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Biosorption of heavy metal ions by chemically modified biomass of coastal seaweed community: Studies on phycoremediation system modeling and design

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ABSTRACT

Biosorption of heavy metals by seaweeds (marine macroalgae) is a potential environmental biotechnology technique for biotreatment of industrial effluents. However, the co-application of biomasses of different seaweeds for bioremoval of these inorganic pollutants from aqueous phase is very limited. In this study, for the first time, a coastal seaweed community composed of *Chaetomorpha* sp., *Polysiphonia* sp., *Ulva* sp. and *Cystoseira* sp. species harvested from the north coast of Turkey was first treated with sodium hydroxide and then used as natural biosorbent material for the bioremediation of zinc-containing synthetic wastewater. Batch biosorption experiments were performed to optimize the conditions of environmental parameters (pH, biosorbent quantity, heavy metal concentration and contact time). The biosorption capacity of biosorbent for zinc ions was highly affected by the operating conditions. Kinetic studies showed that the biosorption process was multistep, fast and diffusion controlled. The pseudo-second-order rate model well described the biosorption kinetics. The equilibrium data of zinc biosorption fitted best with Sips isotherm model and the maximum biosorption capacity of biosorbent from this model was calculated as 115.198 mg g^{-1}. Thermodynamic parameters indicated that the biosorption process was physical and spontaneous. Besides, a single-stage batch biotreatment system was designed and the kinetic performance of this biosorption system was evaluated. The obtained results revealed that the prepared composite biosorbent could be used as efficient novel biosorbent for zinc removal from aqueous effluents.

1. Introduction

Heavy metal pollution is a serious global environmental problem. These inorganic pollutants are often released into water bodies as a result of various anthropogenic activities. In particular, intensive technological and industrial developments have led to excessive use of heavy metal ions and thus increasing water pollution. Heavy metals are often reported to have harmful effects to human and other organisms due to their high toxicity and cumulative effects. Zinc is one of the most common heavy metals present in industrial effluents. It is an essential element for humans, plants and other living beings. The deficiency of zinc in human body leads to several adverse effects such as taste abnormality, diarrhea, lethargy, delayed healing of wounds and growth retardation (Ng et al., 2016). Although it is important for human health, excess zinc is toxic for humans and its main symptoms are nausea, dizziness, electrolyte imbalance and muscle stiffness (Afroze et al., 2016; Girardi et al., 2014).

Seaweeds (marine macroalgae) are important natural biomass resources. They are available in abundance, renewable, non-toxic and low in cost. Marine macroalgae have various bioactive compounds such as polysaccharides, proteins, lipids, polyphenols, carotenoids and vitamins. These phycochemicals have different functional groups including carboxyl, hydroxyl, phosphate and amine that can bind the heavy metals (Areco and dos Santos Afonso, 2010; Sanjeewa et al., 2016). Biosorption is one of the most promising remediation technologies for aquatic areas polluted with heavy metal ions (Gupta et al., 2015). The major advantages of biosorption using the biomass of seaweeds for wastewater treatment are less investment in terms of both initial and operational cost, simple design, easy operation and no effect of toxic substances.

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Turkey is surrounded by seas on three sides (Black Sea, Mediterranean Sea and Aegean Sea), and also it has an internal sea (Marmara Sea). The coastline of Turkey is 8333 kilometers. Numerous species of seaweeds from green algae, brown algae and red algae groups exist in these coastal regions of Turkey. Most of biomasses of seaweeds are collected in the beaches due to eutrophication and harmful effects to the environment and are treated as a waste. In consideration of macroalgae waste biomass is quite a lot in the coastal areas of Turkey, it is clear that the removal of heavy metal ions by biosorption technology from wastewater can be achieved in an inexpensive way.

Almost all previous studies on the removal of heavy metals focused on just one seaweed species (Anastopoulos and Kyzas, 2015; Zeraatkar et al., 2016). Very little attention was paid to the co-utilization of biomasses of different marine macroalgae that aimed to make a more effective biosorbent and save our environment from their detrimental effects. Thus, for the first time, a coastal seaweed community composed of *Chaetomorpha* sp., *Polysiphonia* sp., *Ulva* sp. and *Cystoseira* sp. species harvested from the north coast of Turkey was treated with sodium hydroxide and used as natural biosorbent material for the bioremediation of zinc-containing synthetic wastewater in this paper. The effects of various process parameters including solution pH, biosorbent amount, zinc ion concentration and reaction time on the heavy metal removal ability of biosorbent material were investigated in batch conditions. The equilibrium and kinetic data of zinc biosorption process were modeled using several isotherm models (Freundlich, Langmuir, Sips and Dubinin-Radushkevich) and kinetic models (pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion). The chemical and physical properties of composite biosorbent before and after heavy metal ion biosorption were also studied using the instrumental techniques of Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

