Removal of Heavy Metals from Industrial and Municipal Waste Waters Using an Algal Turf Scrubber

by

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ABSTRACT

The control and remediation of industrial effluents containing heavy metals is a current environmental challenge. Due to the susceptibility of most biological organisms to metal toxicity, existing remediation technologies rely on chemical methods of high cost, yet uncertain environmental soundness.

Algal turf scrubbing (ATS) is a novel, non-chemical remediation method capable of lowering the concentration of a broad spectrum of heavy metals, including Cd, Ni, Cr, Zn and Mo, in polluted waters to undetectable levels. The ATS bioreactor is specifically designed for the culture of a benthic algal community. Metal removal is primarily accomplished by two mechanisms: a) adsorption of metal cations onto the negatively charged surface of the algae, and b) precipitation of metals in elevated pH values resulting from algal photosynthesis. In low ambient metal concentrations algal turf bioconcentration factors can be as high as 10^6-10^8. Ashing or anaerobic digestion of the harvested algae can further concentrate metals. Complete reclamation of metals can be achieved through chemical separation. Low initial and operational costs, convenient management and uncomplicated maintenance contribute to the efficiency of the ATS ethod.

Principle of Operation

The Algal Turf Scrubber^{TM} (ATS) was originally developed by ADEY (1982), at the Smithsonian Institution to maintain the water quality of artificial ecosystems used in research and large aquaria as museum exhibits. Algal turf scrubbing is a new bioremediation method providing nutrient removal, oxygenation, disinfection and detoxification all in one process (SANTAS et al., 1993). The ATS bioreactor is specifically designed for the cultivation of a benthic algal community commonly known as algal turf. Establishment and maintenance of this naturally growing algal community is contingent upon utilization and/or removal, by various mechanisms, of substances traditionally regarded as pollutants. Although the method provides no direct treatment of organic pollutants, a variety of inorganic pollutants, such as heavy metals, nitrates, nitrites, ammonia and phosphates are effectively removed from water through direct uptake by the algal turf. This paper, however, addresses only detoxification, and more specifically the removal by algal turf of heavy metal ions from contaminated water.

The ability of algae to remove metals from water as well as the mechanisms involved are well documented in the literature and are reviewed by MAEDA and SAKAGUGHI (1991). Perhaps the most significant among these mechanisms is algal affinity for heavy metals, a result of metal ion adsorption on the highly negative surface of algal cells (OSWALD, 1988). However, long-term uptake experiments in growing algal cultures show a greater metal accumulation than predicted by adsorption alone, suggesting that some additional

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mechanisms of metal retention may be involved (KHUMMONGKOL et al., 1982). MAJIDI et al. (1990) report that the functional group responsible for metal uptake is most likely a carboxylic group. Members of six of the ten classes of Phycophyta (algae) exposed to cadmium, lead, zinc, silver, copper and mercury ions showed enhanced phytochelatin synthesis thereby removing these metals from solution (GEKELER et al., 1988). On the other hand, heavy metals, especially, lead, cadmium and zinc, can be incorporated in polyphosphate bodies, and subsequently immobilized intracellularly within vacuoles (SICKO-GOAD and LAZINSKY, 1981), or may be detoxified by extracellular products (CAPASSO and PINTO, 1983).

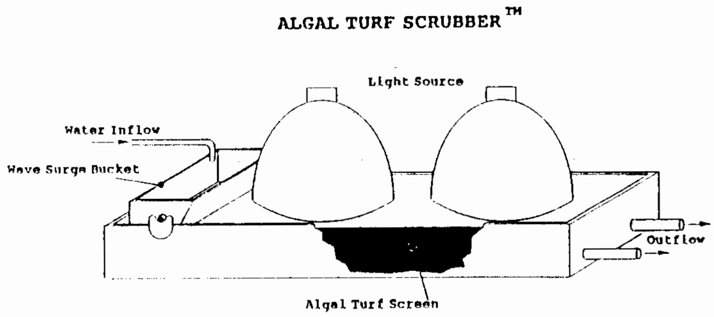
Bioaccumulation factors in *Galaxaura marginata* and *Caulerpa racemosa,* two species relatively abundant in algal turf, varied from 10^2 for Ni to 10^5 for Pb, while Cd uptake was two orders of magnitude greater (GUIMARES et al., 1982). Field examples of filamentous algae, mainly *Spirogyra, Zygogonium, Mougeotia* and *Microspora* species, contained metal concentrations several orders of magnitude greater than ambient levels (FOSTER, 1982). *Chlorella vulgaris* growing in an aqueous medium containing 100 mg Zn and 10 mg Cd/L accumulated 35 x 10^4 mg Zn and 1.8 x 10^4 mg Cd/kg dry weight (MAEDA et al., 1990).

