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Drin pesticides removal from aqueous solutions using acid-treated date stones

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ABSTRACT

This work describes the potential applicability of chemically and thermally treated date stones for removing drin pesticides (aldrin, dieldrin and endrin) from aqueous solutions. The effect of several parameters, such as sorbent particle size, adsorbent dose, shaking speed, shaking time, concentration of pesticide solution and temperature, was evaluated by batch experiments. Pesticide determination was carried out using stir bar sorptive extraction and gas chromatography coupled with mass spectroscopy. Maximum removal efficiency (93%) was reached using 0.1 g of acid-treated date stones (ATDS) (63–100 μm) and 100 mL of aldrin (0.5 mg L^{-1}). The removal efficiency of drin pesticides decreased in the order of aldrin, dieldrin and endrin, and decreased as the temperature rose. Adsorption data were processed according to various kinetic models. Lagergren and Morris-Weber equations were applied to fit the kinetic results. The second order model was the most suitable on the whole, and intra-particle diffusion was found to be the rate-controlling the adsorption process. According to adsorption kinetic data, 3.5 h were considered as the equilibrium time for determining adsorption isotherms. Adsorption data were analyzed by the Langmuir, Freundlich and Dubinin–Radushkevich adsorption approaches. Experimental results showed that the Freundlich isotherm model best described the adsorption process. In addition, thermodynamic parameters such as ΔH, ΔS and ΔG were calculated. Negative values of ΔH and ΔG indicate the exothermic and spontaneous nature of pesticide adsorption on ATDS.

1. Introduction

Organochlorine pesticides (OC) are considered one of the most dangerous products used in crop protection. A large number of these chemicals, such as DDT, technical hexachlorocyclohexane (HCH) and drin pesticides (aldrin, dieldrin and endrin), were widely used throughout the world during the second half of the past century to control malaria vectors as well as for seed dressing to afford protection of stored grains against insect pests. However, today it is commonly known that these OC compounds are very persistent in the environment, tend to accumulate in organisms and have undesired side effects; consequently, their use has been banned in many countries.

Generally, OC pesticides are hydrophobic substances, with low water solubility. Most of them have an octanol ± water partition coefficient (k_{ow}) with log k_{ow} between 3.5 and 6 (Zitko, 2003), which explains their high solubility in lipids. This characteristic, in combination with their toxicity and their high chemical and biological stability, makes organochlorine pesticides prone to bioaccumulation along the food chain, involving a wide range of trophic levels (Biziuk et al., 1996) and engendering negative impacts on the health and well-being of humans (Krieger et al., 2001; Erdogrul et al., 2005; Sudaryanto et al., 2006; El Bakouri et al., 2008a).

Drin pesticides are a class of OC pesticides that have been intensely used in agriculture. They are very hazardous pollutants, toxic to many forms of wildlife, especially aquatic organisms, insects and mammals and persist in the aquatic environment for many years after their application (Shukla et al., 2006). As a consequence, most of them have been listed as persistent organic pollutants (POP) by the United Nations Environment Program (UNEP, 2001). Nevertheless, a large number of these products are still in use as insecticides in fields of most developing countries and also for termites, wood bores and textile pests because of their effectiveness and low application cost. Numerous studies have reported contamination of water resources by these chemicals, even at considerable distances from the point of original application (Golfinopoulos et al., 2003; Sankararamakrishnan et al., 2005; Pazou et al., 2006; Rissato et al., 2006; Zhou et al., 2006; Raposo Júnior and Ré-Poppi, 2007; Xu et al., 2007).

Advanced pesticide removal methods are usually needed to meet environmental quality requirements and improve the ecological system. These include combinations of biological, chemical and physical processes. Adsorption has evolved into one of the most effective physical processes for pesticide removal because the technique uses equipment that is readily available, easy to use

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and not energy-intensive, and also because the treatment is cost effective (Sudhakar and Dikshit, 1999; Carrizosa et al., 2000; Boyd et al., 2001; Shukla et al., 2002; Aslan and Turkman, 2004; El Bakouri et al., 2006, 2007a,b). Additionally, adsorption on activated carbon is the most widespread technology used to purify water contaminated by pesticides and other hazardous chemicals (Heijman and Hopman, 1999; Baup et al., 2000; Sotelo et al., 2002). However, due to the high cost of activated carbon, its use is sometimes restricted for economic reasons. Several recent publications report the use of low-cost and locally available adsorbents, e.g., peat mix, garden waste compost, straw, cow manure, coconut chips, chestnut shells, watermelon rinds, charcoal, etc. (De Wilde et al., 2008; Memon et al., 2007, 2008; Mishra and Patel, 2008; El Bakouri et al., 2009). Nonetheless, the literature is still insufficient to cover this problem, and more work and studies are needed in this field to develop other locally available and economical adsorbents to eliminate pollutants from water.

The purpose of this work was to study the adsorption behavior of Drin pesticides on acid-treated date stones. The effect of several physicochemical parameters, such as sorbent particle size, contact time, temperature and pesticide concentration, was evaluated to better describe the adsorption process. In addition, adsorption isotherms and thermodynamic adsorption parameters were determined to better understand the adsorption mechanism of the studied chlorinated pesticides onto the modified date stones.

