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Optimization of nickel biosorption by chemically modified brown macroalgae (*Pelvetia canaliculata*)

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ABSTRACT

In the present work, various forms of algae *Pelvetia canaliculata* were prepared by different chemical modifications, in order to get the best form of algae for the maximum uptake of nickel. Potentiometric titration revealed that the carboxyl groups were more abundant (3.9 mmol/g) as compared to hydroxyl groups (2.0 mmol/g) on the biosorbent surface. Fourier transform infrared (FTIR) analysis of algae was done to identify the role of different functional groups present on algae surface during nickel biosorption. The protonated algae showed least sorption of nickel suggesting that after acid treatment, some of the binding sites were destroyed. Among the various forms of prepared algae, Na-algae prepared directly from raw algae (without protonation) showed highest uptake of nickel. The release of sodium ions during the uptake of nickel ions has shown that the current biosorption mechanism involves ion-exchange being a stoichiometrical ratio of 2:1 between sodium and nickel ions.

1. Introduction

Heavy metals are essential for various biological activities in living organisms; nevertheless, they are considered as toxic at higher concentrations. The presence of toxic metal ions in the environment has been recognized as deleterious to the ecosystem and human health due to their non-degradability, biomagnification and toxicity. Besides the mining and metal related industries, other sources which discharge metal-laden effluents include leather tanning, battery, glassware, ceramics, electroplating, paints and photographic industries [1]. Compared to conventional techniques such as precipitation or synthetic ion exchange resins, biosorption process offers the economical and efficient approach for the remediation of metal bearing wastewaters because of eco-friendly characteristics, low cost, high uptake capacity, lack of toxicity constraints, less sludge, possible regeneration of biosorbent and availability of biosorbents worldwide [2].

One of the important and widely used biosorbents is marine algae, which possess a high metal-binding capacity for various metals [3–5] with the cell wall playing an important role in binding [6,7]. The high metal binding capacity in algae is due to the presence of various functional groups such as carboxyl, amino, sulfonate and hydroxyl groups, which can act as binding sites for metals. Among different types of algae, brown algae has been found to be very effective biosorbents in removing heavy metals from water and wastewater because of their high alginate content, higher uptake capacities, similar to commercial ion-exchange resins and their unlimited availability in the oceans [2,3,8–10]. Alginate, which is composed of mannuronic and guluronic acids, is a major polysaccharide in brown algae and offers carboxyl groups [11]. It constitutes between 10% and 40% of the brown algal dry weight [12]. Brown algae also contain between 5% and 20% of the sulfated matrix polysaccharide fucoidan [13] about 40% of which are sulfate esters. Alginate and fucoidan are known for their metal binding properties whereby ion exchange between metal ions occurs [14].

To enhance the removal efficiency of metal ions by different algae, various pretreatments have been reported in the literature. Pretreatment may be in terms of hardening the cell wall structure through a cross-linking reaction using epichlorohydrin [15] or increasing the negative charge on the cell surface by NaOH treatment [16], or opening of the available sites for the adsorption by acid treatment [17], and enhancing the ion exchange by initial saturation of biomass with easily replaceable ions such as Ca or Na to facilitate the metal sorption [18].

The importance of any given group for biosorption of a certain metal by a certain biomass depends on various factors such as: the number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the site (i.e., availability), and affinity between site and metal (i.e., binding strength) [19]. Binding strength is one of the important parameters in biosorption process in which ionic (electrostatic) binding and covalent binding are the important ones during metal binding. From different literature sources, it can generally be concluded that the light metals (alkaline

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and alkaline earth metals) bind less strongly than the heavy metal ions [20]. Therefore, the former do not strongly interfere with the binding of the latter.

Metal affinity to the biomass can be manipulated by pre-treating the biomass with alkalis, acids, detergents and heat, which may increase the metal uptake. Further, the surface modification approach has been suggested to be more cost-effective, as the modification agents are normally less expensive than entrapment materials, the sorptive capacity is enhanced, and the mass transfer is not affected [21]. Understanding the binding mechanism can help to obtain stoichiometric information for the preparation of commercially applicable biosorbents and for the optimization of process conditions. In order to determine the binding mechanism, one must identify the biopolymers and functional groups of the biosorbent participating in the binding interaction.

In the present study, different chemical modification methods were employed to raw algae (*Pelvetia canaliculata*) in order to prepare surface modified forms and their potential towards nickel [Ni(II)] biosorption was assessed considering the ion exchange mechanism. Nickel was selected as model pollutant as its salts are used in many industrial applications. Ni(II) is essential for living organisms under permissible limits and it participates in various metabolic reactions such as ureolysis and acidogenesis [22]. However, long term exposure to higher Ni(II) concentrations may lead to various health problems including skin dermatitis, gastrointestinal distress, lung cancer, renal edema and pulmonary fibrosis [23,24]. The World Health Organization's (WHO's) permissible limit for Ni(II) in drinking water is 0.5 mg/L [25]. The biosorption kinetics on raw and modified algae was examined and the role of functional groups in Ni(II) biosorption was discussed based on the data obtained from potentiometric titration, Fourier transform infrared (FTIR) analysis and esterification studies.

