Entrapment of bioadsorbent for removal of heavy metal

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Introduction

Heavy metals are well known for their toxicity as these damage nerves, liver, bones, block functional groups of vital enzymes and are possible human carcinogens (group 2B) Ewan et al. (1996). Various industries such as mining, plating, surface finishing, steel works, smelting, tanning, petroleum refineries and fertilizer complexes discharge heavy metal bearing effluents into the environment. The presence of heavy metals in the aquatic environment has forced international environmental agencies to introduce strict regulations with regard to metal discharge, especially from industrial activities. Various methods have been suggested and applied for the removal of toxic metals from wastewater, such as chemical precipitation, evaporation, ion-exchange, adsorption, electrolysis and reverse osmosis. Due to the specific nature of industrial effluents like low or high pH, variety of cations and anions, oil emulsions, particles, etc. the effective removal of metal ions has proven to be a very difficult and costly process Crist et al., (1996). In recent year, removal of heavy metals from wastewaters through adsorption, particularly biosorption, has emerged as a promising technology. A variety of biomaterials and microorganisms have been explored by researchers for biosorption and bioaccumulation including fungi (Fourest et al., 1994), yeast (Krheminska et al., 2005), algae (Gupta et al., 2001) and mosses (Cossich et al., 2002). Biosorption through live microbial cells can be used to remove heavy metal ions, but maintaining the survivability of the microbial cells during biosorption process is difficult, because they require a continuous supply of nutrients and metal toxicity might take place for microbial cells Arıca et al., (2003). Several researchers have also shown that non-living biomass is also able to bind heavy metals effectively. Therefore, the use of non-living microbial cells can eliminate these problems and can be regenerated and reused for many cycles Papageorgiou et al., (2006); Anjana et al(2007)

Commercial application of these of non-living microbial cells in the powdered form has been hindered by operational limitations associated with their physical characteristics, such as small particle size with low density, poor mechanical strength and low rigidity, solid/liquid separation, difficulty in separation of microbial cells after biosorption and small particle size, which make them difficult to use in the batch and continuous systems McHale et al., (1994). These problems can be solved by entrapment/ immobilization of microbial cells using natural or synthetic polymers. Natural polymers such as alginate, chitosan, chitin, and cellulose derivatives have been mostly used as the matrix for the immobilization of the microbial cells via entrapment Aloysius et al., (1999); Arıca et al., (2004). These polymers are also known to bind metal ions strongly. Entrapment of microbial cells in these polymer supports could also enhance microbial cells performance and adsorptive capacity of the biosorbents systems for the heavy metal ions Baik et al., (2002); Jeon et al., (2002); Tien et al., (2002).

The purpose of the present study is to evaluate feasibility of entrapment of biosorbent. The relatively inadequate studied algae *Spirogyra species* is taken as an example to demonstrate the feasibility of entrapment for overcoming the operational problems. The entrapped biosorbent were tested for Ni and Cd removal from aqueous solutions.

Materials and methods

Alginate beads preparation

Fresh algal biomass of *Spirogyra species* was collected from the freshwater lake, Hisar district, Haryana, India. Before use, it was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content. After this, the biomass was sun dried for 48 hours and milled and sieved through 0.3 mm mesh. 4.0 g dry *Spirogyra species* biomass and 4.0 g sodium alginate powder were mixed in 100 ml double distilled water under gentle stirring at 25^0 C. This slurry was dropped through a burette (opening i.d. 1.5 mm) into 0.5 M $CaCl_2$ solution to form beads of diameter 3.0-4.0 mm. After keeping them overnight in the $CaCl_2$ solution, the beads were rinsed with double distilled water.

Preliminary experiment on metal removal

3Cd SO_4. $8H_2O$ and $NiSO_4.6H_2O$ were used for preparing stock solutions of 1000 mg l^{-1} of Cd and Ni respectively. From stock solution 5 mg l^{-1} solutions were prepared by serial dilutions. Preliminary study on heavy metal removal was done at pH 4.0 and 5 mg l^{-1}initial metal concentration. The experiments were carried out in 250 ml Erlenmeyer flasks. 5.0 g wet algal beads in 100 aqueous metal solutions at room temperature were used for experiment. The test solutions with Spirogyra species beads were shaken on a mechanical shaker for period of 2 hours. After this period test solution were filtered through Whattman filter paper no. 40. The filtrates were analyzed for residual metal concentration on atomic adsorption spectrophotometer.

Results and Discussion

Figure 1-3 shows that application of biosorbent in powder form suffers by operational limitations due to their physical characteristics. Such limitations can be overcome by entrapping them into beads form.

