Journal of Environmental Management 156 (2015) 200–208

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Modeling, kinetic, and equilibrium characterization of paraquat adsorption onto polyurethane foam using the ion-pairing technique

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ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form
2 March 2015
Accepted 13 March 2015
Available online

Keywords:
Paraquat
Polyurethane foam
Adsorption
Ion-pairing

ABSTRACT

We studied the adsorption of paraquat onto polyurethane foam (PUF) when it was in a medium containing sodium dodecylsulfate (SDS). The adsorption efficiency was dependent on the concentration of SDS in solution, because the formation of an ion-associate between the cationic paraquat and the dodecylsulfate anion was found to be a fundamental step in the process. A computational study was carried out to identify the possible structure of the ion-associate in aqueous medium. The obtained data demonstrated that the structure is probably formed from four units of dodecylsulfate bonded to one paraquat moiety. The results showed that 94% of the paraquat present in 45 mL of a solution containing 3.90×10^{-5} mol L^{-1} could be retained by 300 mg of PUF, resulting in the removal of 2.20 mg of paraquat. The experimental data were reasonably adjusted to the Freundlich isotherm and to the pseudo-second-order kinetic model. Also, the application of Morris–Weber and Reichenberg models indicated that both film-diffusion and intraparticle-diffusion processes were active during the control of the adsorption kinetics.

1. Introduction

Nowadays, contamination of aquatic systems can be considered as one of the main problems in modern society, because the shortage of water is a phenomenon already observed in several parts of the world (El-Shahawi, 1997). The discharge of pesticides into water bodies is one process that leads to the contamination of aquatic systems (Brigante and Schulz, 2011).

Paraquat (1,1′-dimethyl-4,4′-dipyridyn, Fig. 1) is a quaternary ammonium salt that is largely employed as a herbicide in various types of cultures, owing to its chemical and physical properties such as high solubility in water (Matolcsy et al., 1988; Bromilow, 2004). Paraquat has been proven to be toxic to mammals, directly affecting the lungs, liver, and kidneys, among other organs (Clark et al., 1966; Melchiorri et al., 1996). Despite the fact that some studies have associated Parkinson's disease with paraquat contamination, it is not possible to affirm that this herbicide is responsible for the development of the disease (Dinis-Oliveira et al., 2006; Mandel et al., 2012).

Different strategies can be used to eliminate and/or remove pollutants from water. Among these strategies, adsorption processes represent one of the most important strategies, especially because of the advantages observed when they are applied. In general, adsorption processes are simple, efficient, and versatile, because the use of different adsorbents allows the removal of solutes with varying chemical characteristics.

Several studies have been conducted to evaluate the removal of paraquat from water by adsorption processes. Various materials have already been used for this purpose, such as clay minerals (Seki and Yurdakoç, 2005; Tsai and Lai, 2006; Brigante et al., 2010; Iglesias et al., 2010), diatomaceous earth (Tsai et al., 2005), rice husk (Hsu et al., 2009), mesoporous silica (Brigante and Schulz, 2011), sawdust (Nanseu-Njiki et al., 2010), activated carbon (Hamadi et al., 2004), and chitosan (Silva et al., 2011).

In order to choose an adsorbent for the removal of chemical species from aqueous media, several aspects must be considered. Undoubtedly, the most important aspect is the solute affinity for the adsorbent, which will determine the efficiency of the process.

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http://dx.doi.org/10.1016/j.jenvman.2015.03.022
0301-4797/

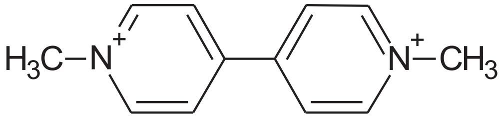

Fig. 1. Structure of paraquat in its ionic form.

Other aspects, such as cost, availability, and the need for pretreatment, are also important. Polyurethane foams (PUFs) satisfy all of these criteria, as they are low-cost, readily available, and do not require pretreatment, and PUFs can easily be obtained in the market in different forms and compositions (Braun et al., 1985). They are able to retain polar and non-polar solutes, owing to the different functional groups present in their structure (Bowen, 1970). PUFs have already been employed, with success, in the adsorption of metallic complexes (Sant'Ana et al., 2003; Sant'Ana et al., 2004a; Sant'Ana et al., 2004b; Almeida et al., 2007), other pesticides (Farag et al., 1986; El-Shahawi, 1993; El-Shahawi and Aldhaheri, 1996; El-Shahawi, 1997; Cassella et al., 2000), dyes (Baldez et al., 2008; Robaina et al., 2009; Baldez et al., 2009; Mori and Cassella, 2009; Silveira Neta et al., 2011; Leite et al., 2012), and other organic pollutants (El-Shahawi, 1994). There is, however, no report regarding the use of a PUF for the adsorption of paraquat or any other cationic herbicide.

