of compressing the biomass which would result in pressure drops with greater pressures needed to pump effluent solution through the bed. In addition, upflow allows for better control of the flow rate as downflow is gravity assisted and would

present a problem since immobilised biomass, with large bead sizes, would allow non-restricted flow of effluent through the bed thus decreasing retention times considerably.

5.7.2 Adsorption of metal ions from synthetic effluent and desorption from the sludge

Waste digested sludge, in a packed-bed configuration, showed capacity to remove heavy metals from synthetic effluent. For all metals investigated, it appears that most of the adsorption occurred within the first 10 min., subsequently decreasing until a plateau was reached after 30 min., (FIG. 4.60). These findings suggest rapid saturation of binding sites for metals and, subsequently, reduction in the sorption capacity of the bioreactor. Studies by Rivera (1983), using the Anflow treatment process, also displayed such rapid sorption rates, yet showed a decrease in soluble COD removal due to heavy metal sorption by the biosolids. Toxic inhibitory conditions of high metal concentrations under anaerobic conditions diminish generation of binding sites and reduce the sorption capacity of the bioreactor. The above does not apply to waste digested sludge under aerobic conditions. The present trials presented the following affinity series viz., $Cr^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Cr^{6+} > Ni^{2+}$. The magnitude of difference in the adsorptive capacities of Cr^{3+} and Ni^{2+} by the adsorbent was noticeable (FIG. 4.60). Trends portrayed by the latter affinity series varied from previous fully mixed findings and other researchers. Mehrotra *et al.*, (1987), under anaerobic conditions showed Zn^{2+} being bound more strongly than Cr^{3+} since Zn^{2+} has a much stronger binding intensity than the latter. McFarlane (1995), using immobilised fungal biomass under similar experimental conditions, showed a different affinity series viz., $Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Cr^{6+} > Cr^{3+}$. The variation in the present findings could

be due to the following. Firstly, being in a packed-bed configuration, there could be a great degree of inconsistency in contact between resident metal ions and sludge surfaces. Secondly, since sludge acts as a cation exchange material and the nature of the surface is of considerable significance in determining the capacity and intensity of binding, addition of polysulfone could alter the surface chemistry of the sludge, thus affecting biosorption.

As observed with previous fully mixed experiments, desorption occurred within 10 min., using the desorbent of choice ie., $0.2N$ H_2SO_4. It appears that most of the metals that had been adsorbed were subsequently desorbed. Cr^{3+} was found to be desorbed most efficiently (FIG. 4.61). This could be attributed to the large amount of Cr^{3+} adsorbed. Similarly, poor Ni^{2+} desorption could be attributed to poor adsorption. The present findings substantiated previous research by McFarlane (1995) who also reported a definite relationship between adsorption and desorption. Thus far, a general conclusion could be drawn and that is that desorption is more agent than metal dependent. Although the latter process is different from fully mixed, the actual mechanisms of desorption are the same and have been discussed previously.

5.8 COMPARISON OF FULLY MIXED AND PACKED-BED PROCESSES FOR METAL ION REMOVAL FROM SYNTHETIC EFFLUENT

Although the adsorbent and desorbent used for both fully mixed and packed-bed processes were the same, variations in process design projected noticeable differences in biosorptive and desorptive efficiencies. Overall tendencies have shown the fully mixed configuration producing far superior biosorption and desorption efficiencies than the packed-bed process

(FIGS 4.45 - 4.61). These findings could be attributed to better contact between metal ions and binding sites on sludge surfaces ie., a greater sludge surface area to metal ion ratio due to agitation, as opposed to packed-bed where metal ions in solution which are being transported through the column are exposed to a reduced sludge surface area. Further comparison would involve a detailed understanding of the kinetics of both processes.

Another noticeable difference between both procedures was the opposing affinity series of the sludge for metal ions. Fully mixed presented the following affinity series in order of preference viz., $Zn^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+} > Cr^{6+}$ as opposed to packed-bed viz., $Cr^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Cr^{6+} > Ni^{2+}$. It should be remembered that biosorption is ultimately dependent on sludge surface chemistry and the physico-chemical factor involved in sludge metal interaction (Kasan, 1993). The addition of polysulfone as an immobilising agent could have altered the surface chemistry of the sludge in the packed-bed process thus influencing the order of preference of the sludge for metal species. In addition, differences in process design would have an effect on physico-chemical factors and ultimately impact on the relative position of metal in the affinity series. Rudd *et al.*, (1984) confirmed that the affinity series of sludges for metals was dictated by physico-chemical factors such as pH, temperature, metal valency and particle size. Variation in desorption efficiencies between both processes could be attributed more to the differences in adsorptive capacities than process design.

