Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents

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Abstract

Inorganic contaminants present in waste streams may be removed by one of three methods, viz. physical, chemical or biological. Chemical and physical techniques have traditionally been employed to remediate such streams. However, due to the crisis of rapidly deteriorating potable water quality, legislation governing the levels of contaminants is becoming progressively stricter. Therefore, alternative methods for treatment have been investigated. Biosorption technology, utilising any natural form of biomass to passively adsorb and immobilise solubilised heavy metals or radionuclides, offers such an alternative. However, the technology needs to effectively compete both on a cost and performance basis with existing methods before industry will accept and implement it. A pilot-plant feasibility study, using waste activated sludge to bioremediate a metal plating effluent, showed that the currently used method of chemical precipitation is more cost-effective. This paper describes the factors that must be considered when selecting bioremediation as a cleanup technology for inorganics.

Introduction

Due to their mobility in natural water ecosystems and their toxicity to higher life forms, heavy metal ions in surface- and groundwater supplies have been prioritised as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions cannot be mineralised. Apart from environmental issues, technological aspects of metal recovery from industrial waste waters must also be considered (Wyatt, 1988). Metal resources are non-renewable and natural reserves are becoming depleted. It is therefore imperative that those metals considered environmentally hazardous, or which are of technological importance, strategic significance or economic value, be removed/recovered at their source using appropriate treatment systems.

Effluent treatment processes are designed to ensure that when waste waters are discharged into natural water courses, any adverse effects are reduced or prevented. The extent of any such effect will be a function of the volume and composition of the influent waste water and the dilution capacity of the receiving water. It is for this reason that similarly operated processing facilities may be required to meet different effluent discharge standards according to their location (Saunders, 1987).

The impact of industry on water sources is immense and it is only through promotion of good pollution prevention practices that contamination and deterioration of these waters will decrease. It is therefore the responsibility of various water authorities to inform industry of the methods available to them and to encourage implementation of such practices to safeguard the water environment. In a recent survey conducted by Umgeni Water (KwaZulu-Natal, South Africa) it was found that regionally, industrial discharges are responsible for 56% of the contamination present in water sources (Fig. 1). However, tremendous effort has been made by this regulatory body to educate senior management within the companies concerned about their legal, social and environmental obligations and ways to improve operational practices (Umgeni Water, 1997).

Before selecting a waste-water treatment system, a considerable amount of laboratory and engineering work must be com-

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**Figure 1**

completed prior to system design or purchase. Preliminary work should include determination of present and future hydraulic flows and contaminant loads and evaluation of water reuse/conservation to maximise system size. Resource recovery and waste minimisation concepts should also be evaluated to reduce consumption and generation of process chemicals and hazardous wastes, respectively. Treatability studies should be conducted to confirm that the process will satisfy effluent standards, the type of chemical or sorbent/membrane envisaged is applicable to the specific waste stream, and to calculate sludge generation rates (Philipp, 1994).

Discussion

Chemical and physical treatment processes

Conventional chemical (precipitation/neutralisation) or physical (ion exchange, activated carbon sorption and membrane technology) treatment techniques are inherently problematic in their application to metal-bearing waste streams. Chemical treatment methods can prove costly to the user as the active agent cannot be recovered for reuse in successive treatment cycles. Also, the end-product is usually a low-volume, highly concentrated metal-bearing sludge that is difficult to dewater and dispose of. After treatment, total dissolved solids (TDS) values of the waste-water may still be unacceptably high due to the poor compaction properties of the sludge cake. Addition of natural or synthetic polyelectrolyte/flocculant may be required to assist with precipitation. Introduction of chemicals increases the conductivity/salinity of water through the production of soluble sulphates and chlorides. This is of particular concern in countries such as South Africa where these waters are reused a number of times. Chemical dosing is a direct function of soluble metal concentrations and must be closely monitored to correlate with diurnal loading patterns. Industrial activities such as metal-finishing operations can produce tremendously variable effluent metal loads, dependent upon the work load. Metal cyanide complexes, common in metal plating streams, cannot be treated using conventional precipitation and clarification techniques (Kuyucak, 1997). Cyanide must therefore be destroyed prior to precipitation, usually based on oxidation of the cyanide ion either partially to cyanate ion or completely to carbon dioxide and nitrogen (Green and Smith, 1972).