While some species of algae, such as *Chlorella* exhibit higher affinity for certain metals (DARNALL; *pers. comm.*), polluted waters usually contain more than one kind of metal ions. Blue-green algae and diatoms are more tolerant to zinc, copper, lead, nickel, cobalt and manganese (REDDY and VENKATESWARLU, 1985). In the same study, it was shown that while *Stigeoclonium* sp. exhibited very good growth at high concentrations of zinc, copper and nickel and at low concentrations of cobalt and lead, *Schizomeris* sp. attained good growth when the concentrations of lead and cobalt were high and low, respectively. The findings of the above studies suggest that the kinds of metal ions may determine the structure of the existing algal community. However, FOSTER (1982) suggests that the degree of metal pollution rather than the polluting metal itself determines the algal species present.

Significant variation exists also in the capacity of various parts of the algal thallus to accumulate metals (BURDIN and POLYAKOVA, 1984a; 1984b). Accumulation is directly proportional to thallus age and size, with larger and older thalli accumulating higher concentrations of metals (YANKOVSKI et al. 1988).

Technical Description of the Treatment Technology

An ATS consists of a tray, a wave generator and a plastic substrate (usually fiberglass screen) lining the bottom of the tray (Figure 1). Natural or artificial illumination drives photosynthesis by algal turf. Algal turf is a multi-species association of algae dominated by attached filamentous forms ranging in size from a few millimeters to a maximum of 10-15 cm (ADEY and HACKNEY, 1988). A diagrammatic view of algal turf growing on fiberglass screen is given in Figure 2. Distinguishing features of algal turf are rapid growth and reproduction, and resistance to grazing through basal persistence instead of protective mechanisms such as toxicity or thallus strength. Surge motion generated by a tipping bucket at the upstream end of the ATS greatly enhances algal turf productivity (ADEY and HACKNEY, 1988; LEIGH et al., 1987). As water flows over the developing community, the algae remove pollutants and release oxygen into the water. Every 7-10 days, the fiberglass screens are removed from the trays, and the algae with the stored pollutants are harvested by scraping. The screens are then returned to the trays, and vegetative regeneration of algal turf begins immediately from basal cells left onto the substrate. Frequent harvesting maintains the community in its young, vigorous growth stage. Should harvesting be neglected for a prolonged period of time, pollutant release from senescent thalli will unavoidably occur.



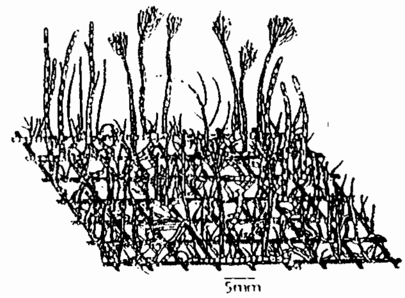


Figure 1.

Figure 2.

Preliminary Experimental Results

The interest for the present study was generated when some data from an experimental microcosm at the Smithsonian Institution indicated bioaccumulation of chromium, molybdenum and nickel by algal turf after high quality stainless steel plates were introduced into the 40,000-gallon exhibit.

Algal turf from the microcosm was harvested and analyzed for Cr, Ni and Mo every 7-12 days for a total of 200 days, while the concentration of the same metals was also monitored within the water column. The results are presented in Figures 3 and 4.

