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Research article

Biosorption removal of benzene and toluene by three dried macroalgae at different ionic strength and temperatures: Algae biochemical composition and kinetics

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ABSTRACT

Release of low–molecular aromatic hydrocarbons (HC) into natural waters brings severe consequences to our environment. Unfortunately very limited information is available regarding the treatment of these pollutants. This work evaluated the use of brown, green and red macroalgae biomass as biosorbents of benzene and toluene, two of the most soluble HC. Raw seaweed biomasses were completely characterized, then evaluated under different temperatures and ionic strengths to assess their potential as biosorbents and to elucidate the biosorption mechanisms involved. Brown macroalgae registered the highest removal capacities for benzene and toluene (112 and 28 $mg \cdot g^{-1}$, respectively), and these were not affected at ionic strength < 0.6 M. Langmuir and Sips isotherm equations well described biosorption data, and the pseudo-second order model provided the best fit to the kinetics rate. Hydrocarbons are adsorbed onto the diverse chemical components of the cell wall by London forces and hydrophobic interactions.

1. Introduction

Water pollution by oil spills is a serious problem in petrochemical activities, with a total volume of oil lost to the environment in 2015 of approximately 7000 tonnes (*ITOPF*, 2016). It has been calculated that around 1–3% (sometimes up to 15%) of crude oil can pass into the dissolved state (Njobuenwu et al., 2005), although low molecular aromatic compounds like benzene and toluene, present higher water solubilities and bioavailabilities than other petroleum hydrocarbon components and, as a consequence, have been classified as a risk to the environment (US EPA, 2013). In–situ removal of these pollutants by adsorption onto activated carbon has been considered a more suitable technology than aeration or photocatalysis, mainly due to the hydrophobic nature of the adsorbent, its high surface area and high affinity to a broad type of pollutants (Cooney, 1999). However, the advantages of activated carbon could be restricted for remediation purposes because it has been associated to secondary ecotoxicological effects in sediments (Lillicrap et al., 2015). Another viable option is the usage of macroalgae utilized as biosorption matrix, a process that constitutes a low cost and environmental friendly alternative for the removal of the dissolved fractions of petroleum (Hubbe et al., 2014). Biosorption involves the passive binding to metabolic inactive materials derived from i.e. industrial or agricultural by-products, forestry, marine or terrestrial biological materials and microbe biomass (Cazón et al., 2014; Holkar et al., 2016; Valili et al., 2013). For the special case of macroalgae biomass, it is widely available (15.8 million tons harvested in 2010), occurs in a wide variety of habitats (ranging from marine to freshwater), and contains different active sites in its cell structures that are accessible for organic biosorption, i.e. hydroxyl, carboxyl and amine (Ghadiryanfar et al., 2016; Henriques et al., 2017).

There are three types of macroalgae: red, green and brown (Davis et al., 2003), but all have cell walls that are complex networks of biopolymers consisting in a skeleton of crystalline and fibrous parts (cellulose, hemicellulose, etc.) and an embedding

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matrix of specific polysaccharides, proteoglycans and others molecular components that depend on the type of seaweed. Red algae possess sulfated galactans (i.e. carrageenan), and xylan or mannan fibrils (also presented in green algae), which also include mixed glucan or ulvan linkages. Brown algae are comprised mainly of sulfated fucans and alginates (Synytsya et al., 2015).

Seaweeds, especially brown algae, have been effectively used as biosorbents for heavy metals (Davis et al., 2003), dyes (Hubbe et al., 2014) and polyaromatic hydrocarbons (Chung et al., 2007). Preliminary studies have shown that seaweed biomass can be successfully used to remove many organic pollutants like phenanthrene, phenol and nonylphenol (Chung et al., 2007; Zhang et al., 2015). Unfortunately, the number of studies on water–soluble hydrocarbon fraction is low, with a knowledge gap relative to the ionic strength and temperature effects on benzene and toluene removal. The potential of this technology can be further improved by evaluating the biomass removal capacity for the most water–soluble hydrocarbons (benzene and toluene) under controlled laboratory conditions to increase our knowledge of its use for remediation purposes.

The main objective of this work was to investigate the influence of ionic strength on the benzene and toluene biosorption capacity of three different types (brown, green and red) of macroalgae biomass. The studies were also conducted at 4 and 25 °C in order to simulate temperature variations that could be registered along the water column in oil contaminated waters (Millero, 2005). Additionally, the chemical and physical characterization of algae was conducted to provide insights into the hydrocarbons biosorption mechanisms. All samples were fully dehydrated, milled and mixed in order to avoid any metabolic bioactivity, and to assure homogeneous determinations.

2. Experimental

2.1. Materials and reagents

Samples of the macroalgaes *Macrocystis pyrifera*, *Ulva expansa*, and *Acanthrophura spicifera* (brown, green and red seaweed, respectively) were collected in La Paz, Baja California Sur, Mexico and Ensenada, Baja California, Mexico. The seaweed samples were rinsed with plenty of deionized water (<11 μS/cm) and dried in an oven at 50 °C during 72 h. Algae biomass was sieved to a particle size of 0.8–1 mm with a Mini-Cutting Mill (Thomas Wiley) before used in characterization and sorption experiments. The model soluble HC were represented by benzene and toluene (Sigma–Aldrich, 99% purity).

