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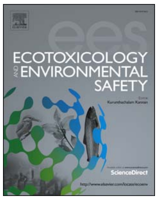

Adsorption of the herbicides diquat and difenzoquat on polyurethane foam: Kinetic, equilibrium and computational studies

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ABSTRACT

This work reports a study about the adsorption of the herbicides diquat and difenzoquat from aqueous medium employing polyurethane foam (PUF) as the adsorbent and sodium dodecylsulfate (SDS) as the counter ion. The adsorption efficiency was shown to be dependent on the concentration of SDS in solution, since the formation of an ion-associate between cationic herbicides (diquat and difenzoquat) and anionic dodecylsulfate is a fundamental step of the process. A computational study was carried out to identify the possible structure of the ion-associates that are formed in solution. They are probably formed by three units of dodecylsulfate bound to one unit of diquat, and two units of dodecylsulfate bound to one unit of difenzoquat. The results obtained also showed that 95% of both herbicides present in 45 mL of a solution containing 5.5 mg L^{-1} could be retained by 300 mg of PUF. The experimental data were well adjusted to the Freundlich isotherm ($r^2 \geq 0.95$) and to the pseudo-second-order kinetic equation. Also, the application of Morris-Weber and Reichenberg equations indicated that an intraparticle diffusion process is active in the control of adsorption kinetics.

1. Introduction

The quaternary ammonium compounds diquat (DQT^{2+}) and difenzoquat ($DFQT^{+}$) are used today as post-emergence herbicides and desiccants in different types of crops (Pérez-Ruiz et al., 1994; Rytwo et al., 2004). They have similar chemical and physical properties such as high solubility in water and high binding potential (Brian et al., 1958; Matolcsy et al., 1998). These herbicides are considered toxic for humans in their cationic forms (Reigart and Roberts, 1999) and are classified by the World Health Organization (WHO) as moderately hazardous (Class II), with a lethal dose (LD_{50}) for oral ingestion in rats of 231 and 470 mg kg^{-1} for diquat and difenzoquat, respectively (World Health Organization, 2009). The contamination of waters with these compounds is a real problem, since they can be easily dissolved in aqueous medium due to the previously mentioned high solubility in water. Therefore, the development of novel strategies for their removal from aqueous medium is needed.

The solid phase extraction is one of the most popular techniques used for the removal of several types of substances from aqueous medium. In this field, the current literature reports the retention of diquat and/or difenzoquat by different materials such as silica (Ibáñez et al., 1996, 1998), vineyard soils (Pateiro-Moure et al., 2009a, b, 2010), montmorillonite minerals (Rytwo et al., 2004; González-Pradas et al., 1999; Rytwo and Tropp, 2001), activated carbon (Parkash, 1974), silver iodide particles (Keizer and Fokkink, 1990) and sepiolite minerals (Rytwo et al., 2002).

The choice of an adsorbent material must be made taking into account several aspects. To select the ideal adsorbent, one should primarily analyze the physical and chemical properties of the material, but should also consider some important features such as cost and environmental characteristics. In this context, polyurethane foam (PUF) presents essential characteristics of a good adsorbent material, because it has very low cost, high adsorption capacity, chemical resistance and versatility, and is able to retain several different types of substances due to the presence of polar and non-polar groups in the structure. Bowen suggested that PUF can be used to retain highly-polarizable molecules (such as aromatic compounds), low electronic density anions and some metallic complexes (Bowen, 1970). Although different mechanisms have already been proposed to explain the adsorbent ability of PUF, several authors support the suggestion that PUF can act as a polymeric extractor phase, similar to a solvent in a liquid-liquid extraction process (Farag et al., 1986; El-Shahawi, 1997, 1993; Rathore et al., 1995). PUF has already been employed in the solid phase extraction of organic substances such as phthalate esters (Gough and Gesser, 1975),

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nitrophenols (El-Shahawi and Nassif, 2003), dyes from industrial effluents (Robaina et al., 2009), flavonoids (Dmitrienko et al., 2012), and pesticides (Farag et al., 1986; El-Shahawi, 1997; El-Shahawi and Aldhaheri, 1996; Cassella et al., 2000). Also, they have been employed in the separation of metallic cations from aqueous medium using different strategies (Cassella et al., 2001; Sant'Ana et al., 2003, 2004; Lemos et al., 2007).

The main goal of this study was to evaluate the possible adsorption of the herbicides diquat and difenzoquat as ion-associates with the counter-ion dodecylsulfate employing polyurethane foam as the solid phase. Several factors that could influence the adsorption process, such as the concentration of surfactant, the adsorbent mass, pH and ionic strength, were evaluated in this work. To characterize the processes, we applied kinetic equations and Langmuir and Freundlich isotherms to the equilibrium condition. A computational study was also performed to reveal the probable species of ion-associates that participate in the adsorption process.

2. Experimental

2.1. Apparatus

The determination of diquat (DQT^{2+}) and difenzoquat ($DFQT^{+}$) in the solutions was performed by spectrophotometry using an Agilent, model Cary 60, UV–visible spectrophotometer (Palo Alto, CA, USA). The instrument was equipped with quartz cuvettes with an optical path length of 10 mm. The spectra were registered in the range of 200–400 nm, and the quantitative analyses were performed at 310 nm for DQT^{2+} and 254 nm for $DFQT^{+}$, which were the wavelengths where the maximum absorptions were observed for the herbicides.

