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Green macroalgae from the Romanian coast of Black Sea: Physico-chemical characterization and future perspectives on their use as metal anions biosorbents

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ABSTRACT

Over the last years, algal blooms occurrences have increased on the Romanian Black Sea coast. In this study, *Ulva rigida* and *Cladophora sericea* green algae were used to investigate the removal of As(III), As(V), Sb(III), Se(IV) and Se(VI) in aqueous solution. In virgin forms, both macroalgae showed good perspectives for application on antimony and selenium uptake from water, although no significant efficiency towards arsenic was observed. Several treatments were applied to the algae to eventually enhance their adsorption capacity. Potentiometric titrations and infrared spectroscopy confirmed favorable chemical modifications in algae surface due to HDTMA and ammonium treatments, although no considerable increase in the biosorption ability was found. *C. sericea*, in virgin form, was selected for further studies on the uptake of Se(IV) and Se(VI). The best results for Se(IV) removal (0.5 mg/g) were found at pH 2–4 and for Se(VI) (0.2 mg/g) at pH 2–3. The equilibrium isotherm for the adsorption of Se(IV), at pH 2 and 20 °C, reported a maximum experimental adsorbed amount of 0.74 mg/g and a Langmuir monolayer capacity of 4 mg/g, which are substantial values considering that the biosorbent (dead marine seaweeds) is a residue and requires no significant processing before use.

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1. Introduction

Water pollution with heavy metals and metalloids represents a serious threat to environmental and human health. Disposal of wastewaters containing critical levels of these pollutants leads to contamination of natural water sources and food chains, causing toxic effects in biota and humans (Anastopolous and Kyzas, 2015).

The conventional methods used to treat heavy metals contaminated wastewaters include precipitation, chemical

reduction, ion exchange and membrane separation. These methods though, can be expensive and complex due to the high volumes of wastewaters to treat, difficulty of removing low concentrations (mg/L or µg/L) and due to different chemical species that can occur, depending on pH and oxidation conditions (He and Chen, 2014; Mandal et al., 2015).

Adsorption on biomass has emerged as a promising clean-up biotechnology (He and Chen, 2014), most of the literature studies being focused on heavy metals such as copper, zinc, cadmium, nickel, cobalt and lead from wastewaters

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Nomenclature

Abbreviations

CEMUP	Centro de Materiais da Universidade do Porto
CP	<i>Cladophora sericea</i> after protonation treatment
CV	<i>Cladophora sericea</i> in virgin form
CV-Se	<i>Cladophora sericea</i> loaded with Se(IV)
EDS	Energy Dispersive X-Ray Spectroscopy
FTIR	Fourier transform infrared spectroscopy
HDTMA	hexadecyltrimethylammonium
NS	not significant
SC	surface charge (mmol/g)
SE	standard error of the regression
SEM	Scanning Electron Microscopy
UA	<i>Ulva rigida</i> after ammonium treatment
UH	<i>Ulva rigida</i> after hexadecyltrimethylammonium treatment
UP	<i>Ulva rigida</i> after protonation treatment
UV	<i>Ulva rigida</i> in virgin form

Symbols

C_a	concentration of HCl solution (mol/L)
C_b	concentration of NaOH solutions (mol/L)
C_{eq}	equilibrium concentration of solute in the liquid phase (mg/L)
C_f	final concentration (mg/L)
C_{in}	initial solute concentration (mg/L)
K_d	Partition coefficient (L/g)
K_F	Freundlich constant related to the adsorption capacity (mg/g (L/mg) ^{1/n})
K_L	Langmuir constant (L/mg)
m	mass of algae (g)
n	Freundlich constant related to the intensity of the adsorption
q	adsorbed amount of solute, per g of alga (mg/g)
q_e	adsorbed amount of solute, per g of alga, in equilibrium (mg/L)
Q_m	maximum biosorption capacity predicted by Langmuir model (mg/g)
R^2	coefficient of determination of the regression
v	volume of solution (L)
V_a	added volume of NaOH solution (mL)
V_b	added volume of HCl solution (mL)
V_T	total liquid volume in the titration cell (mL)

