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## Biosorption of metals from contaminated water using seaweed

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**Heavy metals are major pollutants in marine, lake and groundwaters as well as in industrial and even treated effluents. Biosorption, an inexpensive and reliable method to remove cadmium and lead ions from solution using dry seaweed biomass as adsorbents, was investigated. *Sargassum wightii* exhibited maximum metal uptake at pH 4–5 and the value ranged from 18% to 29% of dry biomass. The kinetics of metal adsorption was fast with 70–80% taking place within 30 min. Based on these results, a biobattery involving perforated columns packed with pulverized dry biomass of *S. wightii* was designed, which could remove metals in the range of 50–97% from a multi-metal ion solution within two and a half hours. The mechanism of metal sorption by seaweeds and the advantages of the present design of seaweed columns are discussed in the light of ecofriendly and cost-effective approach for effluent treatment.**

**Keywords:** Biobattery, biosorption, effluent treatment, heavy metals, *Sargassum wightii*.

HEAVY metals can be extremely toxic as they damage nerves, liver, kidney and bones, and also block functional groups of vital enzymes<sup>1</sup>. Stringent environmental legislation and powers of the authoritative bodies established to enforce these regulations are increasing the demand for new technologies to remove metal from wastewater. For more than a decade, researchers have been looking for cheaper and more effective methods to remediate heavy metal-contaminated waters and reduce the growing public-health risk. Biosorption is proven to be quite effective at removing metal ions from contaminated solution in a low-cost and environment-friendly manner<sup>2</sup>. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent and the possibility of metal recovery<sup>3</sup>.

Bacteria<sup>4</sup>, fungi<sup>5</sup>, marine algae<sup>6,7</sup>, etc. have been studied for their heavy metal uptake capacities and suitability to be used as development of biosorbents. Biosorptive capacities of seaweeds, activated carbon and natural zeolites have been evaluated and are comparable to those of synthetic ion-exchange resins<sup>6</sup>. Marine macro-algae are harvested or cultivated in many parts of the world and are therefore readily available in large quantities for the development of highly effective biosorbent materials. This study inves-

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tigated the biosorptive potential of *S. wightii* (class Phaeophyta) on Cd and Pb and the physical and chemical factors required for sorption. Based on the results, an experimental biobattery with seaweed sorbents was designed to treat a solution containing Cd, Pb, Cu and Zn.

The raw biomass of *S. wightii* was collected from the Gulf of Mannar coast (Rameswaram). The collected biomass was washed with excess tap water and finally with distilled water to remove salt and particulate material from its surface and oven-dried at 80°C for 24 h. The dried samples were then ground and sieved to a particle size of 2–4 mm. These were stored at 37°C in a desiccator for later use.

The Cd, Pb, Zn and Cu stock solutions (1000 mg/l) were prepared by dissolving their corresponding salts (CdCl<sub>2</sub> monohydrate, Pb(NO<sub>3</sub>)<sub>2</sub>, ZnCl<sub>2</sub> and CuSO<sub>4</sub> analytical grade) in distilled water, and standardized by anode stripping voltammetry (VA 757 Computrace attached to 765 Dosimat, Metrohm, Switzerland). Working solutions of each metal at 0–600 ppm concentrations were prepared by adequate dilution of the stock solution with deionized double distilled water (DDW).

All the preliminary experiments were done in 2 l glass bottles containing 1000 ml metal solution, with three replications and were continuously agitated using filtered air (HNO<sub>3</sub>–KMnO<sub>4</sub>–DDW), using aquarium aerators for uniform suspension of the sorbent particles. After each experiment, 15 ml of the sample was collected from each system, filtered (0.45 μ) and kept for analysis by adding one drop of conc. HNO<sub>3</sub>.

The voltammetric procedure consisted of differential pulse anodic stripping voltammetry and determinations were carried out in a teflon cell. A hanging drop electrode was used as working electrode and the potential was measured versus an Ag/AgCl reference electrode and an auxiliary platinum electrode. Concentrations of Zn, Cd, Pb and Cu in the samples were simultaneously measured by standard addition of mixed metal standard. Blanks were run and subtracted from the values determined. Results were expressed as μg/l. Certified reference materials (BCSS-1) were used to provide a check on analytical quality.