Immobilisation of biomass using polysulfone for the packed-bed process could be partially responsible for the comparatively depleted biosorptive capacity when compared to non-immobilised fully mixed configurations. As explained earlier, addition of an agent could

have had a pronounced effect on the surface chemistry of the sludge thus reducing biosorption and altering the affinity series.

Although the fully mixed configuration presented superior metal biosorption, there was a problem with the release of settleable, suspended and dissolved solids into the treated effluent due to the method of agitation and subsequent shearing of biomass in the bioreactor. This release of solids consequently increases the permanganate value (PV_4) of the final effluent and renders it unacceptable for discharge according to stringent municipal regulations. On the contrary, the packed-bed process facilitated no shearing of biomass, therefore releasing no solids, subsequently resulting in a less turbid and improved quality of effluent.

Both processes have proven their capacity for industrial application. The problem of solids, with regards to the fully mixed process, could be alleviated with the use of flocculants but will have economic implications. The limiting aspect of the packed-bed process was its comparatively poor biosorption, although there were minimal solids problems encountered. Further research would warrant an investigation into the feasibility of both processes for large scale industrial application. It was anticipated that the information generated from such a study would be required for future large scale process design, operation and control.

CHAPTER 6

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 SUMMARY AND CONCLUSIONS

All waste digested sludges investigated during the present research showed potential to biosorb metal ions from solution although the differences in biosorptive capacities were not of large magnitude. The biosorption capacity of sludges exposed to single solutions of metals was much greater than mixed metal effluents due to lack of metal complexation and interspecies competition for cellular surface binding sites. In addition, there was a general trend of increase in biosorption of metals by sludges with increases in metal concentrations in solution. The overall comparative adsorptive capacities of the sludges for metal ions in single solutions was S3 > S2 > S4 > S5 > S1. Sludge biosorption ranking was determined by computing metal ion binding strength (k_a) and metal binding capacities of the respective sludges (X_m). Maximum binding capacities of sludges to metal ions, however, did not correlate with maximum bond strengths. The magnitude of difference in surface charge of the sludges was significant. Findings showed S3 to be the most electronegative sludge followed, as expected, by the same descending order as mentioned above. The general affinity series of the sludges for metals follow the descending order of $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cr^{6+} > Cr^{3+}$. Mechanisms of metal uptake were determined by applying the Langmuir adsorption model. It should be noted that only seven of the thirty isotherms conformed to the model. Present results substantiated previous findings and reaffirmed the premise of a definite relationship between sludge surface charge and respective biosorptive

capacities. These findings were of significance since they proved that biosorptive capacity, sludge ranking according to bond strength (k_a) and surface charge, were definitely related due to their identical order of ranking. Therefore, further investigations were restricted to using the three superior biosorbents, viz., S3, S2 and S4.

Further experimentation involved upscaling of the biosorption process and the development of a laboratory scale model in a fully mixed configuration. The results showed comparatively lower biosorptive capacity by the sludges concerned which could be attributed to metal complexation due to mixed metal synthetic effluents being used as opposed to pure metal solutions. The affinity series determined for the latter was in the descending order of $Zn^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+} > Cr^{6+}$. It was concluded that metal adsorption is more dependent on metal ion species rather than the biosorbent. Sludges also displayed metal biosorptive capacities when exposed to industrial effluent, containing Zn^{2+} concentrations as high as 119.4 $mg.\ell^{-1}$. It was noted that the higher the concentration of metal in the effluent, the better the biosorption eg., 4.5 $mg.g^{-1}$ Zn^{2+} biosorbed by S3. Sludge S3 displayed overall superior biosorption therefore further investigation was restricted to its use alone.