Application of membrane technology to metal-bearing waste streams has several major drawbacks. Apart from the expense, membranes are also unable to resist certain types of chemicals and pH values, and are prone to deterioration in the presence of micro-organisms. Compaction, scaling, short operation life and applicability only to feed streams with low concentrations of metal ions are some other problems which can be encountered with membrane installation (Kuyucak, 1997). Energy consumption increases as solution concentrations increase. Skilled labour is required for their successful operation and certain quantities of ions can always be detected in the permeate (Kuyucak, 1997).

Ion-exchange resins have recently found a niche in the market of water and waste-water treatment. However, apart from their cost which can be prohibitive especially to smaller processing plants, resins are vulnerable to oxidation by chemicals, are affected by the presence of magnesium or calcium ions in solution, and are prone to fouling by precipitates and organics (Kuyucak, 1997).

Biosorption of inorganic contaminants

Biological methods of metal recovery, termed biosorption, have been suggested as cheaper, more effective alternatives to existing treatment techniques. Biosorption entails the use of either living or dead micro-organisms and/or their derivatives which complex metal ions using ligands or functional groups situated on the outer surface of the cell (Bolton and Gorby, 1995). This phenomenon has been directly compared with chemical ion-exchange processes (Chang and Hong, 1994). The process requires neither an active membrane transport mechanism nor metabolic energy in order to function and is controlled in a non-directed physico-chemical reaction (Gadd, 1988; 1992). Microbial biomass types investigated for their biosorptive potential include bacteria, yeasts, filamentous fungi and marine and freshwater algal flora (Norris and Kelly, 1979; Strandberg et al., 1981; Tobin et al., 1984; Kasan and Stegmann, 1987; Kasan, 1993; Aldor et al., 1995; Leusch et al., 1995; Kuyucak and Volesky, 1997). Heterogenous microbial population studies using activated sludge have also been reported (Oliver and Cosgrove, 1974; Forster, 1983; Lawson et al., 1984; Gourdon et al., 1990; Forster, 1983; Aldor et al., 1995; Leusch et al., 1995; Kuyucak and Volesky, 1997). Heterogenous microbial population studies using activated sludge have also been reported (Oliver and Cosgrove, 1974; Forster, 1983; Lawson et al., 1984; Gourdon et al., 1990; Kasan, 1993; Bux et al., 1994; Bux and Kasan, 1996; Atkinson et al., 1996). Certain biomass types are evident more suitable than others to a specific application. The affinity that a biosorbtent material exhibits for a specific metal cation will dictate the practicality of its implementation for remediation of a particular waste stream.

Figure 2

Guiding questions to be considered concerning the feasibility of a potential biosorbent for metal/s removal from contaminated effluent
Once laboratory trials are complete and a potential biosorbent has shown the ability to adsorb and sequester the required metal ions from solution, several questions need to be resolved in order to assist the decision concerning its pilot-scale or industrial application. Examples of such questions are illustrated in Fig. 2.

There are basically two categories of industrial waste liquors that will require treatment prior to discharge: large volumes bearing low concentrations of metal contaminants (<100 mg·L⁻¹), i.e. mining waste water, and conversely, small volumes characterised by high TDS values, i.e. metal plating liquors. In the first instance, one would expect to employ a biosorbent exhibiting high affinity for the metal/s concerned (Volesky, 1987). In the latter case, the active material should possess high biosorptive capacity values to ensure saturation of biomass binding sites does not occur prior to cessation of the treatment process (Volesky, 1987). Biomass saturation will result in “auto-desorption” where target metals are displaced by insignificant ions or those with higher binding constants thereby producing effluent waste water containing higher metal concentrations than the influent (Brierley et al., 1993). In both instances, interference by counter-ions such as magnesium and calcium should not occur (Crist et al., 1990). Ammonium and sodium ions are also cations which electrostatically interact with biomass and can displace bound metal if present in sufficient concentrations (Aldor et al., 1995). Biosorbent specificity should therefore be high.

