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Characterization of sorption processes for the development of low-cost pesticide decontamination techniques

Raquel Rojas *, Eva Vanderlinden, José Morillo, José Usero, Hicham El Bakouri

Department of Chemical and Environmental Engineering, University of Seville, 41092 Seville, Spain

HIGHLIGHTS

- Sorption and kinetics of four pesticides on different organic matrices were studied.
- Sorption was related with organic matrix and pesticide characteristics.

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ABSTRACT

The adsorption/desorption behavior of four pesticides (atrazine, alachlor, endosulfan sulfate and trifluralin) in aqueous solutions onto four adsorbents (sunflower seed shells, rice husk, composted sewage sludge and soil) was investigated. Pesticide determination was carried out using stir bar sorptive extraction and gas chromatography coupled with mass spectroscopy. Maximum removal efficiency (73.9%) was reached using 1 g of rice husk and 50 mL of pesticide solution (200 μg L^{-1}). The pseudo adsorption equilibrium was reached with 0.6 g organic residue, which was used in subsequent experiments. The pseudo-first-order, pseudo-second-order kinetics and the intra-particle diffusion models were used to describe the kinetic data and rate constants were evaluated. The first model was more suitable for the sorption of atrazine and alachlor while the pseudo-second-order best described endosulfan sulfate and trifluralin adsorption, which showed the fastest sorption rates. 4 h was considered as the equilibrium time for determining adsorption isotherms. Experimental data were modeled by Langmuir and Freundlich models. In most of the studied cases both models can describe the adsorption process, although the Freundlich model was applicable in all cases. The sorption capacity increased with the hydrophobic character of the pesticides and decreased with their water solubility. Rice husk was revealed as the best adsorbent for three of the four studied pesticides (atrazine, alachlor and endosulfan sulfate), while better results were obtained with composted sewage sludge and sunflower seed shell for the removal of trifluralin.

Although desorption percentages were not high (with the exception of alachlor, which reached a desorption rate of 57%), the K_fd values were lower than the K_f values for adsorption and all H values were below 100, indicating that the adsorption was weak.

1. Introduction

While pesticides are important tools in agriculture used in managing weeds, insects and diseases, continuous exposure to pesticides may cause serious problems for non-target organisms. Pesticides applied to crops find their way to the soil by direct losses, spray drift, runoff or incorporation of contaminated crop residues. According to several field surveys and measurement campaigns around 40–90% of surface water contamination is attributable to direct losses. The main pesticide direct losses are caused by spillages during the filling and cleaning of the spraying equipment and leakages of the spraying equipment (De Wilde et al., 2009). Once present in soil, pesticides migrate from one compartment of the environment to another and act as a source of contamination to air, groundwater, etc., the magnitude of which depends on their residence time in the soil (El Bakouri et al., 2009a; Lima et al., 2011). Therefore, the use of pesticides represents a water quality risk in agricultural areas since these compounds can spread across the ground and contaminate both surface waters and groundwater. Their presence in waters has grown considerably in the last few years and numerous recent studies have reported contamination of water resources by these chemicals (ADEQ, 2013; Jurado et al., 2012; Vryzas et al., 2012).

Prevention of groundwater pollution is much cheaper than restoring polluted aquifers. For that very reason it is of maximum interest to develop techniques that prevent pesticide leaching on land and/or avoid

* Corresponding author at: Departamento de Ingeniería Química y Ambiental, Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Camino de los Descubrimientos s/n, 41092 Sevilla, Spain. Tel.: +34 954481284.
E-mail address: rrojas@etsi.us.es (R. Rojas).

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water contamination during filling and cleaning operations. Adsorption is considered quite an attractive method for removing pesticides from dilute solutions. Although, the use of commercially available activated carbon and zeolites for removing pesticides is still very popular, it is very expensive (Terdkiatburana et al., 2008). Moreover, the high cost associated with its regeneration led to the exploration of new inexpensive materials (Gupta et al., 2006). Therefore, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of pesticides. The use of low cost modified organoclays has been proposed by several authors (Undabeytia et al., 2000; Rodriguez-Cruz et al, 2008; Suciu et al., 2011), but it is particularly interesting if the adsorbents can be recycled wastes as they are free and their use as adsorbents could contribute to solving the problem of waste disposal. Organic matter is the main soil component contributing to the sorption of pesticides (El Bakouri et al., 2009b). Numerous studies have suggested the addition of exogenous organic matter to soil as a possible method to reduce pesticide leaching (Delgado-Moreno et al., 2010; Cox et al., 1997; Tejada et al., 2011). Basing on the same principle of sorption, other studies suggested the development of on-farm biopurification systems to remove pesticides from contaminated water generated at the farmyard (Torstensson and Castillo, 1997; Torstensson, 2000). This technique was called biobed, Phytobac or biofilter. It consists of a biologically active matrix that retains pesticides onto organic matter and soil particles, where enhanced or rapid microbial degradation of the pesticides occurs. The composition and types of organic material present in the biobed are believed to be crucial for retention of chemicals. Matrix substrates that can be used in a biopurification system can have differing organic carbon contents and more importantly, differing pesticide sorption capacities. The same is applicable when using them as soil amendments. In order to optimize and model the fate and transport of pesticides in soil or in the biopurification systems, sorption and desorption of the pesticides on the substrates should be profoundly characterized.