To study the effect of pH, 1 g ground biomass of *S. wightii* was treated with 1 l of single metal ion solutions of Cd and Pb maintained at different pH values ranging from 3 to 11 for a period of 3 h. Monitoring of pH was done at a regular interval of 1 h and was maintained constant using 1.0 N solution of NaOH or HCl. The duration required for effective sorption plays a major role in the efficiency and economy of the sorption process. *S. wightii* (1 g) was treated with 1 l of 100 mg/l concentration of single metal ion solutions of Cd and Pb for a period of 8 h at 4.5 pH. Samples (15 ml) were taken from each bottle at regular intervals of every half hour and subjected to voltammetry. To evaluate the sorption potential of *S. wightii*, single metal ion solutions of Cd and Pb having concentrations of 1, 10, 50, 100, 150, 200, 300, 400, 500

and 600 ppm were treated with 1 g ground biomass of *S. wightii* at pH 4.5 for 8 h.

The biobattery consisted of simple cylindrical PVC bottles (10 cm × 5 cm) each containing a bolting cloth bag filled with 5 g ground *S. wightii* inside (Figure 1). There were provisions at the bottom of the bottles for fitting aeration tubes, and with the help of a screw mechanism the bottles were temporarily attached to the aeration tubes. The bottom and topsides of the bottles were well perforated to effect continuous circulation of water through them. The efficiency of the biobattery was tested in a multi-metal ion solution (to simulate industrial effluents containing more than one metal) containing four metals, Zn, Cd, Pb and Cu, each having 100 mg/l concentration, at pH 4.5, 1 l metal solution was taken in a 10 l capacity long cylindrical glass container. Five bottles were used to treat the metal solution, one after another, each operated for 30 min. After each 30 min, the bottles were changed manually by lifting up the aeration mechanism. Next 15 ml of the water samples was collected every 30 min after the operation of each bottle, filtered and preserved for analysis through anode stripping voltammetry.

Results were expressed as the amount of metal ions adsorbed on dried algae at any time ( $q$ , mg/g), adsorbed metal ions per gram of seaweed at equilibrium ( $q_e$ , mg/g), maximum amount of metal ions the biomass can adsorb ( $q_{max}$ , mg/g), initial metal concentration ( $C_0$ , μg/ml), concentration of metal ions that remain in solution at the equilibrium ( $C_e$ , μg/ml), and fraction of metal adsorbed ( $X_a$ , % =  $(1 - C_e/C_0) \times 100$ ). Biosorption metal uptake ( $q$ ) was calculated from the sorption system mass balance:

$$q = V(C_i - C_f)/S,$$

where  $V$  is the solution volume,  $S$  the amount of solids (biomass), and  $C_i$  and  $C_f$  the initial and final metal concentrations respectively.

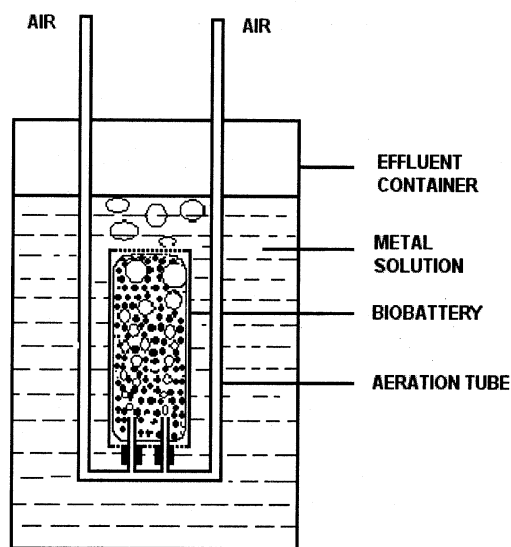


Figure 1. Design of biobattery.

Solution pH level is one of the most important parameters on biosorption of metal ions from aqueous solution<sup>7,8</sup>. The results obtained in this study also confirm the significant role of pH in metal sorption process (Figure 2). *S. wightii* could remove more than 90% of Cd and Pb ions in a pH range of 4–8 with peak values at pH 4 and 5. Compared to cadmium sorption, lead sorption by *S. wightii* showed significant differences with change in pH.  $X_a$ , the fraction of lead adsorbed reached more than 90% at pH values 4 and 5 only. Thus it is evident from the studies that biomass of *S. wightii* exhibits maximum metal uptake capacity at pH range 4–5. Similar results have been reported by different authors<sup>7,8</sup>. The pH dependence of metal uptake can largely be related to the functional groups present in algae and also on the metal chemistry in solution<sup>7</sup>. Majority of metals of interest (i.e. Cd, Co, Cu, Fe, Ni, Pb) display maximal or near maximal sequestration at pH values near the apparent dissociation constant of carboxylic acid observed in brown algal biomass ( $pK_0$  near 5)<sup>9</sup>.