Sulphuric acid, at 0.2*N*, was selected as superior desorbent when compared to HCl and CH_3COOH. Desorption occurred most efficiently within a 10 min., contact period between the adsorbent and desorbent. Results showed that desorption was desorbent dependent rather than sludge dependent. Findings thus far provided the foundation for the development of a biotechnological process to bioremediate metal contaminated effluents. In order to provide a thrust towards potential industrial application, the isolated biosorption and desorption

processes were subsequently combined in a simultaneous process.

Although the desired objective was to obtain a continuous process, this was not possible due to the mineral acid desorbent hydrolysing the surface of the sludge, thereby preventing its reuse. However, a simultaneous process was developed whereby new biomass was introduced to the reactor vessel during adsorption cycles. More significantly, biosorption and desorption occurred concurrently thus reducing the time for treatment. The major disadvantage of the latter fully mixed configuration was the release of solids, by the biomass, into the effluent during adsorption, surpassing regulatory standards as determined by municipal authorities for the discharge of trade effluents. Subsequently, use of a packed-bed process was investigated to alleviate the problem. Although the packed-bed process produced a much clearer effluent with less solids in suspension, biosorptive and desorptive potentials were reduced when compared to the fully mixed process. This was attributed to the immobilisation of the biomass, ultimately affecting interactions between dissolved metal ions and the sludge surface. The affinity series determined for the latter process was $Cr^{3+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Cr^{6+} > Ni^{2+}$.

Findings of the present research have confirmed the potential of waste digested sludge as a suitable biosorbent and have also contributed to the successful development of a novel laboratory scale biotechnological process for the bioremediation of metal contaminated industrial effluents.

6.2 RECOMMENDATIONS

1. Present findings have confirmed the efficacy of using sludge surface charge, as determined by the pH/millivolt method, as an excellent indication of potential biosorbents. This method can therefore be used for rapid assessment of potential biosorbents during future studies.

2. Upscale to industrial application is envisaged by way of a fully mixed simultaneous process. Although biosorptive activity of the sludge is limited, the biomass is, in essence, a waste product and therefore freely available.

3. The packed-bed process presented poor biosorptive potential. Problems encountered with elevated suspended solids concentrations during fully mixed operations can probably be alleviated through the use of flocculants.

4. Fully mixed simultaneous processes, with the use of flocculants, have shown phenomenal potential for the bioremediation of metal contaminated effluents at laboratory scale.

5. Further investigations would warrant comparison of the latter process, regarding both efficiency and economics, with technologies currently treating metal plating effluents. This would entail a thorough economic feasibility study of the industrial application of the proposed process.

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APPENDICES

APPENDIX A

PREPARATION OF REAGENTS

Stock solutions of 1 000 mg.ℓ^{-1} of the six metal salts, $K_2Cr_2O_7$ (BDH, England); $CrK(SO_4)_2.12H_2O$ (BDH, England); $Cu(NO_3)_2.3H_2O$ (BDH, England); $ZnSO_4.7H_2O$ (BDH, England); $NiCl_2.6H_2O$ (BDH, England) and $Cd(NO_3)_2.4H_2O$ (BDH, England), of analar grade, were prepared in one litre A-grade volumetric flasks. Five concentrations of standards viz., 30, 60, 90, 120 and 150 mg.ℓ^{-1} were prepared in 100 mℓ A-grade volumetric flasks using A-grade pipettes.

Methodology

1) Stock solutions are adjusted to room temperature before use.

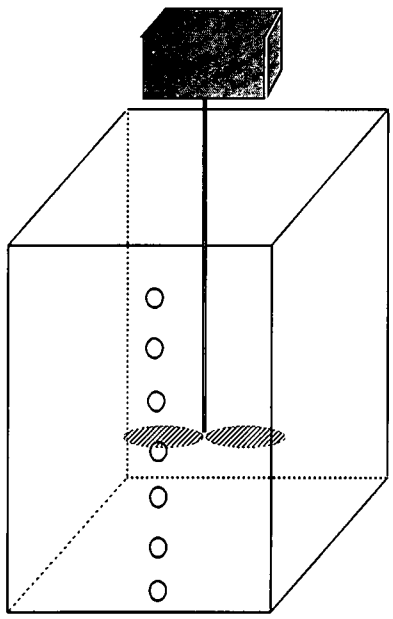
2)

Concentration required (ppm)	Volume stock solution added (mℓ)	Volume deionised water added (mℓ)
30	3.75	96.25
60	7.5	92.5
90	11.25	88.75
120	15.0	85.0
150	18.75	81.25

APPENDIX B

CONSTRUCTION OF BIOREACTOR

Perspex was used for construction of bioreactors.