The adsorption capacities of the inert biomass were determined in different ionic strength solutions: (1) deionized water as a control; (2) NaCl solutions with concentrations from 0.3 to 0.75 M; and (3) artificial seawater solution Instant Ocean® (33 g L^{-1}) ≃0.76 M.

2.2. Algal properties testing

2.2.1. Physical characterization

Surface area ($m^2 \cdot g^{-1}$) and pore size distribution of the macroalgae were calculated by BET isotherms and DFT (Density Functional Theory), respectively, using a Micromeritics ASAP 2020 instrument at 77 K (Brunauer et al., 1938).

Proton binding curves and the point of zero charge (pH_{PZC}) were determined by potentiometric titrations (Mettler Toledo model T50) following the stablished protocol by Flores-Chaparro et al. (2016). A series of 0.1 g biomass samples were placed in 50 mL NaCl solutions with different ionic strengths ($I = 0.01, 0.15, 0.3$ and 0.45 M). The system was allowed to equilibrate for 16 h and then the experiment initiated. The pH solution was adjusted to pH 3 by adding 0.1 N HCl. During the titration, the solution was continuously stirred in N_2 atmosphere to avoid the interference of CO_2. NaOH standard (0.1 N) was used as titrant. The titration curves consisted of about 50–70 experimental points between pH values of 3–11 because of the buffering effect of water at pH < 2 and >12 (Jagiello, 1994). The resulting titration curves were transformed into proton binding curves Q (pH) using the numerical procedure SAIEUS (Solution of the Adsorption Integral Equation Using Splines) which indicates the total amount of protonated sites (Bandosz et al., 1993). Raw biomass was grinded with KBr pellets and studied by a Thermo Nicolet 6700 in transmittance mode in the range of 600–4000 cm^{-1}, with a 4 cm^{-1} resolution and 64 scans. The ash content of samples was determined by a TGA–Thermo Cahn thermo–gravimetric analyzer under an air flow rate of 2 $mL \cdot min^{-1}$, at a heating rate of 5 $°C \cdot min^{-1}$, up to a final temperature of 900 °C. The degree of swelling (S_w) was determined in triplicate runs by weighing a precise mass of 0.5 g of dry biocomposites which was placed in a beaker at 25 °C with 20 mL of distilled water. The swollen materials were removed from water and weighted (W_t) after 24 h. The S_w value was computed by the following equation: $S_w = ((W_t - W_o)/W_o)^*100$, where, W_o is the mass weight of the dry biomass ($t = 0$) and W_t is the weight of the swollen material at time t.

2.2.2. Chemical characterization

An extensive chemical analysis of algae was made to characterize the main molecular structures associated with the HC biosorption. The total nitrogen content in crude protein was determined by the Kjeldahl method (Marinho-Soriano et al., 2006), using a conversion factor of 6.25 to calculate protein content (AOAC, 2006); crude fat and total sugars were estimated through the fatty acid hydrolysis and by the Fehling – Soxhlet extraction procedure (AOAC, 2006; Peña-Rodríguez et al., 2011). Cellulose, hemicellulose and lignin were determined by a semiautomatic fiber analyzer (ANKOM Technology, Macedon, NY, USA), which is based on the use of a neutral and acid detergent methodology reported by Van Soest et al. (1991). Alginate extraction was carried out using the sequence of ion–exchange reactions proposed by Bertagnolli et al. (2014). Sulfated polysaccharides constitute an important fraction of algal biomass. It was for this reason that the main sulfated polysaccharide (fucans) present in brown algae were characterized according to Ale et al. (2011). The biomass soluble fraction was estimated using a TOC–meter (Shimadzu Co. Model TOC–VCSN), conducted by placing 0.1 g of dry macroalgae in contact with deionized water during 48 h and then filtering it through a 0.22 μm pore size filter. The concentration of inorganic elements in the biomass structure were determined through an acid digestion of the ashes (previously obtained by 5 g of biomass in a muffle at 550 °C) during 3 h using 10 mL of a 1:1 ($v \cdot v^{-1}$) mixture HNO_3 and HSO_4 solution. The concentrations of Zn, Ca, Fe, K, Cu, Cr, Ni, Mn, Mg and Na were determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES) by a Varian 730–ES spectrophotometer.

2.2.3. Biosorption uptake experiments

The benzene and toluene capacity of the raw biomass was determined in deionized water and saline solutions of different concentrations (Shell Chemicals, 2012; Xie et al., 1997), including the maximum solubility of each compound (Table S1, Supplementary information). The salting coefficients κ_s of the hydrocarbons were calculated according to the Setchenov equation $log(S_o/S) = \kappa_s C$, where S_0 is related to the solubility of benzene and toluene in water, and is equal to 1800 and 515 $mg \cdot L^{-1}$, respectively (Benbouzid et al., 2012).

An amount of 0.1 g of each biosorbent was added to 35 mL of