2. Materials and methods

2.1. Biosorbent characterization

The surface properties of unloaded and zinc loaded biosorbent samples were visualized by a Scanning Electron Microscope (SEM, Zeiss Evo Ls 10). The infrared spectral studies were performed to determine the major functional groups involved in the biosorption of heavy metal ions. The spectra of raw and zinc loaded biosorbent samples were obtained by Fourier Transform Infrared Spectroscopy (FTIR, PerkinElmer Spectrum 400) in the wavelength range of 4000–400 cm^{-1}.

2.2. Heavy metal ion solution

A stock solution of zinc ions (1 $g L^{-1}$) was prepared from $Zn(SO_4)\cdot 7H_2O$ dissolution in distilled water. Necessary dilutions were made from the stock solution to prepare the working solutions in the concentration range of 10–30 $mg L^{-1}$. The initial pH of each solution was adjusted to the desired value with HCl and NaOH solutions (0.1 $mol L^{-1}$) before mixing the biosorbent. All chemicals used were of analytical reagent grade and were purchased from Merck.

2.3. Seaweed community and modification process

The coastal seaweed community composed of *Chaetomorpha* sp. (green algae), *Polysiphonia* sp. (red algae), *Ulva* sp. (green algae) and *Cystoseira* sp. (brown algae) species was collected from the north coast of Turkey. The harvested fresh macroalgae biomasses were washed with tap water, followed by several washings with distilled water to remove extraneous materials. They were dried at 80 °C in an oven until a constant weight was achieved. The dried macroalgae biomasses were crushed in a laboratory blender and sieved through a 0.5 mm standard sieve. For the pretreatment of these biomaterials, the samples of 1 g of biomasses were treated with 0.3 M solution of NaOH (100 mL) for 24 h under slow stirring. The pretreated biomasses were washed several times with distilled water to remove excess chemical substance and then dried as mentioned above. The obtained final products were thoroughly mixed in equal weight ratios and kept in a glass bottle for the biosorption studies.

2.4. Heavy metal biosorption experiments

Batch biosorption experiments were performed in a set of conical flasks containing 100 mL of zinc ion solutions to optimize various process parameters including pH, biosorbent quantity, heavy metal concentration and reaction time on the zinc removal ability of biosorbent. The flasks were agitated on an orbital shaker at 200 rpm and room temperature for desired contact times. After the experiments, the suspensions were centrifuged to remove the biomasses from the biosorption media and then the residual heavy metal ion concentrations in the solutions were analyzed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Thermo X Series II). The amount of heavy metal ion bound by the composite biosorbent (q_t and q_e, $mg g^{-1}$) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where C_0, C_t and C_e ($mg L^{-1}$) are the concentrations of heavy metal at the initial, a time t and equilibrium, respectively. V (L) is the volume of aqueous solution and M (g) is the mass of biosorbent.

2.5. Phycoremediation system modeling and design studies

The experimental equilibrium data of zinc ion biosorption were modeled by Freundlich, Langmuir, Sips and Dubinin-Radushkevich isotherm models. Biosorption isotherm models can also be used to predict the design of single-stage batch biosorption systems. Thus, a single-stage batch biosorption system was designed for the removal of zinc ions from aqueous solution based on the best fit isotherm model for this study. The pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models were used to model the obtained kinetic data for the biosorption of heavy metal ions. Besides, based on the pseudo-second-order parameters, the kinetic performance for the heavy metal biosorption system was also evaluated. The isotherm and kinetic parameters were obtained by the nonlinear curve fitting tool of SigmaPlot software package. The determination coefficient (R^2) and root mean square error (RMSE) analysis methods were used to determine the best fit models. A high R^2 and low RMSE values indicate the closer agreement of model with the experimental data.

3. Results and discussion

3.1. Properties of composite biosorbent

Fig. 1 indicates the SEM images of biosorbent before (a) and after (b) the biosorption process. The physical structure of biosorbent surface was irregular and rough. This morphological structure provides a larger biosorption surface for the biosorption of heavy metal ions. After the binding of zinc ions, the surface of biosorbent became dull because of the coating of biosorbent particles with the heavy metal ions.