Specifications (internal diameters)

Length	- 916.00 mm
Width	- 300.00 mm
Internal diameter	- 10.00 mm
Width of perspex	- 4.00 mm
Number of ports	- 7

APPENDIX B (cont.)

AGITATION

Lightnin motor (0.18kW) model HP 18, consisting of a 10mm diameter shaft and axial flow impeller. The above was supplied by Aeromix (Pty) Ltd. Rate of agitation was controlled by a Varispeed-606 PC 3 single phase inverter which was supplied by Varispeed.

$$\text{Speed in revolution/min (rpm)} = \frac{60 \times \text{frequency}}{2}$$

APPENDIX C

PREPARATION OF STOCK SOLUTIONS

1 000 mg.ℓ^{-1} stock solutions using metal salts were prepared in one litre A-grade volumetric flasks.

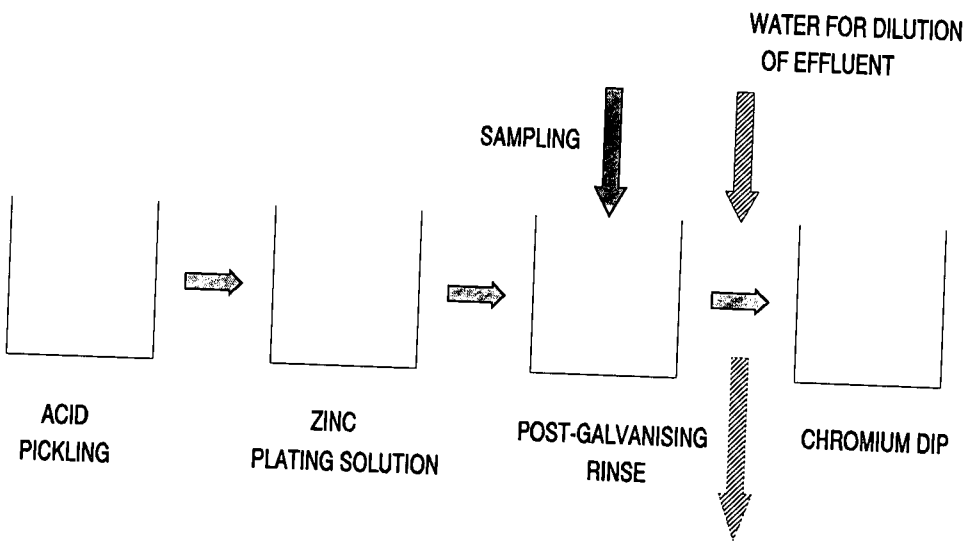
Metal species	Metal salt	Mass added (g.ℓ^{-1})
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	3.801992
Zn^{2+}	$ZnSO_4.7H_2O$	4.397614
Cr^{6+}	$Na_2CrO_7.2H_2O$	4.731168
Cr^{3+}	$CrK(SO_4)_2.12H_2O$	9.604654
Ni^{2+}	$NiCl_2.6H_2O$	4.049876
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	2.744245

Salts were massed by using a four decimal analytical balance and dissolved in deionised water. Similarly, for preparation of synthetic effluent, accurately measured metal salts, as discussed above, were dissolved in a required volume of deionised water to produce an effluent with a final metal ion concentration of 50 mg.ℓ^{-1} of each metal.

APPENDIX D

COLLECTION OF INDUSTRIAL EFFLUENT SAMPLE (SAAYMAN DANKS ELECTROPLATERS)

Samples of effluent were obtained on-line from the galvanising plant, since that section of the plant uses most of the water for dilution of effluent.



The reason for sampling at the post galvanising rinse was due to high concentrations of Zn^{2+}. If the biosorption process is successful, it would alleviate the need for wastage of water for dilution of the effluent.

APPENDIX E

DETERMINATION OF HEXAVALENT CHROMIUM (Adapted SABS 206 and Merck method)

Principle

In slightly acid solution, hexavalent chromium reacts with diphenylcarbazide to produce a reddish-violet colour, the intensity of which is measured spectro-photometrically.

