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Study of Cu(II) removal by *Cystoseira crinitophylla* biomass in batch and continuous flow biosorption

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HIGHLIGHTS

- *Cystoseira crinitophylla* continuous flow column study.
- Copper adsorption capacity reaching 160 mg g^{-1}.
- Thomas and Clark models suitable for breakthrough prediction.
- Complete regeneration even after 35 cycles at pH 4.5.

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ABSTRACT

Copper biosorption by *Cystoseira crinitophylla* dry biomass was studied in a batch sorption experiment as well as a continuous regenerable column configuration. The algal biomass showed a very high adsorption capacity of 160 mg g^{-1} at 600 mg l^{-1} equilibrium concentration at pH 4.5. Sorption isotherms were fitted with the Langmuir and Freundlich model equations showing very good agreement with the data. Flowthrough experiments were performed in a column containing *Cystoseira* protonated dry biomass. The data were fitted with the Thomas and Clark models for heterogenous ion exchange and the role of pH, flow rate, bed height and feed concentration was investigated. Regeneration studies of the column showed 100% efficiency even after 35 sorption/desorption cycles at pH 4.5 and 96% for pH 2.6.

1. Introduction

Water and soil pollution by heavy metals constitutes today one of the greatest environmental problems. Different wastewater treatment processes used may diminish the amounts of heavy metal runoff, however significant amounts of low concentration effluents still find their way to the soil and groundwater and finally into the food chain.

There are several different techniques of heavy metal removal from wastewaters, but there is an increasing interest for metal sorbents based on plants, plant tissues and derivatives known as biosorption and phytoremediation. Biosorption is the passive uptake of heavy metals from aqueous solutions by biological materials (biosorbents). Various types of biomass have been used for the study of biosorption, including algae [1], bacteria [2] and fungi [3]. When metal concentration in the feed does not exceed 100 mg l^{-1} biosorption has been reported to be superior than existing wastewater treatment techniques [4]. Schiewer and Wong [5], have found biosorption techniques to be the only ones capable of providing drinking water at a very low cost. The advantages of the use of marine algae as a biosorbent have been extensively reported as their macroscopic structures offer a convenient basis for the production of biosorbent particles suitable for sorption process applications [6].

Packed bed columns are the common configuration for biosorption applications resulting in a better quality of the effluent utilising efficiently the materials sorption capacity [7].

Valdman et al. [8] used a mini-column of 0.5 cm ID and 1.6 cm in length packed with *Sargassum* sp., which exhibited Cu and Zn uptake capacities of 11.9 and 21.0 mg g^{-1}, respectively. Kaewsarn [9] used a glass column of 1 cm ID packed with 1 g of *Padina* sp. biomass, which exhibited Cu-biosorption capacities ranging between 49.58 and 52.76 mg g^{-1} at different initial copper feed

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concentrations. Volesky et al. [10] with a 2.5 cm ID and 50 cm length column packed with 38 g of dry *Sargassum filipendula* biomass, reported Cu-biosorption capacity of approximately 38 mg g^{-1} during seven regeneration cycles.

However, the strong dependence of the biosorption process on the pH of the feed solution and the differences in selectivity of various algal species [10,11] as well as frequent flow restrictions [12] have not yet allowed algal biomass biosorption to find wide application as a low cost wastewater treatment process for heavy metal removal.

In the present study the metal biosorption properties of *Cystoseira crinitophylla* in a packed bed column are presented by investigating its behaviour during sorption and regeneration cycles for high copper concentration feed solutions as well as batch sorption experiments.

2. Materials and methods

2.1. Reagents

Copper solutions were prepared by adequate dilution of a standard $CuCl_2$, 1 g l^{-1} solution purchased by Merck (9987 Titrisol-Merck) with deionised water.

2.1.1. Biomass

The collection of *C. crinitophylla* samples took place in Palio coasts, Kavala Gulf, in a depth range of 30–80 cm in Spring 2004. After mechanical separation from other organisms, it was washed thoroughly with distiled water, was left to dry at room temperature and further dryed at 50 °C to constant weight. After drying, the biomass was ground, sieved and stored in a dessicator. The particle size of the ground biomass was less than 1 mm. Heavy metal ions naturally occurring in the biomass due to environmental exposure, were removed by immersion under stirring into a 0.1 M HNO_3 solution for 15 min. The biomass was consequently filtered in a 63 μm sieve, washed with distiled water and dried in an oven at 35 °C for 48 h. The protonation process resulted in a 36.8–40.8% mass reduction of the biomass.