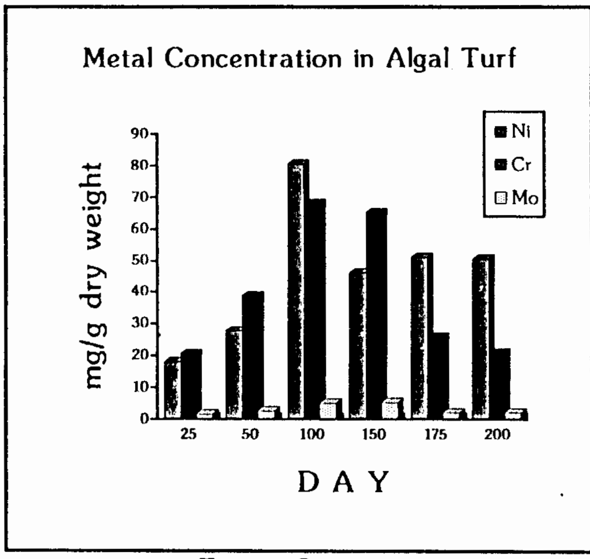


Figure 3.

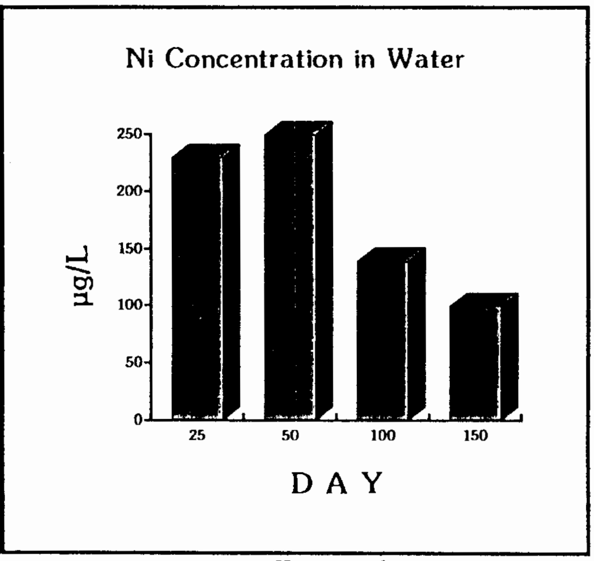


Figure 4.

During the first 100 days, metal concentration in algal tissue increases steadily (Figure 3) thereafter declining as the community becomes senescent. This decline may be attributed to death and decomposition of older thalli followed by metal release back into the water column.

Cr and Mo concentrations remained below the detection limit throughout the experiment and are not presented here. Nickel concentration in the water column declined from 230 µg/L at the beginning to less than 100 µg/L at the conclusion of the experiment (Figure 4). The slight increase in Ni concentration, between days 25 and 50, may be due to accelerated corrosion of the steel plates and/or a delayed metal removal by algal communities.

Metal removal performance of ATS was compared to Anaerobic Gravel Filter (AGF) under two conditions of light availability and the results are shown in Figures 5 and 6.

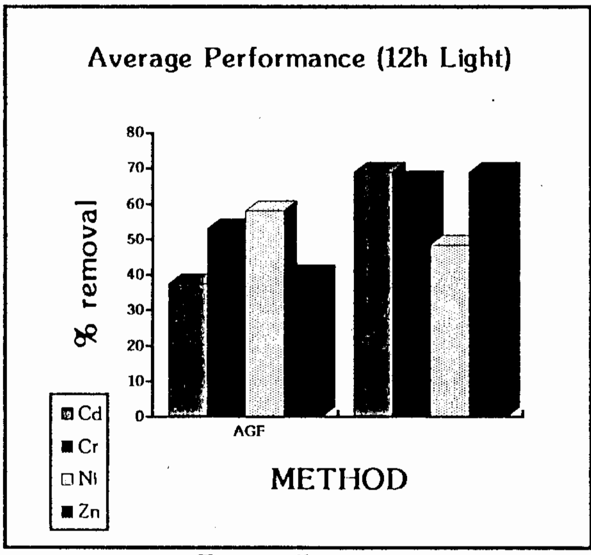


Figure 5.