Alginate is a very promising biopolymer material, that offers such advantages. Alginate is a linear copolymer of a-l-guluronate (G) and a-dmannuronate(M), which constitutes 10–40% of the dry weight of all species of brown algae Volesky et al., (2003). Depending on the algal species used for the extraction of alginic acid its molecular weight as well as its M/G ratio presents great variations. The capability of this copolymer to form stable biodegradable gels in the presence of divalent cations has been known and studied extensively since the seventies Grant et al., (1973); Smidsrod et al., (1972). These gelation properties can be attributed to the simultaneous binding of the divalent cations such as Ca^{2+} to different chains of a-l-guluronate blocks (G-blocks) Veglio et al., (1997). As a result of their configuration, these chains form electronegative cavities, capable of holding the cations via ionic interactions, resulting in cross-linking of the chains into a structure resembling an "egg box" Grant et al., (1973). Due to its ability to form stable structures, cross-linked alginate has been used for the immobilization of biological material for various purposes, including the immobilisation of material with metal binding properties, such as algae, for the removal of heavy metal from wastewater Kuyucak et al., (1989). The present study shows that dry biomass of *Spirogyra species* can be entrapped in the form of beads, which can be successfully use in batch and continuous process for removal of heavy metal. In this study removal of Ni and Cd with entrapped *Spirogyra species* biomass bead are found to 78.50 and 65.25% respectively in above said condition.

Conclusions

The present study concluded that entrapment of the bioadsorbent particularly biomass based adsorbent can solve the operational limitations of adsorption process. Thus, after entrapment, these materials can be used without any operational problem for heavy metals removal and from wastewater.

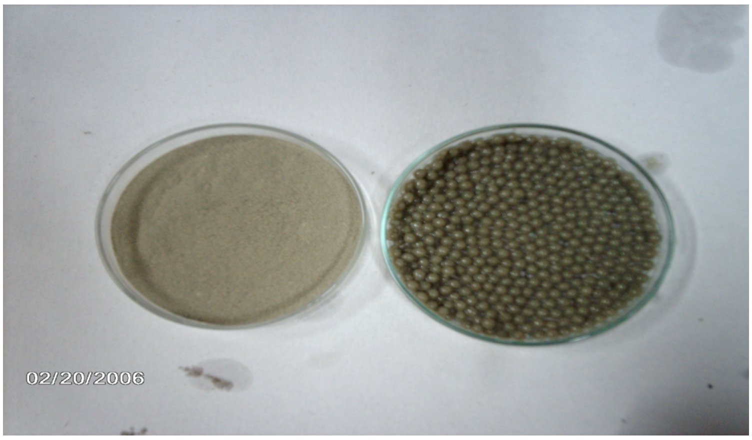

Figure 1. Entrapped and Powder form *of Spirogyra sp.* biomass

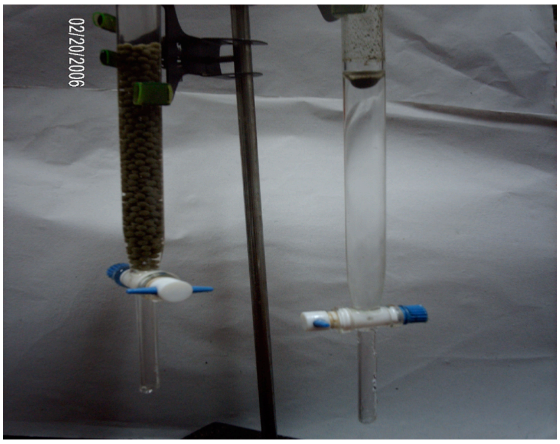

Figure 2. Entrapped and Powder form *of Spirogyra sp.* Biomass in Continuous Process

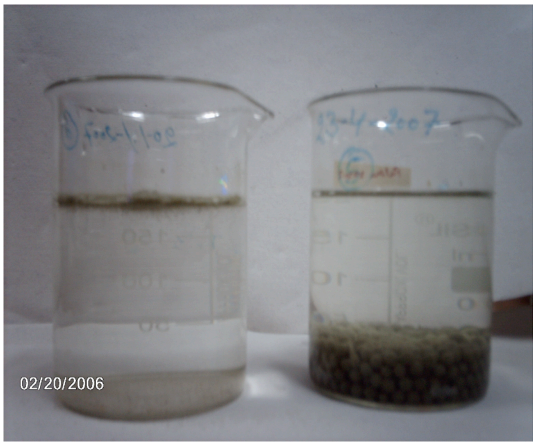

Figure 3. Entrapped and Powder form *of Spirogyra sp.* Biomass in Batch Process.

Acknowledgement: One of the authors, A.K.Y., is grateful to CSIR and AICTE, New Delhi for awarding SRF and NDF respectively.

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