2.1.2. Batch sorption experiments

100 ml Cu^{2+} solution of different concentrations was added in 200 ml Erlenmeyer flasks, containing 0.25 g dried biomass weighed on a Mettler Toledo AB204 balance. Known amounts of 0.5 M HNO_3 were added, until the pH measured on a Metrohm 744 pH metre was stable at the desired values. The flasks were put in a Julabo SW22 shaking bath at 190 rpm, at 25 °C and were left shaking overnight for complete equilibration. Initial and final metal concentrations were measured by Flame Atomic Absorption Spectrometry (FAAS) (GBC Avanta Σ). All experiments were performed in triplicates.

2.1.3. Column experiments

Batches of 2, 4 and 6 g of dry weight of biomass were soaked into 10 ml of deionised water and were placed into columns without applying pressure. Each column consisted of a glass tube of 1 cm internal diameter and 50 cm height, positioned vertically. At the lower part of the tube an inert filter was fitted, before a manually operated flow control valve. On top of the column, a 500 ml funnel was kept constantly full with a Cu^{2+} solution of appropriate concentration. Gravity was the only driving force of the solution through the column. The flow was adjusted by means of the flow control valve at 5.5, 6.25 or 16.5 ml min^{-1} and samples were taken at appropriate time intervals every 100 ml of effluent. The solution was thermostated at 25 ^{0}C and the concentration of the effluent was monitored by means of Flame Atomic Absorption spectrometry (Perkin Elmer 5100). All experiments were performed in triplicates.

For column regeneration, the column was filled with 0.1 M HNO_3 and was sealed for 24 h. It was then washed with 300 ml of bi-distiled water in doses of 100 ml and was used for the consequent biosorption cycle.

2.1.4. Sorption isotherm equations

Several sorption equilibrium models are available for sorption isotherms data analysis. In this work, two isotherm model equations, namely, the Langmuir and the Freundlich, were employed to study the biosorption process. The Levenberg–Marquardt iteration method (Origin 7.0® software) was used in order to calculate the fitting parameters.

The Langmuir isotherm is described by Eq. (1),

$$Q = \frac{q_m bC}{1 + bC} \quad (1)$$

where C represents the Cu^{2+} ion concentration (mg l^{-1}) while b and q_m, are related to the affinity and maximum sorption, respectively. The model, which assumes a monolayer adsorption process on a homogeneous surface, is one of the most commonly used for equilibrium isotherm studies. However, factors such as differences in

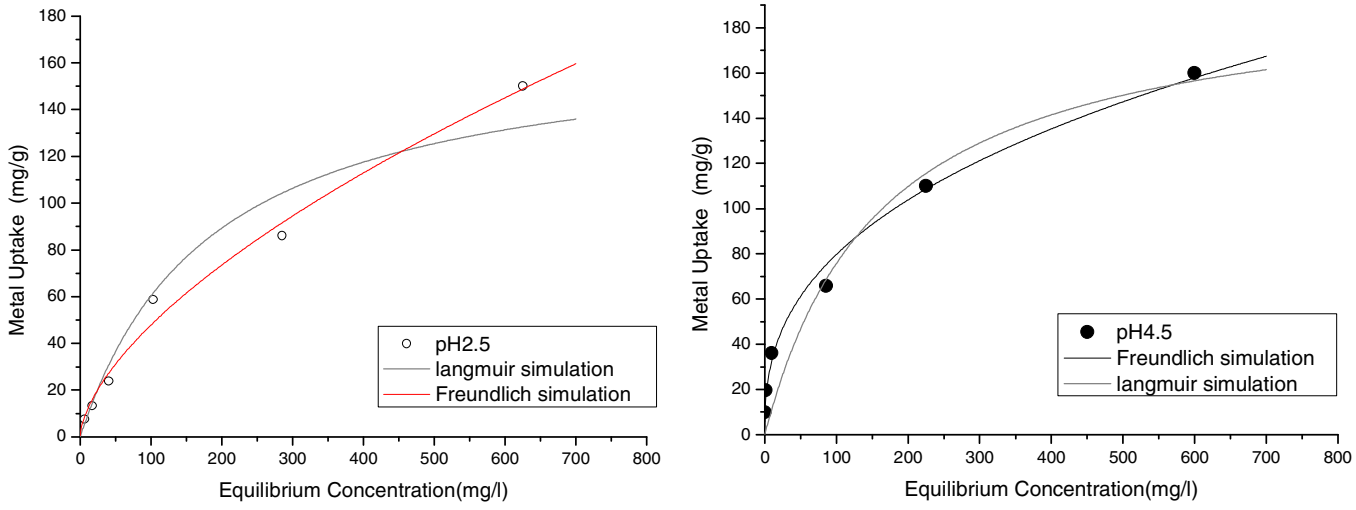

Fig. 1. Cu^{2+} sorption isotherm and Freundlich/Langmuir model equations fitting at pH 2.5 and 4.5.