**Capital expenditure**

Based on fully-mixed, suspended biosorbent systems, initial capital expenditure for process development and setup can be estimated to be equivalent to that of chemical precipitation methods. Both systems require the same basic equipment such as a contact vessel (perspex or stainless steel), a method of agitation (mechanical stirrers with attached impellers), piping and other peripheral equipment such as pH probes and level controllers. During a recent pilot-plant feasibility study, investigating the installation of a metal-plating effluent treatment facility capable of treating 3 000 t effluent/batch (Bux et al., 1997), costs for acquisition of the above-mentioned equipment and construction was R193 000 (cost includes all modifications to existing installations, i.e. sump, piping, etc.) (Hollingsworth, 1996). Note that this final cost was for a manually operated system with no automated parts whatsoever.

Reactor tanks are usually designed to function as secondary settlers/clarifiers (in batch process designs) to assist with sludge separation and disposal. Cone bottom tanks with agitation are therefore recommended. A bi-functional reactor will also reduce space requirements considerably. Most industrial clarifiers are of the inclined-plate or tube design (Philipp, 1994). Compared to circular clarifiers, inclined-plate clarifiers are less costly to install, require less floor space and maintenance and are generally more efficient (Philipp, 1994).

Generally, the more intricate a process becomes the greater the capital requirement. Design and type of process to be employed (batch/continuous) is dictated entirely by choice of biomass and its method of immobilisation (if immobilisation is required). Automation of the treatment facility will also increase costs considerably. Complexity will result in the requirement of a more skilled labour force for process operation. Therefore, in order to keep initial costs to a minimum, engineers and biotechnologists should aim for simplicity of design and operation.

**Process design**

Many different types of process configurations such as fixed bed upflow and downflow reactors, fluidised beds, rotating biological contactors, trickle filters and air-lift (either free or immobilised) reactors have been proposed and investigated for their practicality (Hutchins et al., 1986; Townsley et al., 1986; Gadd, 1988; Huang et al., 1990; Bux et al., 1997). Downflow column reactors should theoretically be the most cost-effective systems to operate due to their total dependance upon gravitational forces to transfer the water body through the bed. All other systems require either pumps or motors with associated power consumption to effectively contact the waste water with the biosorbent. However, in downflow processes the operator has little control over effluent retention times within the reactor (retention time is governed by inter-particle spaces, bed volume/depth and biosorbent density). The waste stream may then be required to pass through numerous treatment cycles or reactors (in series) before desired metal concentrations are obtained. Another disadvantage of this system is the potential for compaction of the bed with consequential backflow of the waste stream due primarily to increased retention times. To alleviate this drop in pressure, the biosorbent should be loosely packed and immobilised in such a way that particles maintain their structural integrity for the duration of the reaction.

The decision whether to use batch or continuous treatment is a function of hydraulic flow, types of contaminants present and space availability (Philipp, 1994). Usually, if flow rates are less than 20 000 l/shift, manual batch treatment is more economical (Philipp, 1994). Manual batch systems are simpler to operate as automated systems are prone to problems such as operator inattention to care and calibration of control instruments. If a manufacturing plant owner wishes to eventually expand his operation, installation of a continuous system from the outset may be the most cost-effective long-term answer.

**Biosorptive capacity**

When determining the feasibility for application of a particular biosorbent, maximum capacity of the agent to sequester metals to its surface will contribute considerably to the total cost of the process. This measured value has a direct influence on the mass (volume) of biomass required per treatment cycle which in turn dictates the quantity of sludge generated for disposal as well as the cost and type of transport required. Even if a biosorbent can be acquired free of charge, e.g. waste sludges, the volume required to be transported may render costs of the process prohibitively expensive. As with any industrial process, the nearer the source of raw material (biomass) to the point of application, the more feasible the process becomes. In order for biosorption to become competitive with existing technologies, loading capacity of the material should be in excess of 150 mg·g⁻¹ (Gadd, 1988) although literature indicates that these types of loading rates by the various biomass types investigated are rare.

