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Removal of glyphosate herbicide from water using biopolymer membranes

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ABSTRACT

Enormous amounts of pesticides are manufactured and used worldwide, some of which reach soils and aquatic systems. Glyphosate is a non-selective herbicide that is effective against all types of weeds and has been used for many years. It can therefore be found as a contaminant in water, and procedures are required for its removal. This work investigates the use of biopolymeric membranes prepared with chitosan (CS), alginate (AG), and a chitosan/alginate combination (CS/AG) for the adsorption of glyphosate present in water samples. The adsorption of glyphosate by the different membranes was investigated using the pseudo-first order and pseudo-second order kinetic models, as well as the Langmuir and Freundlich isotherm models. The membranes were characterized regarding membrane solubility, swelling, mechanical, chemical and morphological properties. The results of kinetics experiments showed that adsorption equilibrium was reached within 4 h and that the CS membrane presented the best adsorption (10.88 mg of glyphosate/g of membrane), followed by the CS/AG bilayer (8.70 mg of glyphosate/g of membrane). The AG membrane did not show any adsorption capacity for this herbicide. The pseudo-second order model provided good fits to the glyphosate adsorption data on CS and CS/AG membranes, with high correlation coefficient values. Glyphosate adsorption by the membranes could be fitted by the Freundlich isotherm model. There was a high affinity between glyphosate and the CS membrane and moderate affinity in the case of the CS/AG membrane. Physico-chemical characterization of the membranes showed low values of solubility in water, indicating that the membranes are stable and not soluble in water. The SEM and AFM analysis showed evidence of the presence of glyphosate on CS membranes and on chitosan face on CS/AG membranes. The results showed that the glyphosate herbicide can be adsorbed by chitosan membranes and the proposed membrane-based methodology was successfully used to treat a water sample contaminated with glyphosate. Biopolymer membranes therefore potentially offer a versatile method to eliminate agricultural chemicals from water supplies.

1. Introduction

Agriculture is a ubiquitous feature of human society throughout the world. From the earliest times, plants that appear naturally and spontaneously in areas occupied by humans, and that do not provide sources of food or fiber, have been considered undesirable and labeled as weeds (Linz and Homan, 2011). Techniques used to control these plants developed slowly over time, until the introduction of new chemical pesticides in the 20th century. These substances are used to effectively control pests and diseases, but can bring associated risks or inconvenience to humans and the environment (World Health Organization, 2009). Many studies of water quality have shown that the most important classes of

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chemical contaminants of aquatic systems are pesticides, hydrocarbons, and metals (Díaz et al., 2007).

The herbicide glyphosate has been available since 1973 and is now the chemical that is most widely used to control weeds, due largely to its non-selectivity and action against all types of plants. However, its long history of use has resulted in some weeds developing tolerance to the chemical (certain genetically modified crops also possess immunity to its effects). As a result, there is a continual increase in the quantities of glyphosate used in cultivations.

The presence of glyphosate in the environment has led to the need to develop techniques for its removal from water sources. Existing water treatment methods include microfiltration, ultrafiltration, reverse osmosis, adsorption by activated charcoal, filtration using sand, and biological degradation. Some of these procedures are expensive and/or require large infrastructure investments, and some are specific to particular contaminants (Moreno Escobar et al., 2005). As a result, there is increasing interest in alternative low-cost techniques. The use of polymeric membranes is potentially an attractive option because they are inexpensive, easy to produce, and have good adsorption characteristics (Feng et al., 2013). These membranes can be manufactured by casting and solvent evaporation, forming a single layer of dense membrane or forming multilayers membrane, inspired by the layer-by-layer technique (Moon et al., 1999).

One of the candidate polymers for the preparation of membranes intended to remove contaminants from water is alginate, a water-soluble linear polysaccharide (Motwani et al., 2008). Another important polymer is chitosan, obtained from the deacetylation of chitin, a polysaccharide that is abundant in nature because it is a structural component in organisms including insects, marine animals, and single-celled microbes (Ma et al., 2014). Advantages of this substance include its non-toxicity, biocompatibility, biodegradability, and wide availability. In its natural state, chitin has a low sorption capacity, with around 10% of free amines due to acetylation of the amino groups (Monteiro Junior et al., 2005).