The aim of the present work is to evaluate the adsorption/desorption characteristics of alachlor, atrazine, endosulfan sulfate and trifluralin on different organic matrices (sunflower seed shells, rice husk and composted sewage sludge mixed with pruning residues) and on soil.

The pesticides were chosen based on their physicochemical characteristics, frequency of detection and toxicity. The pesticides selected for this study have been frequently detected in Spanish, European and American surface and groundwater, and many times above the 0.1 μg L^{-1} groundwater quality standard for individual pesticides or 0.5 μg L^{-1} for the sum of several pesticides (ADEQ, 2013; Vryzas et al., 2012; Jurado et al., 2012; Barco-Bonilla et al., 2013; Moreno-González et al., 2013). What is more, pesticides selected for this study or their precursors were cataloged as Priority Substances under the Directive/39/EU 2013. Furthermore, while most of the developed countries have already banned or restricted the production and usage of these compounds, some developing countries still use these products because of their effectiveness and low application cost (El Bakouri et al., 2009a). The selection of the organic matrices was based on abundance, availability and cost. Sunflower seed shells (OR1) and rice husk (OR2) are industrial residues of sunflower oil production and the rice industry. Agricultural waste materials have little or no economic value and often pose a disposal problem. Applying those as an adsorbent for pesticides could also help to solve the waste disposal problem. Sunflower seed shells were already effectively used as an adsorbent for diazo dye Reactive Black 5 (Osma et al., 2007). Daifullah et al. (2003) successfully used rice husk to remove heavy metals from agriculture and sewage wastewater. Composted sewage sludge (OR3) is commonly used as an organic amendment to agricultural soils. Compost improves the soil quality and microbial activity. As the amount of pesticides sorbed is greater, the soil becomes less toxic for soil-bacteria and earthworms (Tejada et al., 2011). Composted sewage sludge was chosen in this study to evaluate its adsorption characteristics for the four selected pesticides. The fourth adsorbent, soil, is used as a reference, as soil also has adsorbent characteristics (Gevao et al., 2000).

Several recent publications report the use of low-cost and locally available adsorbents for pesticide removal: e.g., rice husk, date seed activated carbon, raw and biotransformed olive cake, etc. (Daifullah et al., 2003; Delgado-Moreno et al., 2010; Salman et al., 2011). Nonetheless, information covering the sorption capacity of the proposed organic substrates for the pesticides selected in this study has not been found in the literature. Some studies report the use of different types of organic matter to evaluate the sorption and mobility of these pesticides (El Bakouri et al., 2007, 2008, 2009b, 2010; Jamil et al., 2011; Kyriakopoulos et al., 2005; Rodríguez-Cruz et al., 2006). However, more investigations on readily available low-cost adsorbents are needed. The present study focuses on locally available natural organic substances at no cost. Which is more, in the case of biobeds, most studies have focused on the adsorption processes (De Wilde et al., 2009; Omirou et al., 2012; Tortella et al., 2012; Karanasios et al., 2013) but not on desorption. The desorption process could be as important as the adsorption process not only to predict transport, but also release, bioavailability and toxicity of sediment-phase pesticides (Gebremariam, 2011), which are crucial aspects for the optimization of biobeds. Characterizing the sorption/desorption of the selected adsorbents could help with the development of a technique to prevent contamination of groundwater by the studied pesticides. This method could help farmers select and properly use organic amendments to minimize environmental impact. To better define the best organic matrices to use as to prevent pesticide leaching, several sorption experiments were performed in this study.

2. Materials and methods

2.1. Chemicals, soil and organic matrices

All pesticide standards used in this work (atrazine, alachlor, endosulfan sulfate and trifluralin) were obtained from Dr. Ehrenstorfer GmbH (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 other solvents and chemicals used were of gas chromatography (GC) or analytical grade and were obtained from Merck (Germany). The water used was purified using a Milli-Q water-purification system (Millipore, USA). Sodium chloride and methanol were purchased from Merck (Germany). Calcium chloride ($CaCl_2$) solution (0.01 M) was freshly made up with ultrapure water to be used as the solution phase for each batch experiment.

The considered pesticides belong to different families and their physicochemical properties are shown in Table 1.

Soil for this work came from an agricultural plot in south-western Spain (N 37° 04′ 32″, W 5° 53′ 41″). Soil was sampled from the upper layer (0–25 cm), air-dried in the laboratory for a week and then dried at 70 °C in a drying oven for three days. Thereafter it was sieved through a 2 mm mesh and mixed well before use.

The organic matrices selected for the work (sunflower seed shells, rice husk and composted sewage sludge) were collected from different sites in Seville province (south-western Spain). Sunflower seed shells, residue of the sunflower oil production, were obtained at a local seed shop, rice husk was provided by Fábrica de Arroces Hervás and composted sewage sludge mixed with pruning residues was obtained from EMASESA (Metropolitan Water Purification and Supply Company of Seville, Spain).

Each organic residue was air-dried for a week and then dried at 70 °C in a drying oven for three days. They were manually sieved and particle sizes of less than 1 mm were used.

Standard soil characterization methods were used to provide information on the physical and chemical nature of the soil and organic