Removal of Ni(II) from Aqueous Solution by Biosorption using two Green Algal Species *Oscillatoria sp.* & *Spirogyra sp.*

DIWAN SINGH
Civil Engineering Department
National Institute of Technology, Kurukshetra (Haryana)
INDIA

Abstract: Removal of Ni(II) from aqueous solutions by biosorption on dried green algae *Oscillatoria sp.* and *Spirogyra sp.* was investigated as a function of contact time, pH, algal dose, initial nickel ion concentration and temperature. The uptake of Ni(II) by *Oscillatoria sp.* is rapid by *Oscillatoria sp. than by Spirogyra sp.* Metal uptake capacity of algal biomass increased with increase in initial metal ion concentrations. *Oscillatoria sp.* was observed to be a far superior biosorbent than *Spirogyra sp.* in the removal of nickel ions. Removal of the metal ions has been found to increase with an increase in temperature by both the biomasses. The sorbed nickel ions were effectively desorbed using 0.1N HCl.

Key-Words: Removal, *Oscillatoria sp.*, *Spirogyra sp.* biosorption, contact time, nickel, pH, metal uptake, temperature.

1 Introduction

Toxic heavy metals removal from wastewater is essential due to their extreme toxicity towards aquatic life and humans. Public awareness and stringent environmental legislations have led to extensive research into developing effective alternative technologies for the removal of these potentially damaging substances from effluents and industrial wastewaters [1]. Conventional heavy metal removal processes from aqueous streams include chemical precipitation, ion exchange, filtration, electrochemical treatment, membrane technologies and evaporation recovery. These processes are expensive or ineffective, especially when the metal concentrations are very low and of the order of 1 to 100 mg/l in the solution [2]. Biosorption is a promising alternative, which utilizes inactive or dead biomass to bind and concentrate heavy metals from the aqueous solutions. Different types of biomaterials have shown different levels of metal uptake. Among the most promising biomaterials studied is algal biomass [3].

Nickel is one of the toxic heavy metals which require most immediate concern. In humans, nickel can cause serious problems such as dermatitis, allergic sensitization, lung and nervous system damages and is also a known carcinogen [4], Nickel is present in raw wastewaters from industries such as nickel electroplating, mining & metallurgy of nickel, stainless steel, battery and accumulator manufacturing, pigments and ceramic industries [5]. The present study was aimed at to investigate the removal of Ni(II) from aqueous solutions using two non-living algal species *Oscillatoria sp.* and *Spirogyra sp.* by batch experiments. The parameters which influence biosorption process such as contact time, pH, initial metal ion concentration, algal dose and temperature were studied. Desorption of Ni(II) from spent algal biomasses was tested using 0.1N HCl as an eluent.

2 Materials and Methods

Algal biomass of *Oscillatoria sp.* was collected from Braham Sarover and *Spirogyra sp.* was collected from Sannihit Sarover of Kurukshetra. These biomasses were washed under running tap water which was followed by washing with double distilled water to remove extraneous matter. The washed biomasses were sun dried and ground to powder in the laboratory pulverizer. The surface area of the biosorbents increases many times in the powdered form. The powdered biomass passing through I.S. Sieve No. 30 (aperture size 300 micron) and retained on I.S. Sieve

No. 15 (aperture size 150 microns) was selected for this study.

Batch forms of kinetic and isotherm sorption experiments were conducted to evaluate effect of contact time, pH, initial nickel ion concentration and temperature. Analytical grade reagents were used in all experiments and double distilled water was used throughout. Stock metal solution (1000 mg/L) was prepared by dissolving 1.000 g of nickel powder (SISCO make, Mumbai) in minimum volume of (1:1) HNO_3. It was diluted to one litre with 1 % (V/V) HNO_3. Ni(II) working solutions were made freshly by diluting the stock solutions. All the experiments, except studies related to the effect of temperature, were conducted at room temperature (28±2°C). Atomic Absorption Spectrophotometer (Model AAS-4129, ECIL, India) was used for metal determinations.

Procedure adopted for Ni(II) biosorption studies:

100 ml. of nickel metal ion solution of a required concentration (mg/L) was taken in Erlenmeyer flask (250 ml. size). To this solution selected algal dose (g/L) was added and it was put on the rotary shaker (140 rpm). After the desired contact time, the sample was taken out and filtered through Whatman 41 filter paper. The filtrate was analyzed for residual metal ion concentration using Atomic Absorption Spectrophotometer.

