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Removal of Nickel (II) from Aqueous Solution Using Marine Alga Sargassum swartzii in Continuous System

V. Sivasubramanian*, M. Jerold, Jacob Varun Dev, M. Aneesh Benny, Mohamed Swalih

Department of Chemical Engineering, National Institute of Technology Calicut, Kozhikode, Kerala-673601, India

*Corresponding author email: siva@nitc.ac.in, Tel.: +91 495 2285406

ABSTRACT

Biosorption of nickel (II) ions from aqueous solution onto *Sargassum swartzii* in continuous mode of operation has been studied. The involvement of various functional groups was elucidated using Fourier transform infrared spectroscopy (FTIR). The surface morphology of the biosorbent was visualized by means of Scanning electron microscopy (SEM). The EDAX analysis was also done to understand the elements and their contribution for the biosorption of Ni (II) ions. The biosorption was maximum at pH 4. The column experimental data was analyzed using Logit model. The results obtained from the experiments showed that *S. swartzii* can be used as effective biosorbent for the removal of Ni (II) ions from wastewater.

Keywords - Biosorption, Packed column, Nickel, Wastewater, Biomass, FTIR, SEM.

1. INTRODUCTION

Technological advances have created lot of environmental issues. Water pollution is one of the impacts due to the vast industrialization. From various metallurgical industries high volume of wastewater containing heavy metal ions are released into the natural environment. Heavy metal has significant effect on the environment and public health due to their toxicity. This heavy metal seems to get accumulated in the food chain and persistence in nature. World Health Organization (WHO) has categorized the heavy metals having immediate effects are cadmium, chromium, cobalt, copper, lead, nickel, mercury, and zinc. Nickel is one among the toxic metal released into environment in various ways such as mining and metallurgical activities. Also nickel is released by various industries such as steel, electroplating, battery and accumulators, pigments, ceramic and porcelain. Nickel has serious effects on human health and sometimes it acts as carcinogen [1]. Hence, it is dangerous for human health. Therefore this is to be removed before discharge of the effluents.

There are various conventional treatment methods for the removal of heavy metals such as chemical precipitation, chemical oxidation, ion exchange, filtration, electrochemical treatment, solvent extraction, reverse osmosis and membrane technologies. However, these methods are not feasible due to high treatment cost, production of toxic sludge and continuous chemical input [2-4]. Biosorption is a newly emerged separation technique for the removal of pollutants from wastewater [5, 6]. It is a reversible binding process. The metal ion from the aqueous solution bound to the biomass surface via functional groups. Various biomaterials such as algae, bacteria [7], fungi [8], and yeast cell [9] were used as biosorbents. In the present study macroalgae (seaweed) are exploited for the removal of nickel ion from wastewater. The objective of the study is to investigate the application of packed bed column for the continuous removal of Ni (II) ion from wastewater using *S. swartzii*. The biosorbents were characterized using SEM, EDAX and FTIR to understand their applicability. The breakthrough profile was analyzed using Logit model.

2. MATERIALS AND METHODS

2.1 Preparation of biosorbent

Raw *Sargassum swartzii* biomass, collected from Mandapam, Tamil Nadu, India, was washed with copious quantity of distilled water and sun-dried and subsequently dried in oven at 60° C for 24 hrs to remove the complete moisture. Dried samples were ground to an average particle size ranging from 0.5 to 1.0 mm and consequently used for the biosorption experiments without any further modification.

2.2 Preparation of adsorbate solution

The stock solution of Ni (II) of 1000 ppm concentration was prepared by dissolving 4.059 grams of analytical grade Nickel Chloride in 1000 ml of RO distilled water. The stock solution was further diluted with RO distilled water to desired concentration for obtaining the standard solutions for absorbance measurement. The sample solutions which were to be treated with the adsorbent were also prepared similarly by dissolving required quantity of the above mentioned salt in RO distilled water.

2.3 Characterization of biosorbent

The surface morphology of biosorbent was characterized using SEM, EDAX and FTIR. Scanning electron micrograph shows the changes in the surface texture before and after biosorption of metals. EDAX gives overall elemental information of biosorbent. FTIR reveals the involvement of functional groups for the biosorption of Nickel (II). Further, to know the presence of elements C, H, N and S, *S. swartzii* was analyzed using C-H-N-S Analyzer (Vario EL III, Elementar, Germany).

