

Effect of Chemical Modification of Functional Groups on Copper(II) Biosorption by Brown Marine Macroalgae *Ascophyllum nodosum*

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Abstract : The principal mechanism of metal ions sequestration by brown algae involves the formation of complexes between the metal ion and functional groups present on the cell wall of the biological material. To understand the role of functional groups on copper(II) uptake by *Ascophyllum nodosum*, some functional groups were chemically modified. The esterification of carboxylic groups was carried out by suspending the biomass in a methanol/HCl solution under stirring for 48 h and the blocking of the sulfonic groups was performed by repeating the same procedure for 4 cycles of 48 h. The methylation of amines was conducted by suspending the biomass in a formaldehyde/formic acid solution under shaking for 6 h and the chemical modification of sulfhydryl groups on the biomass surface was achieved using dithiodipyridine for 1 h. Equilibrium sorption studies for Cu²⁺ using the raw and esterified algae were performed at pH 2.0 and 4.0. The experiments were performed using an initial copper concentration of 300 mg/L and algae dose of 1.0 g/L. After reaching the equilibrium, the metal in solution was quantified by atomic absorption spectrometry. The biological material was analyzed by Fourier Transform Infrared Spectroscopy and Potentiometric Titration techniques for functional groups identification and quantification, respectively. The results using unmodified algae showed that the maximum copper uptake capacity at pH 4.0 and 2.0 was 1.17 and 0.52 mmol/g, respectively. At acidic pH values most carboxyl groups are protonated and copper sorption suffered a significant reduction of 56%. Blocking the carboxylic, sulfonic, amines and sulfhydryl functional groups, copper uptake decreased by 24/26%, 69/81%, 1/23% and 40/27% at pH 2.0/4.0, respectively, when compared to the unmodified biomass. It was possible to conclude that the carboxylic and sulfonic groups are the main functional groups responsible for copper binding (>80%). This result is supported by the fact that the adsorption capacity is directly related to the presence of carboxylic groups of the alginate polymer, and the second most abundant acidic functional group in brown algae is the sulfonic acid of fucoidan that contributes, to a lower extent, to heavy metal binding, particularly at low pH.

Keywords : biosorption, brown marine macroalgae, copper, ion-exchange

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