3 Results and Discussions

3.1 Effect of Contact Time

Fig. 1 shows the effect of contact time on the percentage removal of Ni(II) from aqueous solutions with initial Ni(II) concentrations of 10 mg/L by algal biomasses at an algal dose of 5g/L. The percentage removal of Ni(II) by *Oscillatoria sp.* was more than 90 % of final removal at equilibrium time within first 20 minutes where as it was around 70 % by *Spirogyra sp.* of algae for the algal dose 5 g/L. It can be seen that maximum percentage removal of Ni(II) was achieved within a period of 120 minutes. Therefore, for the following experiments, the contact time was taken as 120 minutes.

3.2 Effect of Initial pH Values

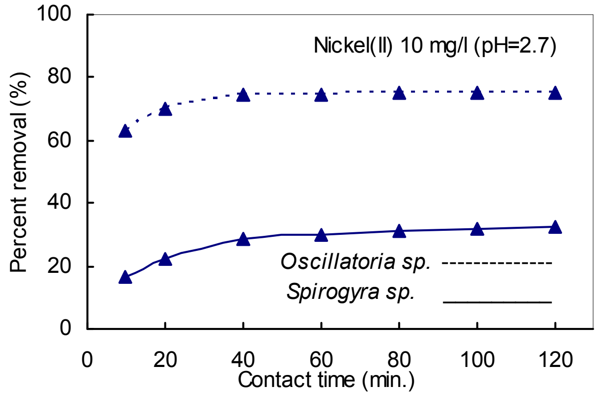

Fig. 1 Effect of contact time on removal of Nickel(II) algal dose 5 g/L.

The pH of the aqueous solution is an important parameter affecting the biosorption process [4, 6]. Effect of initial pH (pH 1-12) on removal of Ni(II) by biomasses from aqueous solutions is given in Fig. 2. A sharp increase in Ni(II) removal by algal biomasses was observed upto pH 4.0 and further it increased slowly being maximum at pH 6.0 (Optimal). Beyond pH 6.0 a slow decline in removal of nickel ions was observed upto pH 12.0 in the case of *Oscillatoria sp.* where as a sudden increase was observed in the case of *Spirogyra sp.* Nickel will transform into hydroxide complex at higher pH and could not be considered for biosorption behaviour of the cells [7]. The results indicated that the nickel biosorption by non-living cells of algal biomasses was affected by initial pH of the solution and may be due to ionic attraction. Therefore, at low pH values the cell surface becomes more positively charged, reducing the attraction between metal ions and

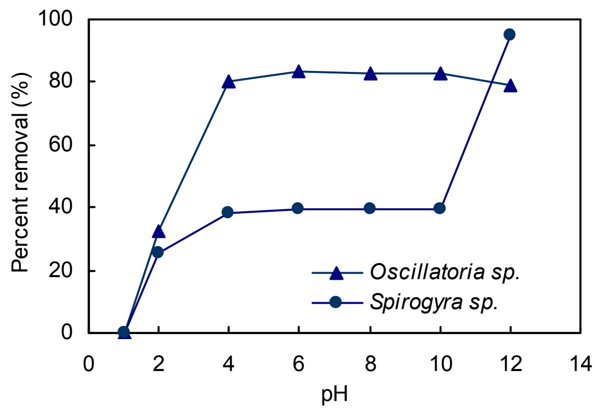

Fig. 2. Effect of initial pH on removal of Nickel(II) algal dose 5 g/L and initial Ni(II) conc. 10 mg/l

functional groups on the cell walls whereas higher pH helps in metal biosorption, since the metal surface is more charged.

3.3 Effect of Algal Dose and Initial Metal Ion Concentration

Effect of algal dose was investigated in the initial metal ion concentrations range of 10-100 mg/L and is shown in Fig. 3 & 4. It can be observed that percentage removal of Ni(II) increases with increase in algal dose. The increases in removal of Ni(II) with increasing dose of the sorbent is expected because for a fixed initial solute concentration, increasing sorbent doses provides greater surface area or sorption sites. It is evident that *Oscillatoria sp.* invariably maintained an upper hand in respect of metal removal over *Spirogyra sp.* at all the algal doses. With an algal dose of 10 g/l, the removal of Ni(II) was observed as 86.8% by *Oscillatoria sp.* whereas it was only 43.4% by *Spirogyra sp.* from aqueous solution of Ni(II) conc. of 100 mg/l. The differences between algal species in the metal ion binding capacity may be due to the properties the properties of the algae (e.g. structure, functional groups and surface area, depending on the algal division, genera and species). Cell walls of algae contain polysaccharides as basic building blocks, which have ion exchange properties and also proteins and lipids and therefore offer a host of functional groups capable of binding to heavy metals. These functional groups such as amino, carboxylic, sulphydryl, phosphate etc. differ in their affinity and specificity for metal binding [6].