A basic summary of the costs incurred for the application of activated sludge to metal biosorption operations is provided in Fig. 3. Costs were calculated during the economic study mentioned previously (Bux et al., 1997). Depicted values represent percentage contribution to the total daily treatment cost of R918 (excluding energy consumption and capital expenditure). Transport costs include hire of a 5 t truck (excluding fuel) required to travel a daily round-trip distance of 70 km. Labour includes the wage of one semi-skilled plant operator. Inorganic flocculant,
required to reduce TSS concentrations in the effluent once treatment cycles are complete, is of nominal consequence to the overall cost. Sludge generation and disposal must be minimised before pilot or industrial plant development is undertaken due to the significant contribution they make to the final cost of the process. Waste sludges can, however, be either dried or dewatered in order to reduce the volumes produced. A number of dewatering devices, including various filter presses (recessed plate, rotary vacuum, plate and frame), filters (belt, tube paper, cartridge, bag and diatomaceous earth) and centrifuges, are available to the user once the sludge filtration characteristics and percentage of dry solids in the cake are known (Philipp, 1994). In many instances, it is more cost effective to further dewater or dry the filter cake. Most commercially available drying equipment will reduce the weight and volume of the filter cake by 60 to 80% (Philipp, 1994). The two types of dryers presently available are the continuous direct fired design (incenerator) and the indirect fired batch design (Philipp, 1994).

Biomass immobilisation

Costs of biosorbent preparation must also be considered. To date, the majority of research conducted has concentrated on the use of granulised biosorbents packed in columns thereby resembling ion-exchange resins. Although cell entrapment imparts mechanical strength and resistance to chemical and microbial degradation upon the biomass, costs of immobilising agent cannot be ignored. Free cells are not suitable for use in a column in that due to their low density and size they tend to plug the bed resulting in large drops in pressure (Pons and Fusté, 1993). Support matrices suitable for biomass immobilisation include alginate, polyacrylamide, polysulfone, silica gel, cellulose and gluteraldehyde (Gadd and White, 1993). Current prices for such agents are shown in Table 1 (Sigma Chemical Company, 1996).

Lu and Wilkins (1995), upon assessing the biosorptive capacity of waste yeast biomass entrapped in alginate gel, found that the gel itself could sequester metal species (9.01 mg g⁻¹ for Cu²⁺, 7.50 mg g⁻¹ for Cd²⁺ and 7.08 mg g⁻¹ for Zn²⁺). These capacities were greater than native and immobilised yeast samples. They attributed the decrease in yeast-binding capacity to cross-linking of potential metal-binding sites on the cell surface and their subsequent masking by the gel. Cross-linking will have a similar effect on the gel.

Biomass is usually mixed with immobilising agents at densities of 4 to 6% biomass to 1% carrier (w/w) (Lu and Wilkins, 1995) thereby reducing the amount of agent required. Care must be exercised not to exceed these ratios as it could result in poor quality beads with biomass “leaching” into the surrounding solution.