Sensitivity

The limit is 0.01 mg.ℓ^{-1} when a 5 cm light path is used for photometric measurement at 540 nm.

Procedure (conducted in triplicate)

a) Preparation of Calibration Curve: Standard

Make a 1 : 10 dilution of the initial standard solutions of 10, 20, 30, 40 and 50 ug/mℓ resulting in 1, 2, 3, 4 and 5 ug.mℓ^{-1}.

1. Add 5 mℓ of each of the standards into 25 mℓ conical flasks.
2. Follow with addition of 1.666 mℓ of H_2SO_4.
3. Add 1.501 mℓ of deionised water.
4. Add 0.166 mℓ of diphenylcarbazide reagent.
5. Allow to stand for 5 min.

b) Preparation of test sample

1. Dilute test sample 1 : 10 ie., 0.5 mℓ of sample added to 4.5 mℓ deionised water.
2. Balance of the additions are the same as for the standard preparations.
3. If number of samples is large, add reagent prior to reading sets of samples, so samples do not stand for too long resulting in the colour fading.

APPENDIX E (cont.)

Read spectrophotometrically at 540 nm and use deionised water as a blank.

If necessary, oxidise trivalent chromium with ammonium peroxodisulphate. This is usually done when chromium is present in the trivalent form only.

Plot a curve of the absorbances against the masses (in *u*g) of chromium present in the respective standards. Subsequently, read concentrations of the test sample from the standard curve.

APPENDIX F

MOBILITY OF SLUDGE BETWEEN BIOREACTORS

Due to the coagulative nature of wet sludge, 20 mm internal diameter silicone tubing was used to prevent blocking. In addition, a high velocity "washing machine" pump (5 $\ell.min^{-1}$) had to be adapted to transport the sludge between bioreactors. The sludge had to be in suspension and agitated during transfer from adsorption bioreactor to desorption bioreactor.

APPENDIX G

IMMOBILISATION OF BIOMASS

Dried sludge was milled through a Retsch Cross Beater Mill (Model SK-1), equipped with a 2 mm sieve and receptacle. The milled sludge was subjected to further sieving through a 2 mm sieve. Particle size of sieved sludge retained in the sieve was 1 - 2 mm. Biomass used for immobilisation constituted ($<$ 1 mm) sludge particles from the sieve collection pan.

APPENDIX H

PREPARATION OF POLYSULFONE SOLUTION

Fifty grams of polysulfone resin (Acros) were added to 500 mℓ concentrated N,N-dimethylformamide (AR, Saarchem), in a one litre Schott bottle. The lid was closed to prevent evaporation. Dissolution of the resin was achieved by constant stirring on a magnetic stirrer (Agimatic, N), with slight heating and left overnight.

APPENDIX I

DESORPTION SAMPLING PROCEDURE

1. During sampling, agitation had to be discontinued for a minimum period (maximum 40 secs).
2. Twenty millilitre samples were dispensed in polypropylene vials using a Gilson micropipette P10 000.
3. Samples were stored at 4°C for further analysis.

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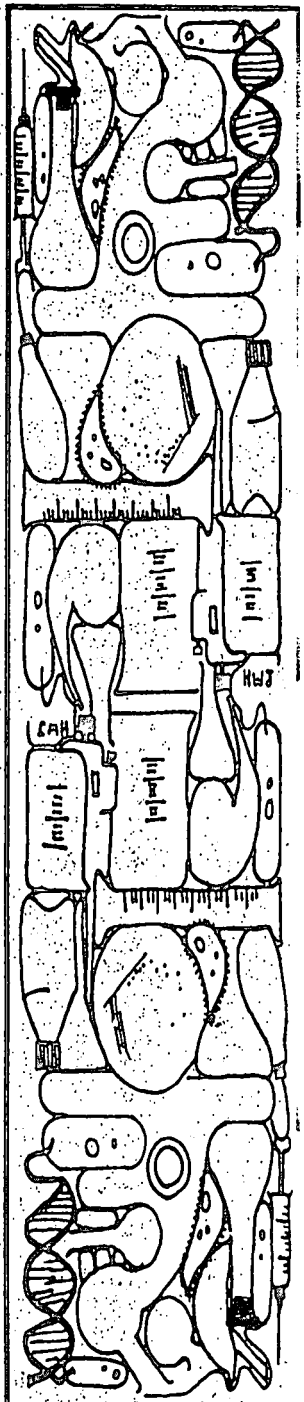