In the present study, it was found that 80% of the cadmium ions was removed within the first 30 min (Figure 3). Equilibrium was reached within 180 min, where  $q_e$  was 93.685 mg/g. The initial quick phase was followed

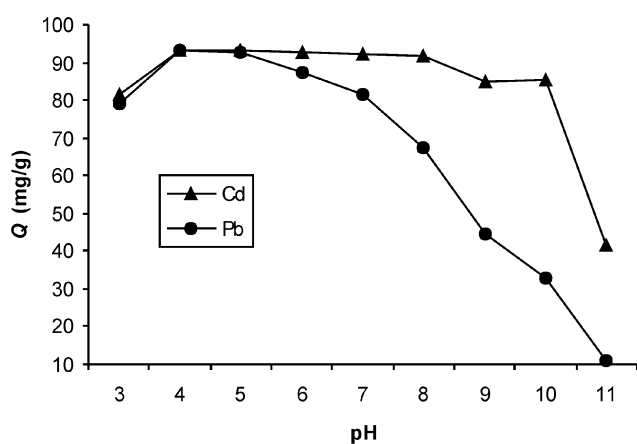


Figure 2. Effect of pH on sorption potential of *Sargassum wightii*.

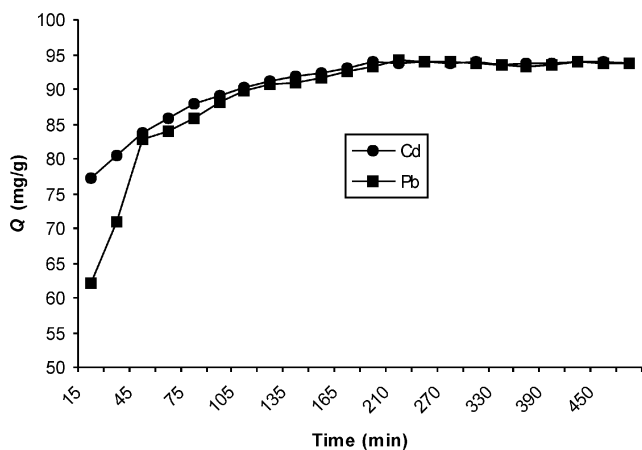


Figure 3. Optimizing effective time for sorption.

by a slower phase where only 20% of the metal ions could be removed. Similar results for cadmium adsorption have been reported by Matheickal *et al.*<sup>7</sup> and Cruz *et al.*<sup>10</sup>. Lead sorption kinetics can also be divided into two stages, one in which the sorption rate is high, followed by a second stage with a much lower sorption rate (Figure 3). Compared to cadmium, lead sorption kinetics was slower in the first phase, as only 70% of the ions was removed in 30 min.

These observations are consistent with the concept of homogeneity of the algal surface, which contains a variety of functional groups. These groups that serve as adsorption sites may differ both with respect to the strength of the metal sorptive bond and the rate of adsorption onto the sites. This will result in different rates of metal uptake by the biosorbent and in general can be classified into fast and slow uptake<sup>7</sup>. The initial rapid metal uptake observed in this study has significant practical importance, as it will facilitate sorption adsorption columns, ensuring efficiency and economy.

When *S. wightii* was treated in cadmium and lead solutions having different initial concentrations, sorption capacity of the biomass increased with increase in initial metal concentration up to 400 ppm and remained constant for higher concentrations (Figure 4). The biomass could remove more than 80% of the metal ions in solutions up to 200 ppm.  $q_{max}$  obtained for cadmium was 181.483 mg/g and for lead 290.532 mg/g. Holan *et al.*<sup>11</sup> have reported  $q_{max} = 195$  mg/g for cadmium in the case of brown alga, *Ascophyllum nodosum*.  $q_{max}$  for *Sargassum natans* with cadmium was 115 mg/g. In a study conducted by Yu *et al.*<sup>8</sup>,  $q_{max}$  values for different species were 130.397 mg/g for *Lessonia flavicans*, 132.644 mg/g for *Durvillaea potatorum* and 129.273 mg/g for *Ecklonia maxima*. The reported  $q_{max}$  values for lead sorption are 280 mg/g for *A. nodosum*<sup>12</sup>, 336 mg/g for *Fucus vesiculosus*<sup>12</sup>, 362.512 mg/g for *Lessonia nigresense*, 321.16 mg/g for *Durvillaea potatorum* and 300.44 mg/g for *L. flavicans*<sup>8</sup>.