2. Methods

2.1. Chemicals

All pesticide standards used in this work (aldrin, dieldrin and endrin) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Working solutions were prepared by diluting the stock solution first with methanol and then with ultrapure water. The percentage of solvent in the final pesticide solution was less than 0.1%. The standard stock and working solutions were stored at 4 °C and used to prepare dilute solutions and to spike water samples to the required concentrations. All the organic solvents were of analytical grade and were obtained from Merck (Germany). Methylene blue was purchased from Fluka. The water used was purified using a Milli-Q water-purification system (Millipore, USA).

2.2. Adsorbent preparation

Date stones selected for this work were from an indigenous variety of palm fruits (Boufeggous) available in Morocco markets. The collected date stones were kept at ambient temperature in the laboratory for a week and then dried at 70 °C in a drying oven for three days before crushing them in an electric mixer. The stones were sieved with vibratory sieves (Fritsch, Germany). Particle sizes of less than 250 μm were used for the thermal and chemical modification experiments. The thermal treatment was performed by heating the samples at 300 °C in a closed muffle furnace to increase the surface area (Chern and Wu, 2001). A higher temperature will remove some unburnt carbon and most of the micro pores in the sorbent, which may result in the reduction of surface area, leading to a decrease in the sorption (Memon et al., 2007). The sorbent material was then treated with 1 mol L^{-1} HCl at room temperature (25 ± 2 °C) for 8 h to remove the ash content. The digested sorbent was filtered and washed with a generous amount of ultrapure water. The chemically and thermally activated material was dried at 100 °C for 12 h, sieved and stored in a vacuum desiccator until needed.

The specific surface area of the date stones was determined by the methylene blue adsorption method. This technique is used widely for solids of various kinds, such as oxides, graphite, yeast, activated carbon, calcium carbonate, etc. (Graham, 1955; Savitsky et al., 1981). A detailed description of this method can be found elsewhere (El Bakouri et al., 2008b,c).

2.3. Measurements

The pesticide removal efficiency of each natural organic substance was determined by gas chromatography using stir bar sorptive extraction. This technique consists of the adsorption of pesticides contained in the recovered solution by using a stir bar (Twister) obtained from Gerstel (Mullheim a/d Ruhr, Germany). The commercial Twister consists of a glass-encapsulated magnetic stir bar 2 cm long externally coated with polydimethylsiloxane (PDMS). The Twister was placed in an Erlenmeyer flask containing 50 mL of the supernatant solution. The extraction was performed over a period of 12 h with a stirring speed of 800 rpm at room temperature (25 ± 2 °C) using a 15-position magnetic stirrer (Huertas et al., 2007). After extraction, the Twister was placed in an empty glass thermal desorption tube (187 × 4 mm i.d.). TD-GC-MS analysis was performed using a Gerstel TDS 2 thermal desorption system equipped with a Gerstel MPS 2 autosampler and a Gerstel CIS 4 programmable temperature vaporization (PTV) inlet. Gas chromatography was performed with an Agilent 6890 gas chromatograph with a 5973 mass-selective detector (Agilent Technologies). The thermal desorption system was programmed to increase at 60 °C min^{-1} from 40 to 280 C, and remained at this temperature for 7 min. Meanwhile, the desorbed analytes were trapped on a liner (Tenax and quartz wool filling) in the CIS 4 PTV injector at 30 °C. Finally, the CIS 4 was set to increase the temperature from 30 to 300 °C (held for 7 min) at 12 °C s^{-1} to inject the trapped analytes into the GC column in solvent vent mode. Separation was accomplished on a DB-5 MS fused silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies). After completion of the desorption stage, the oven temperature was kept at 70 °C for 2 min and after that set to rise from 70 to 150 °C at 25 °C min^{-1}, then to 200 °C at 3 °C min^{-1}, and finally to 300 °C at 8 °C min^{-1}. This temperature was maintained for 10 min. The flow of helium (carrier gas) was adjusted using RTL software so that chlorpyrifos-methyl was eluted at a constant retention time of 16.59 min. The mass spectrometer was operated in selected ion monitoring (SIM) mode with electron ionization. The amount of pesticide adsorbed was considered to be the difference between that initially present in solution and that remaining after equilibration. The pesticide detection limits (DL) were estimated by using the equation:

$$\mathrm{DL} = y_{\mathrm{B}} + 3 \cdot S_{\mathrm{D}} \tag{1}$$

in which y_{B} represents the blank signal (signal of water without target analyte) and S_{D} the standard deviation of the blank (Miller and Miller, 1994). The detection limit was verified by using the EPA method (EPA, 2003). A volume of spiked water was prepared to yield seven replicate aliquots with a concentration equal to the estimated detection limit. The DLs were then determined by multiplying the standard deviation by 3.143 (the Student's *t*-statistic at the 99th percentile for $n - 1$ degrees of freedom). The resulting DLs were 0.002 μg L^{-1} for aldrin and dieldrin and 0.003 μg L^{-1} for endrin. In this work the precision and accuracy were evaluated for all the analyzed compounds. The relative standard deviations (RSD) were less than 15% with recovery rates ranging from 94 to 107. These values are frequent in chromatographic methods (Lambropoulou and Albanis, 2005; León et al., 2006) and therefore the accuracy is acceptable.

2.4. Kinetic study

The kinetic experiments were performed by a batch technique according to the Organization for Economic Cooperation and