HEXAVALENT CHROMIUM: ITS ECOTOXICOLOGICAL EFFECTS AND REMOVAL BY BIOSORPTION

By

NEETU TEWARI
Center for Rural Development and Technology

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Dedicated
To

My baba, for his love
My papa, for his principles that has guided his life
My maa, for her sacrifices that has led her children into intellect pursuit

CERTIFICATE

This is to certify that the thesis entitled "**Hexavalent Chromium: Its Ecotoxicological Effects and Removal by Biosorption**", submitted by **Neetu Tewari**, to the Indian Institute of Technology, Delhi for the award of degree of Doctor of Philosophy is a record of bonafied research work carried out by her. She has worked under our guidance and supervision, and has fulfilled the requirement for the submission for the thesis. The results contained in this thesis have not been submitted in part or full to any other university or institute for award of any degree or diploma.

Padma Vasudevan

(Prof. P. Vasudevan)
Centre for Rural Development and Technology,
Indian Institute of Technology, Delhi
New Delhi-110016
India

(Prof. B.K. Guha)
Department of Chemical Engineering
Indian Institute of Technology, Delhi
New Delhi-110016
India

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N Tewari

Neetu Tewari

ABSTRACT

The presence of heavy metal ions in surface water continues to be the most pervasive environmental issue of present time. Heavy metals like mercury, lead, cadmium, copper, chromium and nickel are toxic even in extremely minute quantities. Chromium is widely used in electroplating, leather tanning, and metal finishing and chrome preparations. Chromium exists in two stable oxidation states Cr (III) and Cr (VI). The Cr (VI) state is of particular concern because of its toxicity. Chromium occurs in these effluents in concentrations higher than its permissible limit. The recommended limit of Cr (VI) in potable water is 0.05mg/l. It is a potential carcinogen and its deleterious effects on all form of life are well documented. Various methods used for removal of chromium ions include chemical precipitation, reverse osmosis, ion exchange and adsorption. These techniques often involve high capital and operational cost. Among them adsorption is most promising, but it involves costly adsorbents. Thus attention has been focused on evaluating some cost effective and efficient alternatives. Biosorption refers to different modes of non-active metal uptake by microbial biomass, where metal sequestration by cell can take place through adsorption, ion exchange, coordination, complexation etc. Metal ions diffuse to the surface of microbial cell where they bind to the active sites on the cell surface formed by the presence of various functional groups such as carboxylate, hydroxyl, amino and phosphate, which exhibit affinity for the metal ions. The use of dead biomass is advantageous as the process is free from nutrient supply and moreover there is no toxicity constraints in the organism employed. So in present study Bagasse, Soil, Vermi-compost, Biogas slurry, Saccharomyces cerevisiae and Mucor hiemalis were chosen, for their ease of availability and cost effectiveness. And their performance has

been compared with conventionally used sorbents like Activated carbon, Activated alumina and Bentonite.

Sorption experiments were conducted in batches for optimization of sorption parameters and to study equilibrium, kinetics and thermodynamics of sorption process. For reutilization of sorbents experiments on desorption were also conducted. It was observed that for all the sorbents sorption of Cr (VI) was maximum at agitation speed of 120 rpm. The total removal of Cr (VI) increased, with increase in initial concentration of Cr (VI) and the dose of sorbents. The optimum pH for all the sorbents, except activated alumina was 2.0. For activated alumina it was 4.0. Equilibrium was achieved with in 1-2 hours of contact. All the Cr-adsorbent systems showed better correlation to Langmuir isotherm model. M. hiemalis showed the highest uptake of Cr (VI). Its maximum uptake capacity ranged from 47.4 to 53.5 mg/g. Its sorption capacity was higher than that of commonly used sorbent, Activated carbon. The uptake capacity of Activated carbon ranged from 15.0 to 19.6 mg/g. The kinetics of the Cr (VI) sorption in all the cases was found to be of pseudo-second order. Temperature also influenced the sorption of Cr (VI). The value of free energy change was negative while enthalpy and entropy in all the cases was positive. This indicates that sorption of Cr (VI) on the selected sorbents is a spontaneous and endothermic process. The activation energy for sorption of Cr (VI) on different sorbents used was in the ranges from 7.0 to 14.5 kJ/moles. Desorption study indicates that alkaline eluents are better for desorption of Cr (VI) from previously loaded sorbent. 0.1 N NaOH could elute approximately 98% of the Cr (VI). The Solid/Liquid ratios of 8 and 10 were found to elute the maximum amount of Cr (VI). When desorption was studied for more than one cycle, it was found that Mucor hiemalis showed the best *performance and could be used for five desorption and sorption cycles with out appreciable loss in its sorption capacity.*

Study of ecotoxicological effects of chromium on aquatic plants is important to get an idea on effects of bioaccumulation of Cr. For this purpose Lemna sp. have been widely used as bioindicator. In the present study Lemna minor was used as test plant. The effect of Cr (III) and Cr (VI) on growth and the biochemical parameters like total chlorophyll, total soluble starch, total free sugar, total soluble proteins and total free amino acids was observed. Cr (III) and Cr (VI) accumulation by Lemna minor was also noted. It was found that Cr (III) at all selected concentrations was non-toxic to the plant. While Cr (VI) at and beyond 10mg/l adversely affected the above mentioned parameters. Accumulation of Cr (VI) was higher than the Cr (III). Accumulation of Cr (VI) and Cr (III) from 50 mg/l after seven days of treatment was 1225 and 75 µg/ g dry wt for Cr (VI) and Cr (III) respectively. This may be due to the high mobility and high solubility of Cr (VI).

In conclusions the present work indicates that Mucor hiemalis could be used on an industrial scale for Cr (VI) removal from effluents. However, they work only at low pH (pH 2.0). The performance of biosorbents Mucor hiemalis, Biogas slurry and Vermi-compost was better than the conventional sorbents like Activated carbon and Activated alumina. The aquatic plant Lemna minor could be used for removal for Cr (VI) from polluted water bodies. It may be used as bioindicator for metal pollution.

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