The solutions were shaking on a horizontal roller mixer supplied by a Biomixer (Curitiba, Brazil), and the pH measurements were performed with a Digimed pH meter (Santo Amaro, Brazil), model DM-22, equipped with a glass electrode, also supplied by Digimed.

Design and manipulation of chemical structures was done using the graphical program Chemcraft (http://www.chemcraftprog.com, 2016). Computations were carried out using the Gaussian 09 software (Gaussian Inc., Wallingford, CT, USA).

2.2. Reagents and solutions

All reagents used in this work were of analytical grade or higher and employed without further purification. The deionized water employed in the preparation of the solutions was purified in a Direct-Q 3 System (Millipore, Bedford, USA) and had resistivity of 18.2 MΩ cm or higher.

Stock solutions of 1000 mg L^{-1} of DQT^{2+} (2.90×10^{-3} mol L^{-1}) and $DFQT^{+}$ (2.80×10^{-3} mol L^{-1}) were prepared by dissolving a suitable mass of the respective salts in exactly 50 mL of deionized water. Both reagents (diquat dibromide monohydrate and difenzoquat methyl sulfate) were purchased from Sigma-Aldrich (Steinheim, Germany). Stock solutions of the herbicides were stored in the refrigerator at approximately 4 °C.

The stock solution of 1000 mg L^{-1} (3.45×10^{-3} mol L^{-1}) of sodium dodecylsulfate (SDS) was prepared by dissolving 0.250 g of the reagent, purchased from Vetec (Rio de Janeiro, Brazil) in 100 mL of deionized water. The solution obtained was transferred to a 250 mL volumetric flask and the volume was made up to the mark with deionized water. The stock solution of SDS could be used for seven days without degradation. It was maintained at ambient room temperature (22 ± 1 °C) and protected from the light.

An open-cell polyether type polyurethane foam (Guararapes Ltda, Brazil) with 22.5 mg cm^{-3} density was employed in all experiments. The foam was comminuted in a blender with purified water for 10 min. Then, the comminuted PUF was dried at room temperature for 24 h. After drying, PUF was stored in a suitable flask and protected from light.

2.3. General procedure

Sorption experiments were performed by shaking 45 mL of the solutions containing known concentrations of either DQT^{2+} or $DFQT^{+}$ and SDS with powdered PUF. The mixture was shaken on a horizontal mixer at 90 rpm and the remaining concentrations of diquat and difenzoquat in the solutions were determined by spectrophotometry at 310 and 254 nm, respectively. The determination of the herbicide concentration was performed at predefined time intervals, which were set according to the information desired. All experiments were carried out at ambient laboratory temperature, which was always 22 ± 1 °C. Removal percentage (R) of the herbicides was calculated using the Eq. (1).

$$R(\%) = 100 - \left[\left(\frac{C_t}{C_0}\right) x100\right] \tag{1}$$

where R is the removal percentage, C_0 is the initial concentration of the herbicide in the solution, and C_t is the remaining concentration of the herbicide in solution at time t.

3. Results and discussion

3.1. Influence of SDS concentration in solution

As mentioned previously, PUF is an effective material for the retention of different substances from aqueous medium, especially because it contains polar and non-polar groups in its structure [17]. The removal strategy employed in the present work was chosen taking into account that the retention of diquat and difenzoquat would depend on the formation of an ion-associate between the cationic herbicides and an anionic counter ion (dodecylsulfate, from SDS), since the solutes alone are highly soluble in water and are not retained by the hydrophobic PUF. The ion-associate formation has been previously observed in studies with dyes (Bračko and Špan, 2000; Gohain et al., 2008) and their adsorption on polymeric solid phases was previously documented (Baldez et al., 2009, 2008; Leite et al., 2012; Reis et al., 2011).

In order to evaluate the influence of SDS concentration in solution on DQT^{2+} and $DFQT^{+}$ retention by PUF, we performed experiments varying the SDS concentration between 0 (without SDS addition) and 1.40×10^{-3} mol L^{-1}. The other experimental conditions were: (i) mass of PUF of 200 mg; (ii) shaking speed of 90 rpm and (iii) no pH adjustment. The initial concentration of the herbicides in solution was 5.5 mg L^{-1} for both diquat (1.60×10^{-5} mol L^{-1}) and difenzoquat (1.55×10^{-5} mol L^{-1}). The mixtures were shaken for 120 min and we determined the concentration of the herbicides remaining in the solutions at 0 (initial concentration), 2, 4, 6, 8, 10, 15, 20, 30, 45, 60, 90 and 120 min. The obtained results are displayed in Fig. 1.

In general, the increase in the SDS concentration in solution caused the increase of the removal percentage of both substances (Fig. 1). This fact is certainly related to the higher percentage of ion-associates formation in solution when an excess of SDS was added to the medium. As the ion-associates are more efficiently retained by PUF than the cationic herbicide alone, the removal percentage increased. We observed the maximum removal of both herbicides for SDS concentrations of 200 mg L^{-1} (7.0×10^{-4} mol L^{-1}) or higher, which represents ratios [SDS]/[herbicide] of approximately 45. This high value showed that the addition of an excess of the counter ion enhanced the formation of the ion-associates. A concentration of 200 mg L^{-1} of SDS was then set for all further experiments. In this condition, we could observe maximum extraction for both herbicides, which was approximately 95%.

It is also important to highlight that approximately 25% of the diquat present in solution was removed (Fig. 1a) when no SDS was added. On the other, we did not observe the retention of difenzoquat when no SDS was added. One possible explanation for these behaviors is related to the charge density of the two compounds. As diquat is present in