Ecotoxicology and Environmental Safety 131 (2016) 72–78

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Polyurethane foam loaded with sodium dodecylsulfate for the extraction of 'quat' pesticides from aqueous medium: Optimization of loading conditions

Jonas O. Vinhal [a,b], Claudio F. Lima [a], Ricardo J. Cassella [b,*]

[a] Departamento de Química, Universidade Federal de Viçosa, Av. Peter Henry Rolfs s/n, Viçosa, MG 36570–000, Brazil
[b] Instituto de Química, Programa de Pós-Graduação em Química, Universidade Federal Fluminense, Outeiro de São João Batista s/n, Centro, Niterói, RJ 24020–141, Brazil

ARTICLE INFO

Article history:
Received 10 January 2016
Received in revised form
12 May 2016
Accepted 13 May 2016

Keywords:
Cationic herbicides
Polyurethane foam
Sodium dodecylsulfate
Sorption

ABSTRACT

The cationic herbicides paraquat, diquat and difenzoquat are largely used in different cultures worldwide. With this, there is an intrinsic risk of environmental contamination when these herbicides achieve natural waters. The goal of this work was to propose a novel and low-cost sorbent for the removal of the cited herbicides from aqueous medium. The proposed sorbent was prepared by loading polyurethane foam with sodium dodecylsulfate. The influence of several parameters (SDS concentration, HCl concentration and shaking time) on the loading process was investigated. The results obtained in this work demonstrated that all studied variables influenced the loading process, having significant effect on the extraction efficiency of the resulted PUF-SDS. At optimized conditions, the PUF was loaded by shaking 200 mg of crushed foam with 200 mL of a solution containing 5.0×10^{-3} mol L^{-1} SDS and 0.25 mol L^{-1} HCl, for 30 min. The obtained PUF-SDS was efficient for removing the three herbicides from aqueous medium, achieving extraction percentages higher than 90%. The sorption process followed a pseudo second-order kinetics, which presented excellent predictive capacity of the amount of herbicide retained with time.

1. Introduction

Agrochemicals have been intensively used worldwide in order to combat several types of plagues and maintain high productivity of food. However, their excessive, and sometimes unnecessary, use has generated a number of environmental problems. Certainly, one of the most critical problems derived from the use of agrochemicals is the contamination of natural waters, which occurs when they achieve the aquatic systems due to the discharge from manufacturing facilities, surface runoff, or accidental spills (Kim et al., 2008).

Some ammonium quaternary salts, such as paraquat (PQT^{2+}), diquat (DQT^{2+}) and difenzoquat ($DFQT^{+}$) (Fig. 1), are largely used as herbicides, desiccants and defoliants. They have appropriate chemical and physical properties, such as the high solubility in water, low vapor pressure and high binding capacity, which makes them very useful for application in a variety of cultures (Bromilow, 2004; Matolcsy et al., 1998). The 'quat' herbicides are considered toxic for humans by the World Health Organization (WHO) and can affect lungs, brain, liver, kidneys and other organs (Melchiorri et al., 1996; WHO, 2009). So that, the development of new technologies for their removal from aqueous medium is an important subject to be studied.

The removal of pesticides from aqueous medium is not a simple problem to be solved. In many cases, the use of conventional methods based on UV irradiation, chemical coagulation, sedimentation and/or filtration is not efficient. In these cases, the employment of liquid-solid extraction processes is an alternative, which is especially difficult when the solutes present high solubility in water, such as the cationic herbicides evaluated in the present study. Even though, the current literature reports the use of various sorbents of different natures for the retention of 'quat' herbicides from aqueous medium (González-Pradas et al., 1999; Hao et al., 2015; Nakamura et al., 1999; Moraes et al., 2013; Hsu and Pan, 2007; Hamadi et al., 2004; Leite et al., 2013; Aouada et al., 2009).

The use of polyurethane foams (PUF) in chemical separations dates from 1970, when the pioneering work of Bowen (1970) introduced the use of this polymer for the solid-phase extraction of a number of substances from aqueous solutions. According to Bowen, PUF present the essential characteristics for its use as sorbent material, such as high sorption capacity, chemical and thermal

---

* Corresponding author.
E-mail address: cassella@vm.uff.br (R.J. Cassella).

http://dx.doi.org/10.1016/j.ecoenv.2016.05.012
0147-6513/© 2016 Published by Elsevier Inc.

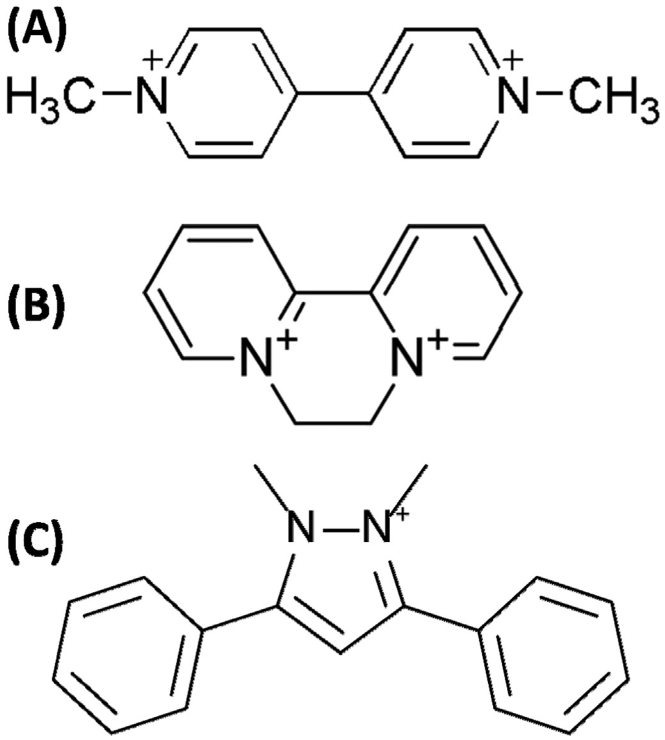

Fig. 1. Chemical structures of the herbicides studied in this work.

resistance, and ability to retain various types of substances due to the presence of polar and non-polar groups in their structures. Additionally, PUF is a very low-cost material and can be easily purchased.