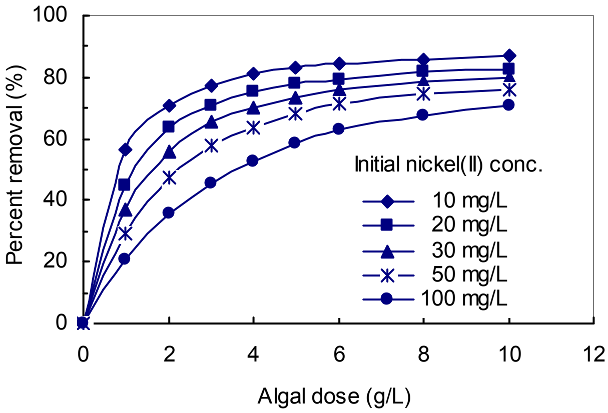

Fig. 3 Effect of algal dose (*Oscillatoria sp.*) on nickel(II) removal at initial pH 6.0.

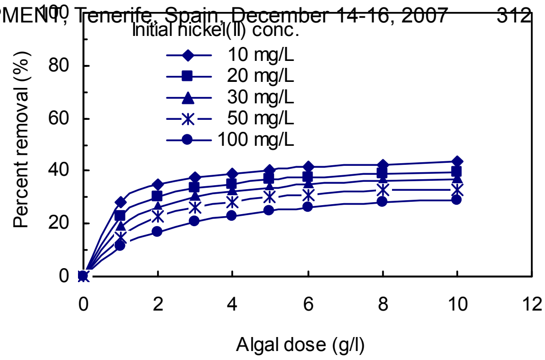

Fig. 4 Effect of algal dose (Spirogyra sp.) on nickel(II) removal (%) at initial pH 6.0.

It can be observed that the amount of Ni(II) uptake per unit of the algal biomass decreases (Fig. 5 & 6) with increase in algal dose. The decrease in Ni(II) uptake by biosorbent with increase in algal dose may be due to the dilution of the metal ions with added algal biomass. Maximum uptakes of Ni(II) by algal biomasses were observed as 20.8 mg/L and at an algal dose of 1g/L from

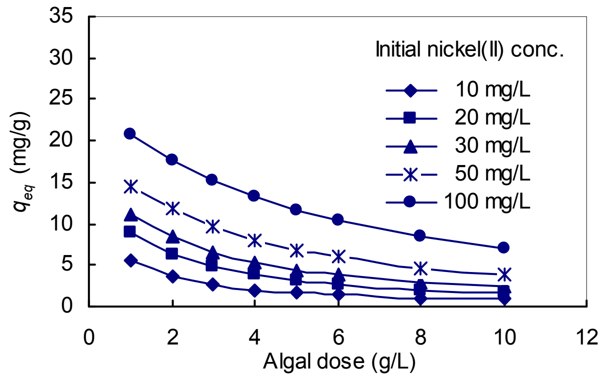

Fig. 5 Effect of algal dose and initial metal ion concentration on specific uptake (q_{eq}) of nickel(II) by *Oscillatoria sp.* at initial pH 6.0.

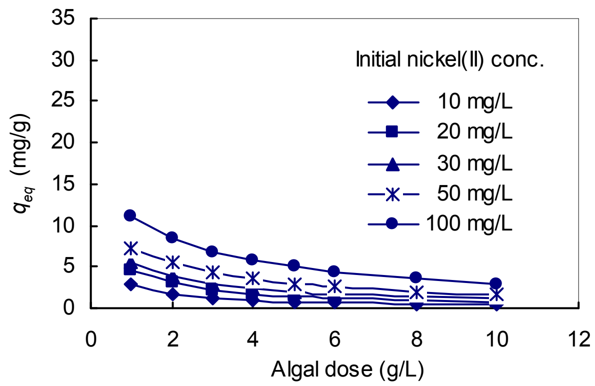

Fig. 6 Effect of algal dose and initial metal ion concentration on specific uptake (q_{eq}) of nickel(II) by *Spirogyra sp.* at initial pH 6.0.

the solution with initial metal ion concentration as 100 mg/L.

3.4 Effect of Temperature

Effect of temperature on biosorption of Ni(II) by algal species was studied in the temperature range of 20- 40ºC). Initial Ni(II) concentration, pH and algal dose were kept as 10 mg/L, 6.0 and 2.0 g/L respectively. It can be seen that high temperature enhanced the Ni(II) biosorption by algal biomass (Fig. 7). The increase in metal ions removal was observed more by *Oscillatoria sp.* than *Spirogyra sp*. The increase in biosorption with temperature indicates an endothermic process. Temperature affects a number of factors that are important for metal biosorption. These include the stability of the metal ion species; the ligands and ligand metal complex as well as the solubility of the metal ions. In general higher temperature favors greater solubility of metal ions in solution and hence weakens the biosorption of the metals ions [8]. Thermodynamically, biosorption will be favored by high temperature if the binding is endothermic but weakened if it is exothermic. The favoring or not by high temperature for the biosorption process is, therefore, dependent on the relative contribution of the carboxylate or amine-ligands on the cell wall/surface. The overall effect of temperature would therefore be the total sum of these favoring and unfavoring factors.