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An Investigation of the Efficacy of Waste Digested Sludges as Metal Biosorbents

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ABSTRACT

Metal contamination of wastewater from factories and metal related industries, loss of precious metals in mine wastewater and accumulation of heavy metal sludge in conventional wastewater treatment works are critical problems at present and will clearly continue to grow due to the unacceptable nature of present technical solutions to these problems. In keeping with the general theme of bioremediation of metal contaminated effluents, the objective of the present research was to investigate the biosorptive potential of waste digested sludges. Single metal solutions of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+} and Cr^{6+} were exposed to selected waste sludges at a concentration of 5 000mg.ℓ^{-1} for a period of three hours. All sludges investigated showed potential to remove metal ions from solution, although they varied in their biosorptive capacities. The general trend of biosorption of metal ions from pure solutions by the sludges was found to follow the descending order of $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cr^{6+} > Cr^{3+}$. It was also observed that certain sludges displayed preferential behaviour ie, displaying affinity for certain metal species. Sufficient biosorptive potential was shown by waste digested sludge to warrant further research focused on optimisation of a laboratory scale process for removal of metals from industrial effluents.

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Assessment of Waste Digested Sludge as a Biosorbent of Metal Ions from Solution.

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ABSTRACT

Waste digested sludge is waste activated sludge which has been subjected to anaerobic digestion and is stabilised. This sludge is a waste product. The objective of this investigation was to assess the potential of this waste material as a biosorbent of metal ions from solution. Three anaerobic sludges were selected from the surrounding wastewater works and individual bioreactor trials were performed on each sludge. These trials were conducted at room temperature, with agitation in 30 litre bioreactors containing synthetic metal solutions of Zn^{2+}; Cu^{2+}; Cd^{2+}; Ni^{2+}; Cr^{3+} and Cr^{6+} and milled sludge. Concentrations of metal ions in solution and dry biomass was 50 $mg.l^{-1}$ and 25000$mg.l^{-1}$ respectively. Of the three sludges examined, the biosorbent which displayed maximum adsorption of 2.0$mg.g^{-1}$ was selected for subsequent investigation. Another aspect of this study involved metal desorption from metal bound sludge, using a range of desorbents, and subsequent reuse of the biomass to establish a continuous biosorption/desorption process. Desorbents assessed were hydrochloric acid, sulphuric acid, acetic acid and sodium chloride. Sulphuric acid at a concentration of 0.2N proved to be the superior desorbent. However, a second adsorption cycle on the desorbed sludge indicated that the desorbent affected the metal binding property of the biosorbent. Therefore, reuse of biomass was not possible. A method was developed whereby biomass was mobilised and transported from one bioreactor to another in such a manner so as to facilitate the simultaneous operation of biosorption and desorption. Although both processes performed different tasks, the conditions of operation are similar. Agitation was optimised at 265rpm, the volume of desorbent was a third the volume of the effluent and a rinse of deionised water was used between bioreactors which also aided in mobilisation and transportation of the biomass. Rinse water was drained and reused for removal of biomass from the desorption tank. Samples were analysed by atomic absorption spectroscopy and a colorimetric method was employed to distinguish Cr^{3+} from Cr^{6+}. The results indicated that metal ions were biosorbed in order of preference viz., $Zn^{2+} > Cd^{2+} > Cu^{2+} > Cr^{3+} > Ni^{2+} > Cr^{6+}$. Results showed maximum adsorption of metal after 45 minutes. In some cases, after 45 minutes, metal biosorbed ($mg.g^{-1}$) remained constant, i.e. no further adsorption occurred due to saturation of metal binding sites, and in other instances there was a decrease in metal concentration indicating, possibly, that desorption was occurring. These results were reproducible and it was concluded that the selected waste digested sludges used, biosorbed cations according to the abovementioned affinity series. Sulphuric acid displayed maximum desorption of the zinc, cadmium and copper ions and reduced chromium and nickel by substantial amounts when compared to amounts biosorbed. This study proved to be economically and ecologically favourable. The continuous biosorption/desorption process is currently being optimised for application to the metal plating industries for bioremediation of the metal laden effluents.