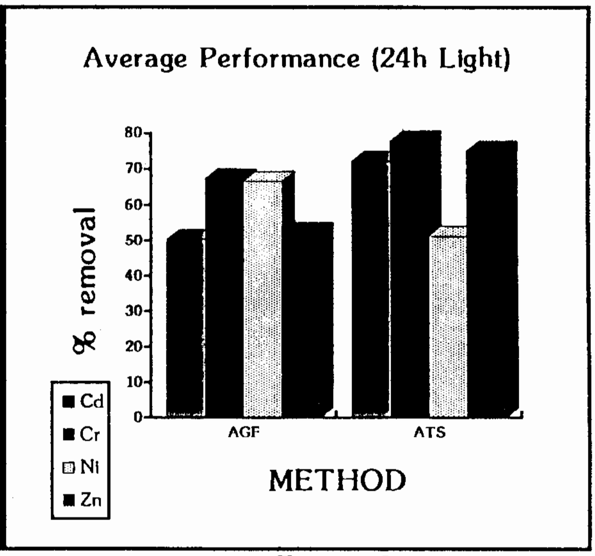


Figure 6.

Removals in the ATS units range from a low of 48.6% for Ni to a high of 77.8% for Cr^{+6}. Average mg metal found per kg of algal mass harvested for 12 and 24h light respectively were: Cd, 1475 and 1405; Cr^{+6}, 877 and 1335; Ni, 762 and 675; Zn, 1816 and 1693. Algal biomass production averaged 9.53 g m^{-2}, and it increased to 13.80 g m^{-2}, which represents an increase of 31% in periods of 12h and 24h light, respectively (Sack et al., 1992). From the above Figures, it is obvious that ATS is the option of choice between the two alternative technologies for heavy metal removal.

Concluding Remarks

- Despite the lack of conclusive evidence, the preliminary results presented above demonstrate that ATS has the potential and can successfully be used as a method to reduce considerably the concentration of heavy metals in water.

- The structure of algal turf communities is affected by the composition of the effluent and the metal concentrations in it. Therefore, ATS metal removal efficiency is expected to fluctuate depending on the origin and composition of the particular effluent. However, overall system functionality is not greatly impaired due to the beneficial indirect effects of increased photosynthesis and pH values. Photosynthesis provides a protection mechanism against metal toxicity by counteracting the inhibitory effect of heavy metals on chlorophyll metabolism and photosynthetic activities (AZEEZ and BANERJEE, 1987). Also, metal toxicity decreases with increasing pH (AHLF, 1985). Carbon dioxide removal during intense photosynthesis in ATS, results in elevated pH values, providing additional protection against metal toxicity.

- Employment of a natural community in the ATS, as opposed to monoculture, assures the success of the system as a technology to remove heavy metals. Fluctuations of environmental parameters induce structural shifts, i.e. changes in the species composition of natural communities. Species intolerant of the new conditions are restricted or eliminated, while more tolerant forms prevail. Compositional shifts of algal turf in response to increased incidence of ultraviolet (UV) radiation were observed by SANTAS (1989). The initial response of algal turf to the increased stress posed by UV radiation was a reduction in species richness and a decrease in productivity. However, three weeks after the change, previously subdominant species became dominant, and the productivity of the community as a whole was restored to its original levels.

- The algal biomass generated during the process of metal removal is expected to be about 10g dry weight m^{-2} day^{-1}, depending on available light conditions. This biomass can be treated anaerobically to further reduce the volume of the solid byproduct and to produce methane. Disposal of the residues from the anaerobic digesters can be handled through any other existing method for handling hazardous waste. Alternatively, development of a chemical process for reclaiming metals from the anaerobic digester sludge may be possible.

- Low initial operational costs, convenient management and uncomplicated maintenance are some of the multiple benefits that contribute to the uniqueness of the method. The technology is likely to find applications in many areas of water and waste water treatment.

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