Differences in metal uptake exhibited by different species of brown algae can be attributed to the guluronic acid

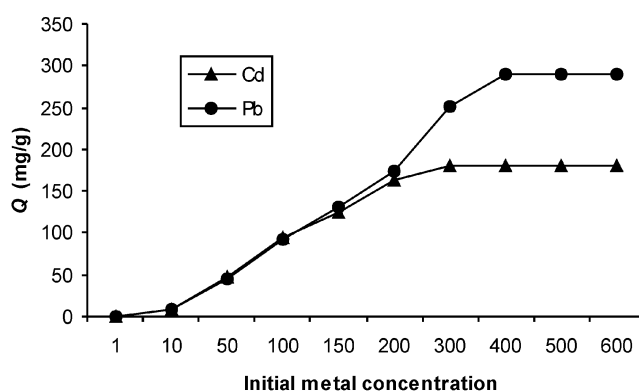


Figure 4. Effect of initial metal concentration on biosorption of *S. wightii*.

content in their cell wall. Alginic acid or alginate, the salt of alginic acid, is the common name given to a family of linear polysaccharides containing 1,4-linked *b*-D-mannuronic (M) and *a*-L-guluronic (G) acid residues. The affinity of alginates for divalent cations such as  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , etc. has increased with the guluronic acid content<sup>13</sup>.

For the design of biobattery experiments the operational parameter levels were selected based on results from preliminary studies. Usually industrial effluents contain a number of metal compounds, which will interfere with the sorption potential of the sorbent. Therefore a multi-metal sorption system was selected for the biobattery study, as it would more closely represent the composition of industrial effluents<sup>14</sup>.

In the biobattery experiment, the maximum metal reduction was observed in the case of cadmium and lead (Figure 5). The result was promising as the final metal concentrations after two and a half hours (five battery operations) were 50.73 ppm for Zn, 2.37 ppm for Cd, 21.56 ppm for Pb and 26.90 ppm for Cu, the percentage reduction being 49.27, 97.63, 78.44 and 74.10 respectively. Among the four metals treated, Cd was the most adsorbed metal followed by Pb, Cu and Zn, indicating the affinity range of the biomass for metal ions. However, in the second battery run, both Cd and Pb concentrations remained unchanged (reduction being 0.287 and 0.920 ppm respectively), whereas Cu, followed by Zn got reduced to 38.17% and 23.79% respectively. This result clearly shows that the metal affinity of the sorbent plays a second role when the initial metal concentrations of other ions are high.

Reduction in metal uptake observed during the successive battery operations could be attributed to lowered metal/biosorbent ratio in solution. According to Fourest and Roux<sup>15</sup>, reduction in biomass concentration in the suspension at a given metal concentration enhanced the metal/biosorbent ratio, and thus increased the metal uptake per unit

biosorbent as long as the latter was not saturated. Thus reducing the biomass concentration with reduction in the metal concentration can be suggested to improve metal uptake in the final stages of biobattery operations.

The inhibitory role of other ions on sorption process can be well understood by comparing the metal uptake capacities of the biosorbent in the case of single (Figure 3) and multi metal ion solutions (Figure 5). Though *Sargassum* could adsorb a maximum of 71.04 mg Pb ions within 30 min from 100 ppm single metal ion solutions of Pb, the value got considerably reduced in multi metal ion solutions (61.60 mg). In multi-metal mixtures, heavy metal ions compete for a limited number of binding sites in the biomass. Depending on the composition of the solution and the form of biomass, this competitive ion exchange may severely reduce the efficiency of the metal-removal process<sup>16</sup>. Though the performance of the battery in multi-metal ion solution was satisfactory, its efficiency in the case of industrial effluents will be affected by the presence of other elements and complex molecules in the solution<sup>17</sup>.

The merits of the biobattery designed for the present study are the following:

- (1) The present design of the biobattery is capable of adsorbing complex metal ions, industrial effluents can be treated for the control of metal pollution.
- (2) The biosorbent is capable of adsorbing metals rapidly within the first 30 min, which will facilitate shorter adsorption columns.
- (3) Replacement of cartridges every 30 min can still improve the efficiency and economy of the system.
- (4) Operation of the battery is so simple that each cartridge can be replaced without affecting the continuity of the process.
- (5) Though desorption experiments were not done in this study, it has been already proved that the adsorbed metal can be retrieved using suitable elutants and the cartridge can be reused.