2.4 Packed Column Operation

Biosorption experiments were conducted in a glass column of packed bed. The column was fabricated with an internal diameter of 1.5 cm and length of 15 cm. The bed was filled with the *Sargassum* biomass for the biosorption of nickel ions. Glass wool was supported and the column was closed to maintain good liquid distribution. The Ni (II) solution of known concentrations at pH 4 was introduced using peristaltic pump (Rivotek-50171 002; Riveria, India) to the column at a flow rate of 10 mL/min. The pH was adjusted using 0.1N HCl/NaOH solution in multiparameter portable meter (Model H19829, Hanna Instruments, USA). Effluent samples were collected at regular time intervals to determine the residual dye concentration in the effluent solutions using Atomic absorbance spectrometer (Varian, Australia). The influent to the column was continued until there was no further adsorption, i.e. the operation was stopped when the effluent concentration exceeded a value of ~99.5 mg/L or higher.

3. RESULTS AND DISCUSSION

3.1 Characterization of biosorbent

3.1.1 SEM Analysis

The morphological changes in surface of the biosorbent was analysed by means of scanning electron microscopy (SEM). A SEM perusal of *S. swartzii*, before and after biosorption, noticeably envisages the morphological changes in the surface texture of algal biomass. The surface of the biosorbent was rough and rigid prior to the biosorption as shown in Fig.1a whereas a smooth and slimy morphological appearance was observed after biosorption as shown in Fig.1b. The SEM micrograph clearly revealed the surface texture and morphology of the biosorbent at different magnifications. The SEM analysis revealed important information on surface morphology where there is a formation of thin layer on the surface. The evidence form SEM illustrates the formation of cloudy layer was due to the loading of metal.

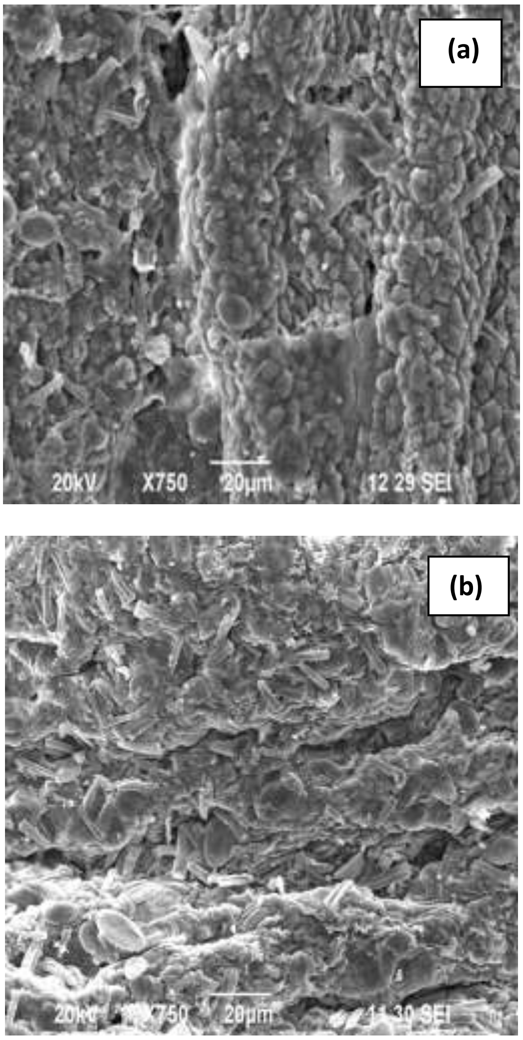

Fig.1. SEM images of *S.swartzii* (a) before Ni (II) biosorption and (b) after Ni (II) biosorption.

3.1.2 FTIR Analysis

The functional groups present in the biosorbents are studied using the Fourier Transform Infrared Spectroscopy (FTIR) at a wavelength of (400 – 4000 cm-1). The capacity of biosorption depends on the functional group reactivity and the surface porosity of the biosorbent. FTIR spectra of fresh biosorbent and Ni (II) adsorbed biosorbent are shown in Fig. 2a and 2b respectively. From the vibration spectra, it is observed that various functional groups present in the biosorbent plays a vital role in the biosorption of Ni (II) ions [10].