(Sari and Tuzen, 2008, 2009; Anayurt et al., 2009; Vilvanathan and Shanthakumar, 2015; Paduraru et al., 2015). Very good results have been reached using brown algae, in comparison to green and red algae (Davis et al., 2003; He and Chen, 2014). Although the biosorption of cationic metals is relatively well established, the removal of metalloid oxyanions, such as arsenic, selenium and antimony by marine macroalgae was not explored enough up to now. In addition, many of the research papers published on the removal of these species by biosorbents (including marine seaweeds) have been conducted using unreal adsorbate levels (hundreds of mg/L, which hardly can be found in contaminated waters), as noticed by Ungureanu et al. (2015a) and Santos et al. (2015), so the results are not illustrative of the expected performance. The most promising results on the removal of Sb, Se and As have been found for iron-coated and impregnated materials (activated carbons, resins, oxides and Fe-binary oxides).

Antimony, selenium and, especially arsenic, are found in trace amounts in the environment, due to natural reasons or, in higher and toxic concentrations, generated by anthropogenic sources. Mining activities, combustion of fossil fuels, oil refining and agricultural activity are known to generate waters contaminated with these elements (Ungureanu et al., 2015a; Santos et al., 2015), whose remediation is of unquestionable importance. In aqueous solution, As, Sb and Se are mainly found in two oxidation states: As(V) and As(III), Sb(III) and Sb(V) and Se(IV) and Se(VI), respectively; the reduced form, of each one of the elements, is more toxic than the oxidized one (Bencze, 1994; Jain and Ali, 2000; Jensen et al., 2005).

In this study, green algae, in raw and modified forms, were studied as biosorbents for As(III), As(V), Sb(III), Se(IV) and Se(VI) from aqueous solutions. The high availability and short life cycle make algal biomass a quantitative available resource. Due to the intensification of the eutrophication process on the coast of the Black Sea, the hard substratums that were populated mostly by brown algae have been replaced by green and red algae (Bologa and Sava, 2012). The study includes a characterization of the algae and an evaluation of their biosorption potential both in natural and chemically modified forms.

2. Materials and methods

2.1. Biosorbent preparation

Ulva rigida and *Cladophora sericea* were collected on the Romanian coast of the Black Sea in August 2014. The seaweeds were washed with distilled water until the wash water reached a conductivity value close to that of distilled water. The conductivity was measured using a calibrated HI 8733 conductivity meter (Hanna Instruments, Italy). After the washing process, the seaweeds were dried in the oven at 55 °C at least for 24 h. Finally, the algal material was grinded to a smaller particle size (0.5 cm approximately). The algae were dried again and kept in a desiccator. These algae samples were termed as UV (*U. rigida* virgin) and CV (*C. sericea* virgin).

Three different chemical treatments were applied to the algae: (i) protonation, (ii) treatment with HDTMA (hexadecyltrimethylammonium, cationic surfactant), and (iii) treatment with ammonium.

Protonation was carried out for both *U. rigida* and *C. sericea*. HNO₃ 1 M solution was put in contact, under stirring, with 8 g/L of algae, for 6 h. The seaweeds were then washed and separated by filtration until the filtrate reached a pH value of 4–4.5, and finally dried at 60 °C in the oven (Ungureanu et al., 2015b). The protonated *U. rigida* and *C. sericea* forms were respectively designated as UP and CP.

The chemical modification of *U. rigida* by the cationic surfactant was performed by contacting a 5.0 g/L HDTMA solution (prepared by dissolution of hexadecyltrimethylammonium bromide, analytical grade, Sigma–Aldrich) with algae (dosage of 10 g/L) for 24 h, under mechanical stirring. The mixture was filtered, the seaweed washed with distilled water and dried at 60 °C. The treated alga was designated as UH.

The chemical modification by ammonium was carried out in a similar procedure, using an algae dosage of 10 g/L and 0.1 mol/dm³ ammonia solution (prepared by dilution of a commercial NH₃ 25% solution, analytical grade, Sigma–Aldrich) and a stirring contact time of 24 h. After solid–liquid separation by filtration and washing, *U. rigida* treated with NH₃ (named as UA) was dried in the oven at 60 °C.

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