Membranes prepared using alginate and chitosan have been developed for the removal of herbicides such as diquat, difenzoquat, and paraquat from water (Moraes et al., 2013; Cocenza et al., 2012). The aim of the present work was to investigate the potential of membranes composed of alginate, chitosan, and an alginate/chitosan combination for the treatment of water contaminated with glyphosate as well as to explore the factors controlling the glyphosate adsorption on these membranes.

2. Experimental

2.1. Materials

Analytical grade glyphosate (Pestanal®), sodium molybdate, and ninhydrin were purchased from Sigma Chem. Co. Deionized water was obtained from a Milli-Q system (Millipore). Other reagents used were analytical grade.

2.2. Quantification of glyphosate and calibration curve

The method used to quantify glyphosate was described previously (Bhaskara and Nagaraja, 2006). A stock 500 μg/mL solution was used to prepare eight samples containing different concentrations of the herbicide (1, 5, 10, 15, 20, 25, 30, and 35 μg/mL), which were then added to separate test tubes containing 1 mL of ninhydrin (5%, m/v) and 1 mL of sodium molybdate (5%, m/v). The mixtures were placed in a water bath at *ca.* 100 °C for 5 min and were cooled naturally to ambient temperature, and made up to 10 mL in volumetric flasks. Quantification of glyphosate was performed in a Varian Cary 50 spectrophotometer, operated at a wavelength of 570 nm. Eight replicates were used to construct the analytical curve.

2.3. Preparation of the membranes

The membranes were produced using the method proposed by Moon (Moon et al., 1999). The solutions employed were: chitosan (1 wt%), with a minimum degree of deacetylation of 85%, in 2 vol% acetic acid; and sodium alginate (1 wt%), dissolved in 0.1 mol/L NaOH.

The solution (50 mL of alginate or chitosan) was spread on a Petri dish and then dried at 50 °C. In the case of the multilayer alginate/chitosan membrane, 25 mL of chitosan solution was spread first and the drying process was interrupted to add 25 mL of alginate solution to enable electrostatic interaction between the polysaccharides, then the polymers were dried until the membrane formation. After manufacture, the membranes were stored in Milli-Q water at neutral pH under refrigeration.

2.4. Adsorption kinetics

The adsorption kinetics experiments were performed with 0.0004 g (approximately 1 cm^2) samples of the three types of membrane (alginate, chitosan, and alginate/chitosan), using 30 μg/mL solutions of glyphosate (50 mL) placed in 125 mL Erlenmeyer flasks. The controls were flasks containing the herbicide alone. The flasks were agitated on an orbital shaker at 100 rpm and 25 °C. Aliquots (1 mL) of the aqueous solution were removed every 30 min for derivatization and quantification of the herbicide (as described in Section 2.2), after which the adsorption kinetics curves were constructed. All the experiments were performed in triplicate.

In order to better understand the mechanism of sorption of glyphosate by the membranes, the data were fitted using the pseudo-first order and pseudo-second order kinetic models, described by Equations (1) and (2), respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{1}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 {Q_e}^2} + \frac{t}{Q_e} \tag{2}$$

In the above equations, K_1 (min^{-1}) is the pseudo-first order rate constant, K_2 is the pseudo-second order rate constant (g*min/mg), Q_e is the maximum amount of product adsorbed (mg/g), and Q_t is the amount adsorbed at time t (mg/g). The time is given in minutes (Ho and Mckay, 1998).

2.5. Sorption isotherms

The adsorption isotherm experiments employed solutions of glyphosate at concentrations of 5, 15, 25, and 35 μg/mL, with 50 mL aliquots placed in separate 125 mL Erlenmeyer flasks together with 1 cm^2 portions of the different membranes. The experiments were performed in triplicate, and flasks containing glyphosate alone were used as controls. The samples were agitated for 4 h at 100 rpm and 25 °C, after which 1 mL aliquots were withdrawn, derivatized, and analyzed. The glyphosate concentrations obtained were used to construct the adsorption isotherms.

The data were investigated using the Langmuir and Freundlich isotherm models. The Langmuir model (Equation (3)) describes adsorption by a surface possessing a finite number of identical sites, with each adsorbate molecule occupying a single site, hence forming a monolayer of adsorbate on the surface of the adsorbent (Adamson, 1976).