The main goal of this work was to optimize and characterize, in terms of kinetics and the equilibrium, the adsorption of paraquat from an aqueous medium by PUF, using dodecylsulfate as the counter ion. Additionally, a computational study was carried out in order to reveal the possible species that is actually adsorbed and to provide information about the adsorption mechanism.

2. Experimental

2.1. Apparatus

Determination of the paraquat concentration in the solutions was performed by spectrophotometry using an Agilent UV–visible spectrophotometer (model Cary 60, Palo Alto, CA, USA). The spectra were registered in the range of 200–400 nm, and the absorbance at 257 nm was employed for quantitative purposes. All measurements were performed with a standard quartz cuvette with an optical path length of 10 mm.

Agitation of the solutions was carried out on a horizontal roller mixer by Biomixer (Curitiba, Brazil). Capped polyethylene flasks with a 50 mL capacity were employed in the experiments. The total volume of solution used in each experiment was always 45 mL.

The Spartan 6.0 software (Wavefunction Inc., CA, USA) was used to design the chemical structures for the input files employed in the computational calculations (Shao et al., 2006). This software was also used to perform conformational analysis of the molecules present in each system. Finally, Gaussian 09 (Gaussian Inc., Wallingford, CT, USA) software was used to run all density functional calculations (Frisch et al., 2009) and Chemcraft was used to view and edit the Gaussian output files.

2.2. Reagents and solutions

All reagents used in this work were of analytical grade or higher and were employed without further purification. The deionized water employed in the preparation of solutions was purified in a Direct-Q System (Millipore, Bedford, USA).

A 1000 mg L^{-1} (3.90×10^{-3} mol L^{-1}) paraquat stock solution was prepared by dissolving 50 mg of the reagent (Sigma–Aldrich, Steinheim, Germany) in approximately 20 mL of deionized water. Afterwards, the obtained solution was quantitatively transferred to a 50 mL volumetric flask and the volume was made up to the mark with deionized water. The stock solution was stored in a refrigerator. The paraquat solutions employed in the experiments were prepared through the convenient dilution of the stock solution with deionized water.

A 1000 mg L^{-1} (3.90×10^{-3} mol L^{-1}) stock solution of sodium dodecylsulfate (SDS) was prepared by dissolving 0.250 g of the reagent (Vetec, Rio de Janeiro, Brazil) in approximately 100 mL of deionized water. Then, the solution was transferred to a 250 mL volumetric flask and the volume was made up to the mark with deionized water. This solution was stable for 1 week when stored at an ambient laboratory temperature (22 ± 1 °C) in a light-free location. Diluted solutions of SDS, employed in the adsorption experiments, were prepared through the convenient dilution of the stock solution with deionized water.

Open-cell, polyether-type PUF (Guararapes Ltda, Brazil) with a density of 22.5 mg cm^{-3} was employed in all experiments. The foam was comminuted in a blender with purified water. Then, the powdered PUF was dried at ambient temperature and sieved through a 2 mm plastic sieve. The treated PUF was stored in a plastic flask, which was maintained in a light- and dust-free environment.

2.3. General procedure

The adsorption experiments were performed by shaking 45 mL solutions, containing known concentrations of paraquat and SDS, with adequate mass of powdered PUF. The shaking was performed with a horizontal mixer operated at 90 rpm. The concentration of paraquat that remained in the solution after shaking was determined by spectrophotometry (at 257 nm), at certain time intervals, as stipulated in each experiment according to the information desired. All experiments were carried out at ambient temperature, which was always 22 ± 1 °C. The removal percentage (R) was calculated using Equation (1):

$$R(\%) = 100 - \left(\frac{C_t}{C_o} \times 100\right) \tag{1}$$

in which C_0 is the initial concentration of paraquat in the solution and C_t is the concentration of paraquat in the solution at a given time.

3. Results and discussion

3.1. Influence of SDS concentration

The most important process variable, related to the adsorption procedure, investigated in this work, is the formation of an ion-associate between the cationic paraquat and the dodecylsulfate anion, because the highly soluble paraquat cation cannot be retained by the hydrophobic PUF, as previously observed in a study on the adsorption of cationic dyes by PUFs (Baldez et al., 2008, 2009; Mori and Cassella, 2009; Leite et al., 2012). Therefore, the addition of a correct concentration of SDS to the medium was fundamental in order to enhance paraquat adsorption by PUF. This parameter was evaluated in the range of 0 (no addition of SDS) to 400 mg L^{-1} ($0–1.40 \times 10^{-3}$ mol L^{-1}). The mass of PUF employed in the experiment was 200 mg, the shaking speed was 90 rpm, and the initial concentration of paraquat in solution was 5.5 mg L^{-1} (or 2.15×10^{-5} mol L^{-1}).

The adsorption efficiency increased with increasing SDS concentration up to 200 mg L^{-1}. Above this SDS concentration, the removal efficiency remained virtually constant, once the variation