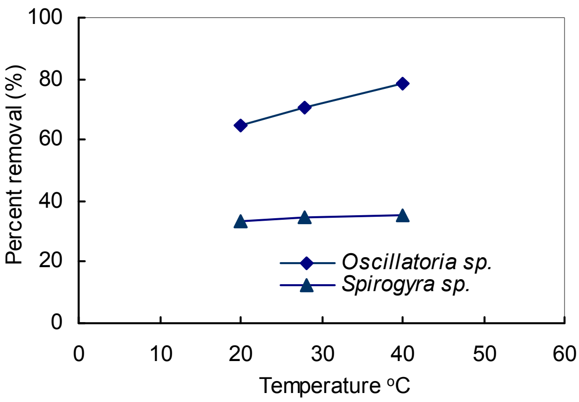

Fig. 7. Effect of temperature on removal of Ni(II) by *Oscillatoria sp.* (Ni(II) initial conc. 10 mg/L)

3.5 Desorption

Recovery of the metal ions sorbed onto the biomass is one of the important aspects of any successful biosorption process development [9]. The studies on the effect of pH on biosorption of nickel (II) on *Oscillatoria sp.* and *Spirogyra sp.* showed that binding of the metal is favored at higher pH. This suggests that metal binding at high pH might be reversed at lower pH. Therefore, in the present study, 0.1 N HCl was used to desorb metal ions. More than 90% recovery of Ni(II) sorbed on algal biomasses was observed.

4 Conclusions

In the present study, it was observed that removal of Ni(II) by the non-living *Oscillatoria sp.* and *Spirogyra sp.* is highly dependent on pH. It is also affected by factors such as contact time, initial metal ion concentration and temperature. *Oscillatoria sp.* was observed to be a far superior biosorbent than *Spirogyra sp.* in the removal of nickel ions. With an algal dose of 10 g/L, the removal of Ni(II) was observed as 86.8% by *Oscillatoria sp.* whereas it was only 43.4% by *Spirogyra sp.* from aqueous solution of Ni(II) conc. of 100 mg/l. Desorption of the sorbed Ni(II) by 0.1N HCl indicated that recovery of Ni(II) from spent biomass is possible. It can be concluded that non-living *Oscillatoria sp.* of algae can be considered as an inexpensive, effective and easily available in abundance biosorbent for the removal of Ni(II) from aqueous solutions.

References:

1. Singh, Diwan, Removal of Zinc(II) from aqueous solution using non-living *Oscillatoria sp., Journal of Environmental Research and Development,* 1,4, 2007 pp. 342-348.
2. Volesky B., *Biosorption of Heavy Metals*. CRC press, Boca Raton, USA, 1990.
3. Vijayaraghavan K., Jegan J., Palanivelu K. and Velan M., Batch and column removal of zinc from aqueous solution using a brown marine alga *Turbinaria ornate. Chemical Engineering Journal*.106, 2005, pp. 177-184.
4. Malkoc E., Ni(II) removal from aqueous solutions using cone biomass of *Thuja orientalis*, *Journal of Hazardous Materials*, B 87, 2006, pp. 127-137
5. Singh, Diwan, Removal of Ni(II) from aqueous solution using non-living *Oscillatoria sp.*, *Pollution Research*, 26, 2, 2007, pp. 301-304
6. Donmez G.C., Aksu Z, Ozturk A. and Kutsal, T., A comparative study on heavy metal biosorption characteristics of some

algae, *Process Biochemistry*.34, 1999, pp 885-892.

7. Chen X. C., Wang Y. P., Lin Q., Shi J. N., Wu W. X. and Chen Y. X., Biosorption of zinc(II) and Zinc(II) from aqueous solution by *Pseudomonas putida* CZI, *Colloids and Surfaces B. Binterfaces*. 46, 2005, pp 101-107.
8. Lau P.S., Tsang C.C.K., Tam N.F.Y. and Wong Y.S., Effect of Metal Interference, pH and Temperature on Cu and Ni Biosorption by *Chlorella vulgaris* and *Chlorella miniata. Environmental Technology*. 20, 1999, pp 953-961
9. Sar P., Kazy S.K., Asthana R.K and Singh S.P., Metal adsorption and desorption by lyophilized *Pseudomonas Aeruginosa*, *International Biodeterioration & Biodegradation*, 44, 1999, pp 101-110.