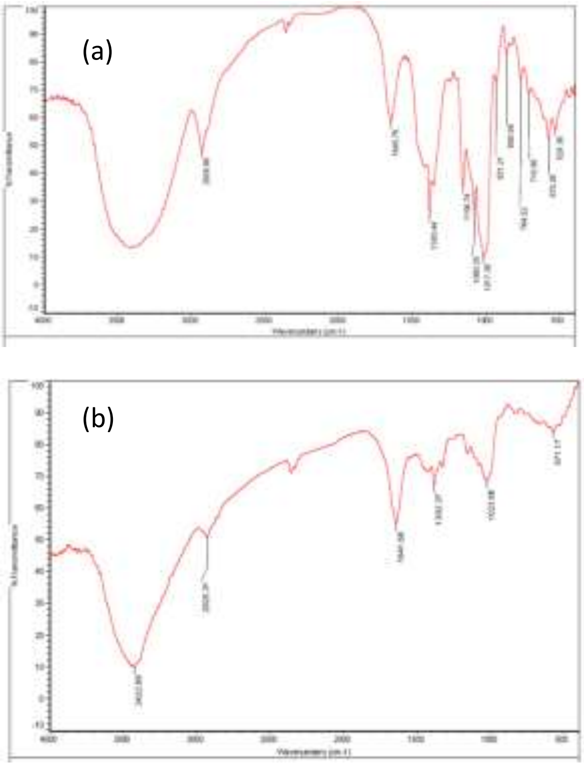

Fig.2. FTIR analysis of *S. swartzii* (a) before Ni (II) biosorption and (b) after Ni (II) biosorption.

3.1.3 EDAX Analysis

The adsorption efficiency of *S. swartzii* was confirmed by EDAX analysis results. The EDAX spectra of *S. swartzii* are shown in Fig.3. This micrograph revealed that the appearance of Ni (II) ion on the surface of the *Sargassum* biomass. EDAX spectra showed the presence of O, C, Ca, K, and Zn in the adsorbent which are known as the principle elements of the adsorbents.

3.1.4 CHNS Analysis

The CHNS analysis provides the percentage of elements in the biomass. Table.1 shows the elements present in the *S. swartzii* biomass. Basically, these carbon moieties may be stored in monomeric form or in the polymeric form. However, the polymeric form has more advantageous because polymers have a lesser effect on osmotic potential than monomeric form. In brown algae, the carbon contents are available in the alginic acid [11].

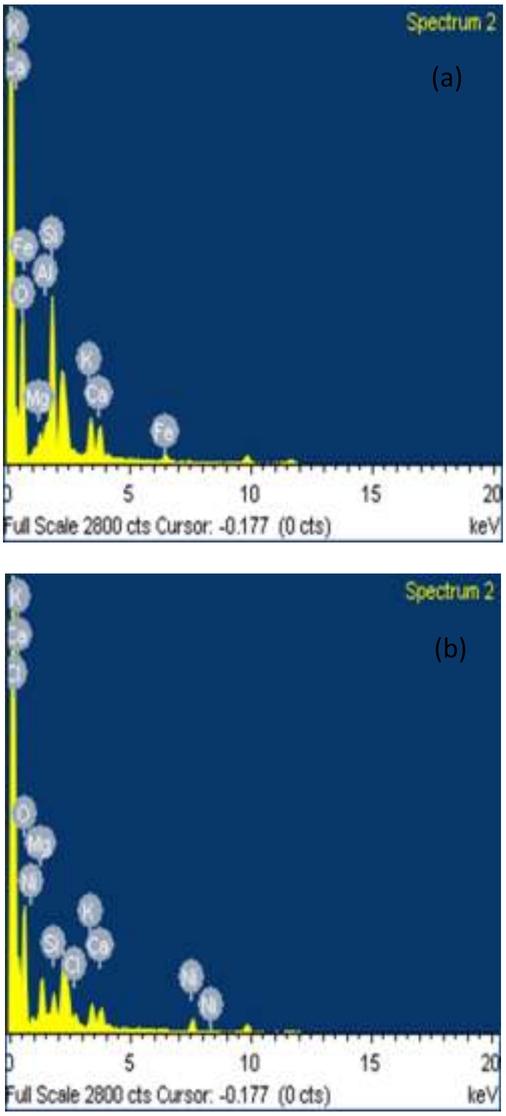

Fig. 3. EDAX analysis of *S. swartzii* (a) before Ni (II) biosorption and (b) after Ni (II) biosorption