The biobattery can be considered as an ecofriendly and cost-effective technique for treating industrial effluents.

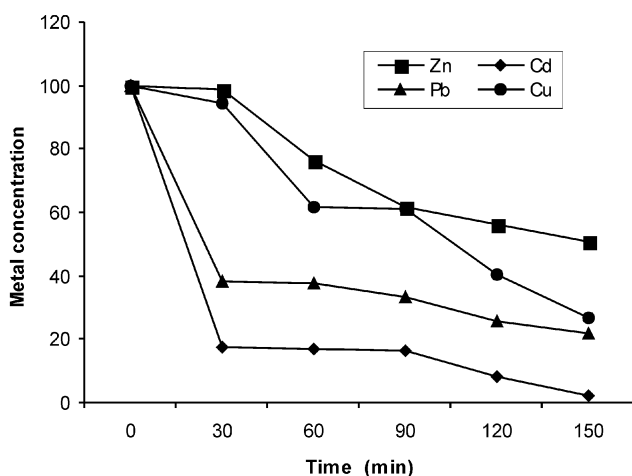


Figure 5. Effect of biobattery on a multi-metal ion solution.

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## Co-existing compressional and extensional regimes along the Himalayan front *vis-à-vis* active faults near Singhauli, Haryana, India

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**The present study demonstrates the significance of morpho-structural analysis using remotely sensed data along with selected field investigations in delineating traces of active faults, which are oblique to the Himalayan Frontal Thrust (HFT) in the northwestern Frontal Himalaya. Topographic features indicate movement along a normal fault with upthrown southern**

**block. This extensional behaviour of faulting is in contrast with the ongoing southward thrusting along the HFT with Siwalik sediments in the hanging wall overriding the alluvial fans in the footwall. Various tectonic landforms and relative positions of Quaternary deposits in the area corroborate that the Frontal Himalayan region has ruptured repeatedly in the recent past.**

**Keywords:** Himalayan Frontal Thrust, morpho-structural analysis, Singhauli active fault, Siwalik Group.

Active faults, which are ubiquitously distributed in diversified domains of the Himalaya, are important in that they provide signatures of the ongoing post-collision tectonic activity. Landforms such as river terraces, alluvial fans, fault scarps and other morphotectonic features such as triangular facets, sag ponds, shutter ridges, pressure ridges and pull apart basins, deflected drainages, etc. are closely related with these faults. Geomorphic and morphotectonic analyses of landforms provide insights into rates, style and pattern of deformation due to active tectonics. Identification of active faults that have moved within the current tectonic regime (CTR), i.e. during Holocene also helps in assessing whether or not tectonic movements are likely to occur and cause seismicity which is generally associated with these faults and ascertain the seismic risk in the surroundings. In the Outer Himalaya or the foothills lying between the Himalayan Frontal Thrust (HFT) in the south and the Main Boundary Thrust (MBT) in the north, numerous active faults and neotectonic features have been reported<sup>1–11</sup>, which have generated major and great earthquakes<sup>12,13</sup>.

During the study of active tectonics in the Himalayan foreland basin, we came across interesting situations at a number of places just adjacent to the HFT, which defines the zone of convergence between the Himalaya and the Indo-Gangetic Alluvial Plains (IGAP), where evidences of normal faulting occur. This faulting has produced topographic features well displayed on Indian Remote Sensing (IRS) satellite images, aerial photographs and topographic maps. We report here a fault zone, referred to as the Singhauli Active Fault (SAF), which traverses through the Middle Siwaliks exposed on the hanging wall of the HFT and is further traceable into the alluvial fans and fan terraces of a number of streams flowing from the Siwaliks into the plains on the footwall of the HFT.

The multi-spectral satellite data of IRS-1D-LISS-III and PAN (date: 04 October 2002) and air-photos supported by the Survey of India topographic maps constituted the important data source for the present study. The satellite data have been digitally enhanced for feature extraction. On the aerospace data a number of lineaments and fault traces have been delineated. Various primary and secondary tectonic landforms have been mapped besides segmented fault scarps being recognized at places. Finally, selected ground-truth checks have been carried out to substantiate our interpretation.

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