Cost of biosorbent

Sources and type of biomass play a major role in determining the overall cost of the biosorbent material. If the biomass needs to be specifically cultured for this purpose, manufacturers will incorporate maintenance and production expenses in the total cost, as well as a commercial fee. These costs can be minimal where certain biomass types such as photo-autotrophic algae (e.g. Chlorella and Oscillatoria spp.) can be successfully grown for large-scale commercial use due to their minimal growth requirements (water, sunlight and CO₂) (Vonshak, 1992). Marine algae such as Sargassum fluitans (Aldor et al., 1995) and Ascophyllum nodosum (Kuyucak and Volesky, 1988a), have shown biosorptive potential although the costs of harvesting the biomass may prove inhibitory to its application. Many industrial waste-biomass types have been investigated for their biosorptive potential. These include the yeasts, Saccharomyces cerevisiae from the food and beverage industry (Kuyucak and Volesky, 1988b) and Candida albicans, a clinical isolate (Gelmi et al., 1994); the moulds, Rhizopus arrhizus from the food industry (Tobin et al., 1984), Penicillium chrysogenum from antibiotic manufacturers (Pighi et al., 1989) and Aspergillus niger from citric acid and industrial enzyme producers (Kurek et al., 1982); the bacteria, Bacillus spp., utilised in amino acid and antibiotic fermentations (Brierley JA, 1990) and Streptomyces noursei from the pharmaceutical industry (Mattuschka and Straube, 1993). Waste activated (Bux et al., 1997) and anaerobically digested sludges (Bux, 1997), originating from waste-water treatment operations, have also been investigated. These potential biosorbents can usually be obtained relatively free of charge from the respective producers since they already present disposal problems to them. The only costs incurred should be those of drying, if required, and transport.

### Table 1

| PRICES FOR COMMERCIIALLY AVAILABLE IMMOBILISING AGENTS (RANDS @ R4.50/$) |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Alginate (per kg)               | 409.00         | 5 472.00       | 2 600.00       | 256.00 - 675.00 | 58.00          | 162.90         |
| Polyacrylamide (per kg)         | 5 472.00       | 2 600.00       | 256.00 - 675.00 | 58.00          | 162.90         |
| Polysulfone (per kg)            | 2 600.00       | 256.00 - 675.00 | 58.00          | 162.90         |
| Silica gel (per kg)             | 256.00 - 675.00 | 58.00          | 162.90         |
| Cellulose (per kg)              | 58.00          | 162.90         |
| Gluteraldehyde (per litre)      | 162.90         |                |                |                |

Figure 3

Percentage contribution to the final cost of a bioremediation process utilising waste activated sludge as biosorbent determined during feasibility studies (Bux et al., 1997)
Upflow anaerobic sludge blanket (UASB) pellets can also be integrated into a biosorption process. The pellets are already of uniform particle size and in a natural immobilised state, therefore not requiring any further preparation. They are suitable for application in continuous column reactor configurations. However, the low biosorption capacity (1.9 mg·g⁻¹ for zinc and cadmium) may limit its application (Bux et al., 1996).

Commercialised biosorbents

Two commercial biosorbents presently available include AlgaSORB™ (Chlorella vulgaris) and AMT-BIOCLAIM™ (Bacillus biomass) (Kuyucak, 1997). Both biosorbents can efficiently remove metallic ions from dilute solutions (10 to 100 mg·l⁻¹) and reduce their concentrations to below 1 mg·l⁻¹ (Hutchins et al., 1986; Kuyucak, 1997). AMT-BIOCLAIM™ is capable of accumulating gold, cadmium and zinc from cyanide solutions and is therefore suitable to metal-finishing operations. Both systems are also capable of metal ion selectivity, even in the presence of “hard water” components such as magnesium and calcium. AlgaSORB™ has been shown in laboratory experiments to reduce levels of cadmium and mercury to concentrations below those specified for drinking-water standards.

Two other commercialised biosorbents include “MetaGene”® and “RAHCO Bio-Beads” which have shown to be effective at removing heavy metal ions when applied to both electroplating and mining waste streams. Both these products have undergone extensive laboratory and field trials although information regarding their industrial application is limited.

Biomass regeneration and reusability

Regeneration and reusability of the biosorbent material must also be considered when assessing the efficiency and feasibility of a treatment process. If the active agent can be regenerated through a desorption cycle without destroying the integrity of the cell wall and hence, surface metal binding sites or ligands, the process will become more lucrative. Note, however, that cell immobilisation and entrainment will offer some resistance to desorption techniques such as dissolution in strong acids and/or bases.