Table.1 CHNS analysis of *Sargassum swartzii*

Element	Percentage (%)
C	30.11
H	4.66
N	0.96
S	0.45

3.2 Breakthrough curve profile

Fig.4 shows the breakthrough curve of the biosorption of Ni (II) ions onto the surface of the *S. swartzii* biomass. The exhaustion time was higher due to the increase in the bed depth. However, the adsorption capacity was highly influenced by bed depth. This was due to the accumulation of metals in the packed bed column and the quantity of the biosorbent in the column. The breakthrough time and the exhaustion time seem to increase with increase in bed depth. The sorption zone tends to move downwards, which resulted in the release of the effluents as shown in Fig. 4. The plot C/C_0 versus time for a constant flow rate, describes the increase in the ratio of C/C_0 as adsorbate zone moves through the column. Hence, a steep 'S' shaped curve was obtained.

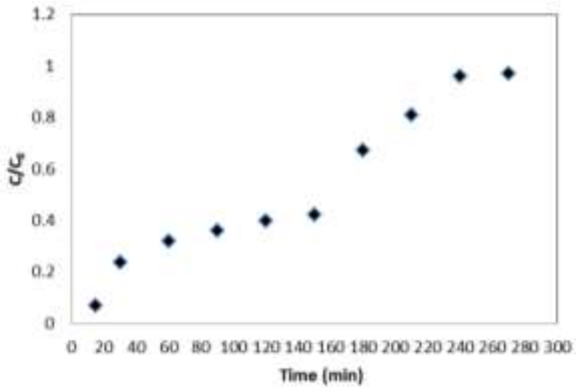

Fig.4 Breakthrough point for Nickel (II) Biosorption

3.3 Evaluation of adsorption column design parameters

The design parameters were determined and optimized for large scale adsorption. From the literature it is found that more mathematical models are available for the design of adsorption columns. In the present study, logit model was used for the design of fixed bed column [12, 13]. The logit equation can be written as:

$$\ln\left[\frac{C/C_0}{1-C/C_0}\right] = -\frac{KC_0X}{V} + KC_0t \qquad (1)$$

Where, C is the Concentration of Nickel (II) at any time t C_0 is the Initial Nickel (II) Concentration (mg/L); V is the Feed velocity, K is the rate constant of biosorbent ($1/mg^{-h}$), N is the Biosorbent capacity constant (mg/L).

Re-arranging (1),

$$\ln\left[\frac{C}{C_0-C}\right] = -\frac{KN_0X}{V} + KC_0t \qquad (2)$$

Plot of ln $C/(C_0 - C)$ vs. t gives a straight line with slope KC_o and intercept ($- KN_0$ X /V) from which K and No can be calculated. The values of adsorption rate constant (K) and adsorption capacity constant (N_o) were obtained as 1.5×10^{-3}(L/mg^{-h}) and 32046 mg/L and 1623 mg/L (1.623 kg/m^3) respectively. These values could be used for the design of adsorption columns. The adsorption capacity was found to be good. Hence, it could be concluded that *Sargassum* biomass is effective for Ni (II) removal.

4. CONCLUSION

From the present study, it was observed that the raw marine brown alga, *S. swartzii*, can be used as an effective biosorbent for the treatment of wastewater containing nickel (II) ions. The dried biomass S. swartzii has good mechanical stability to withstand the fluid flow. The SEM analysis before and after adsorption confirms that the biosorption of Ni (II) ions onto the surface of the biosorbent. The involvement of functional group in the sorption of Ni (II) was characterized using FTIR analysis. In addition, EDAX analysis revealed the elements involved in the biosorption process. The experimental results obtained were modeled using the logit model provides a description of the column parameters.

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