Initially, unmodified PUF were widely employed in the development of a number of methodologies for the separation of organic and inorganic substances from aqueous medium (Braun et al., 1985). Unmodified PUF have been directly applied in the retention of phatalate esters (Gough and Gesser, 1975), pesticides (El-Shahawi and Al-Dhaheri, 1996; El-Shahawi, 1997; Cassella et al., 2000; Farag et al., 1986; Portugal et al., 2008), metal complexes (Soriano and Cassella, 2013; Sant'Ana et al., 2003, 2004a, 2004b), nitrophenols (El-Shahawi and Nassif, 2003), flavonoids (Dmitrienko et al., 2012) and other substances (Gesser et al., 1971; Silveira Neta et al., 2011; Baldez et al., 2009). Subsequently, the necessity of solving more specific problems leaded to the development of new PUF-based sorbents, obtained from the modification of PUF surface or structure. According to Braun et al. (1985) the modification of PUF with specific reagents improves their sorption characteristics, yielding a sorbent with increased selectivity, higher sorption capacity and faster sorption rates.

Two approaches can be used for modifying PUF surface. It can be functionalized or only impregnated (loaded-PUF) with the desired reagent. In this field, certainly, the most part of works have been devoted to the preparation of impregnated/functionalized PUF with specific reagents for the retention of metal cations from aqueous solution (Moawed et al., 2006; Azeem et al., 2010, 2013; Lemos et al., 2006; Saeed et al., 2005, 2005; Sant'Ana et al., 2004a, 2004b; Lemos and Ferreira, 2001). Nevertheless, is also important to remark that some few works reports the modification of PUF with reagents for the sorption of organic substances (El-Shahat et al., 2001; Robaina et al., 2009; El-Bouraie, 2015).

The goal of this work was to optimize the preparation method of PUF impregnated with sodium dodecylsulfate (SDS) for the retention of cationic herbicides (paraquat, diquat and difenzoquat) from aqueous medium. Additionally, a preliminary study on the sorption kinetics was performed, in order to characterize and model the sorption process using the novel sorbent.

2. Experimental

2.1. Apparatus and instruments

The determination of herbicides concentration was carried out with an UV–vis spectrophotometer Cary 60 (Agilent, Santa Clara, USA), using a 10-mm quartz cuvette. The spectra were registered in scan mode from 200 to 400 nm and the quantitative analysis were performed employing the absorbances measured at 257, 310 and 254 nm, for PQT^{2+}, DQT^{2+} and $DFQT^{+}$, respectively.

An orbital shaker, model NT 151, supplied by Nova Técnica (São Paulo, Brazil), was employed for shaking the unloaded PUF with HCl/SDS solutions in the loading process of the foam. The extraction experiments were performed by shaking the solutions containing the herbicides with loaded PUF using a horizontal roller mix, model MR-II, provided by Biomixer (São Paulo, Brazil).

2.2. Reagents and solutions

All reagents used in this work were of analytical grade or better. They were employed without any further purification. Deionized water employed in the preparation of the solutions was obtained in a Direct-Q 3 System (Millipore, Bedford, USA) and always presented resistivity equal or higher than 18.2 MΩ cm.

The 1000 mg L^{-1} stock solutions of paraquat, diquat and difenzoquat were prepared, individually, by dissolving an appropriate mass of each standard reagent (in the form of their respective salts) in deionized water. They were stored in the refrigerator at a temperature of approximately 4 °C. The reagents were supplied by Sigma-Aldrich (Steinheim, Germany).

Similarly, the 1000 mg L^{-1} stock solution of SDS (Vetec, Rio de Janeiro, Brazil) was prepared by dissolving a suitable mass of the reagent in deionized water to complete 250 mL in a volumetric flask. Stock solution of SDS was stored at ambient room temperature (21 ± 2 °C) and protected from incidence of light. In this condition, the solution remains stable for five days.

The hydrochloric acid solutions used in this work were prepared by dilution of concentrated HCl (Tedia, Fairfield, OH, USA) with purified water.

A polyether type polyurethane foam with a 22.5 mg cm^{-3} density (Guararapes Ltda, Brazil) was used in all experiments. In order to increase the surface area exposed to the sorption, the foam was crushed in a home blender with deionized water for 10 min. After crushing, PUF was left to dry on a trail, which was maintained on the bench at ambient laboratory temperature for 24 h. Then, it was employed for the loading with SDS.

2.3. PUF loading with SDS

PUF loading was performed by shaking 200 mL of a solution containing SDS and HCl with 200 mg of unloaded PUF in a 500 mL Erlenmeyer flask. The concentrations of SDS and HCl, as well as the shaking time, were optimized in the present work. After loading, the obtained loaded PUF was dried at ambient laboratory temperature, stored in a plastic flask and kept in a light-free environment until its use in the sorption experiments.

2.4. Sorption experiments

In order to verify the efficiency of the loaded foams for the sorption of the 'quat' herbicides, experiments were carried out using PQT^{2+} as model molecule. The experiments were carried out by shaking 45 mL of the solution containing the herbicide