The purpose of desorption is to re-solubilise biomass-bound metals in greatly reduced, more manageable volumes; and to recover metals if and when of economic significance. Stripping of biomass can be achieved with a relatively inexpensive acid such as H₂SO₄ which can be purchased at R0.70 per ℓ for a 1 M solution. Sulphuric acid is known to effectively desorb metals and industry is very familiar with its use (Tsezos, 1984; Bux et al., 1995). If biomass can be obtained free of charge and preparation and transport costs are minimal, metals can be stripped using destructive techniques such as incineration or exposure to strong acids/bases (Gadd, 1988). Destructive techniques will increase sludge disposal costs.

Biosorption kinetics

In comparison to conventional processes biosorption reaction kinetics are fairly rapid, usually in the order of seconds or minutes. Research has shown that the majority of metal ions are removed within the first 15 min of the reaction. Gourdon et al., (1990) showed that 95% of total cadmium was biosorbed by activated sludge within a 5 min contact time. According to Mattuschka and Straube (1993), high, rapid sorption rates are typical for adsorption of dissolved substances on a solid material. Observed adsorption patterns are usually biphasic and appear similar, i.e. an initial rapid metabolism-independent stage followed by a slower second stage with equilibrium usually been attained in a few minutes (Mowll and Gadd, 1983; Tsezos, 1985; Kasan and Baecker, 1989; Tsezos and Wang, 1991). The effect of initial metal ion concentration affects reaction kinetics significantly. High initial concentrations establish stronger driving forces for mass transfer (Atkinson et al., 1996) and result in faster kinetics than do lower metal concentrations (Tsezos and Deutschmann, 1990). From a power and time consumption point of view, rapid kinetics will obviously prove favourable to the daily running costs of the treatment plant.

Biomass surface charge

Since the principal driving force for metal ion biosorption is the net negative surface charge of the biomass (Bux and Kasan, 1994), it follows that the higher the biomass electronegativity the greater the attraction and adsorption of heavy metal cations. Bux and Kasan (1994) showed a definite relationship between the electronegativity of activated sludge surfaces and their metal biosorptive capacities. They found that sludge with the highest negative charge demonstrated superior biosorption. The polymeric structure of biomass surfaces, consisting primarily of proteins, carbohydrates, nucleic acids and lipids, imparts a negative charge due to the ionisation of organic groups such as carboxylic, aliphatic, aromatic and amino groups and inorganic groups such as hydroxyl and sulphate groups (Hughes and Poole, 1989). Measurement of the biosorbent net charge should therefore provide a rapid indication of the potential of a specific biomass type for application in a treatment process. Isothermal studies should, however, be conducted in conjunction with charge evaluations to elucidate the actual capacity of the biosorbent to remove solubilised metals.

Regarding biosorptive potential, it is interesting to note that Pümpel et al. (1995) devised a rapid agar screening method investigating the biosorptive characteristics of microbial isolates. Although the technique is not quantitatively conclusive, metal precipitation results can be observed and read within 15 to 20 min.

Conclusions

It is evident that environmental biotechnology is a diverse discipline requiring the integration into one field of several loosely related scientific fields. These fields include microbiology, biochemistry, molecular ecology, environmental science, chemical and environmental engineering, physical chemistry and analytical chemistry (Goldstein et al., 1991). Successful bioremedial technologies will therefore only transpire through collaboration and technology transfer with/from experts in the respective fields.

Because government legislation regarding effluent contamination levels is changing regularly, adoption of a flexible, long-term treatment strategy is essential for industrialists. They should treat waste management as a business issue and make decisions based on fundamental principles, economics and liability considerations, not based on specific current requirements (Steward and Ritzert, 1994).

The development of microbe-based metal ion recovery systems will ultimately depend on many factors such as capacities, efficiencies and metal selectivity of the biosorbent, ease of recovery and regenerative properties of the biomass, economic...
and performance equivalence to existing chemical and physical processes, and immunity from interference by other effluent components or operating conditions (Gadd, 1988). The most lucrative market opportunities for biosorbents presently appear to be in secondary or polishing treatment applications and metal removal operations from dilute waste streams (Brierley CL, 1990). However, through continued research and increasing environmental awareness by both the authorities and public alike, this situation is likely to change in the near future with biosorption technology becoming more beneficial and attractive than currently employed technologies.

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