2. Experimental methods

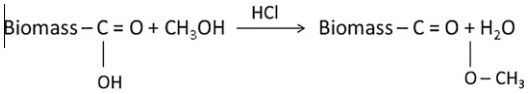
2.1. Biomass preparation

The brown seaweed *P. canaliculata* was collected at the Northern coast of Portugal. *P. canaliculata* is a common brown seaweed (*Phaeophyta*) growing on the rocks of the upper shores of Europe from Iceland to Spain, including Norway, Ireland, Great Britain, the Netherlands, France and Portugal. The sun-dried seaweed was washed with deionized (D.I.) water to remove sand and excess salts followed by drying over night at 45 °C in an oven (BINDER ED53). The biomass was then crushed using a mill (Retsch, ZM 100), sieved (Retsch, AS 200) to obtain the size fraction of 1–2 mm, and stored until use. It was termed as raw algae. Using the raw algae, some biomass was subsequently protonated by soaking into 0.2 M HNO_3 under constant shaking (VWR Advanced digital system) for different cycles of different time periods. After each cycle, the solution was replaced with freshly prepared solution. The biomass was then rinsed with D.I. water several times until pH reached ~4.0 and, later, it was dried at 45 °C. The prepared algae were termed as protonated (H^+) algae.

The biomass was also converted to different ionic forms (Na-, K-, Ca- and Mg-) using the raw as well as the protonated form by soaking them into 0.5 M of respective chloride solutions (NaCl, KCl, $CaCl_2$ and $MgCl_2$) solution for 2 cycles of 24 h each under slow stirring. 1.0 M of respective metal hydroxide solutions (NaOH, KOH, $Ca(OH)_2$ and/or $Mg(OH)_2$) were used to control the solution pH (~5.5–6.0) where protonated algae were used. After each cycle, the old solution was replaced with freshly prepared new solution. Afterwards, the Na-, K-, Ca- and/or Mg-loaded algae was rinsed with D.I. water until achieving a low conductivity solution and pH about 4.0 (in case of H^+-algae), and about 6.0–6.5 (in case of raw algae). Finally, the algae were dried at 45 °C for 24 h and stored until use. The prepared algae were termed as metal-loaded algae (Na-, K-, Ca- and/or Mg-loaded algae). Details of modification methods are listed in Table 1. Attempts were also made to prepare the protonated Na-algae by varying the experimental conditions and results are presented in Table 2. Sodium salts were used as these are highly soluble in water as compared to Mg and Ca salts.

2.2. Blocking of carboxyl and sulfonate groups in algae

Esterification of carboxyl group was carried out by suspending the biomass (2 g) in methanol (130 mL) and concentrated hydrochloric acid (1.2 mL) and equilibrated for 6 h at 25 °C [26]. Esterification of carboxyl acids present on the cell wall occurs according to following reaction:



Afterwards, the biomass was washed with D.I. water nine times in batch conditions (10 g/L; 20 min/wash) and dried at 45 °C for 12 h. The modification of sulfonate groups was done by the method reported elsewhere [27]. For the esterification of sulfonate groups, biomass (2 g) was suspended in methanol (130 mL) and concentrated hydrochloric acid (1.2 mL) and equilibrated for four cycles of 48 h continuous agitation, with replacement of the methanolic HCl between cycles [27]. Researchers [27] have also reported that the methanolic HCl treatment of the algal biomass resulted in significant decrease of the sulfonates concentration. They reported that after three successive treatments, there were no sulfonates detectable [27]. The sorption experiments with the modified biomass were carried out in batch conditions, as described in Section 2.7 for the nickel biosorption experiments.

2.3. Biomass digestion

To determine the amount of metal ions present in raw and metal-loaded biomass, the samples were digested in a microwave oven (Anton Paar, Multiwave 300) after adding 5.0 mL D.I. water, 4.0 mL HNO_3 (Merck) and 12.0 mL HCl (Merck) to 0.5 g of sample. The samples were cooked at 140 °C for 2 h and then the samples were left to cool. The metal concentrations in the digests were determined by atomic absorption spectrometry (AAS) (GBC 932 Plus, Perkin Elmer) after filtration through cellulose acetate membrane filters (Ref. Albet-CA-045-25-BI). The obtained results are shown in Table 3.

2.4. Solutions preparation

Nickel(II) solutions were prepared by dissolving a weighed quantity of $Ni(NO_3)_2{\cdot}6H_2O$ (Merck with purity > 98%) in D.I. water. The pH of each test solution was adjusted to the required value with diluted HCl and NaOH solutions. 0.5 M of NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions were prepared by dissolving respective chloride salts (Merck with purity > 99.5%). 1.0 M NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$ solutions were prepared by dissolving the respective hydroxide salts (Merck with purity > 99.5%).

2.5. Fourier transform infrared (FTIR) analysis

The chemical groups on the algae surface were detected through FTIR spectroscopy (IRAffinity-1, Shimadzu, with EasiDiff