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Sorption potential of alkaline treated straw and a soil for sulfonylurea herbicide removal from aqueous solutions: An environmental management strategy

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HIGHLIGHTS

- Low cost adsorbents were synthesized for sulfonylurea pesticide removal.
- Surface characteristics of treated straw (wheat, corn) samples were assessed.
- Adsorption mechanism of chlorsulfuron was revealed and discussed.

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ABSTRACT

The adsorption potential of alkaline treated straw (wheat and corn) in mixture with soil, has been investigated for the removal of sulfonylurea molecules from an aqueous solutions. The surface characteristics were investigated by scanning electron microscopy and Fourier Transform Infrared - FTIR, while the adsorbent capacity was evaluated using batch sorption tests and liquid chromatography coupled with mass spectrometry. Surface analysis of alkaline treated straw samples by scanning electron microscopy - SEM showed the increasing of the surface roughness improving their functional surface activity. An increase (337.22 mg g^{-1}) of adsorption capacity of sulfonylurea molecules was obtained for all studied straw. The Langmuir isotherm model was the best model for the mathematical description of the adsorption process indicating the forming of a surface sorption monolayer with a finite number of identical sites. The kinetics of sulfonylurea herbicide followed the pseudo-second order mechanism corresponding to strong chemical interactions. The results sustained that the alkaline treated straw have biosorption characteristics, being suitable adsorbent materials.

1. Introduction

Pesticides are fundamental tools in agricultural practices used to control weeds, diseases and insects; however, constant exposure may deplete soil functions and environmental quality. For ground and surface water contamination, both direct and indirect losses of pesticides are responsible. The predominant direct losses of pesticide include spillages during the filling, cleaning and leakages of the spraying equipment (Mandal et al., 2017). Runoff, spray drift or incorporation of contaminated crop residues are the main sources of direct losses (De Wilde et al., 2009). Once they reach the ground, pesticides migrate from one compartment of the environment to another and act as a source of contamination to air, soil and water bodies, etc., the magnitude of which depends on their residence time in the soil (El Bakouri et al., 2007, 2008, 2010). Thus, soil remediation using environmentally and friendly techniques are necessary to improve the ecological system.

A wide range of methods such as combination of biological, chemical and physical processes have been proposed for soil decontamination. Many of these methods are expensive or have some drawbacks, such as low selectivity, high amounts of sludge or incomplete removal (Cara et al., 2015). Among all, adsorption is one

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of the most effective physical process for pesticide removal from aqueous solution, because the technique uses equipment that is available, easy to use and cost effective (Rojas et al., 2014). The technology that is frequently used to purify soil-water contaminated by pesticide is adsorption on activated carbon. Although it has great capacity of adsorbing but the high cost associated and difficulties of regeneration sent to search new materials.

Because of its simplicity, adsorption using low cost adsorbents has gained important credibility, being an efficient alternative and minimization of secondary waste. There are three steps involved in pesticide adsorption onto adsorbent surface: (1) the transport of the pollutant from the bulk solution to the adsorbent surface; (2) adsorption on the particle surface; and (3) transport within the adsorbent particle (Harja et al., 2015). The adsorption process implies the presence of an adsorbent that binds pesticide molecules by physical attractive forces, ion exchange and chemical binding (Todorciuc et al., 2015).

Recently, non - conventional and low - cost adsorbents such raw materials and modified materials obtained by different treatments were frequently used as adsorbents for wastewater treatment.

Wheat, corn and soybean are widely cultivated throughout the world and are a major food item. Straw a byproduct, is mainly used as a raw material for feeding animals and for the paper industry. The straw has been reported to have potential for metal and pesticides sorption (Farooq et al., 2011). Recent publication reports the use of wheat straw for the removing of methylene blue, beying a very promising adsorbent with definite selectivity for cationic dyes simultaneously (You et al., 2016). Batch adsorption experiments were performed by Rojas et al. (2015), De Wilde et al. (2009) to study the adsorption potential of readily available adsorbents (garden waste compost, straw, rice husk, peat mix, composted sewage sludge) for removal of linuron, bentazone, chlorfenvinphos, chlorpyrifos and trifluralin. Agri-wastes biochars *viz.*eucalyptus bark, corn cob, bamboo chips, rice husk and rice straw were investigated for their sorption behaviour of atrazine and imidacloprid (Mandal et al., 2017). Thus, rice, wheat and corn straw biochars have great potential for environmental implications and can be exploited as adsorbents for pesticide water purification.

In this study, soil and modified raw material were used as low cost adsorbents for the removal of sulfonylurea molecules from aqueous solution. Sulfonylureas are a large family of herbicides, widely used for the control of broad leaf weeds in various crops (Leonard et al., 2017). Applied at low doses varying from 2 to 75 g of active ingredient per hectare, sulfonylureas possess high herbicidal activity, broad spectrum of action, good selectivity and low mammalian toxicity. Chlorsulfuron is often considered as the representative of the family since it is one of the most-sold sulfonylurea herbicides. This compound is a post-emergence herbicide commonly used on corn crops at 60 g active ingredient ha^{-1}. Its solubility (31.8 mg L^{-1}) and sorption coefficient (0.42 mL g^{-1} according to the soil characteristics) make this compound relatively mobile and bioavailable in soil and water (Leonard et al., 2017).

In order to increase the adsorption capacity of raw materials, a simple alkaline treatment was used. The influence of sulfonylurea molecules concentration and equilibrium contact time was studied at room temperature, in a series of batch sorption tests. Two adsorption isotherm models were used for the mathematical description and the experimental data were analyzed using the pseudo-second-order and first-order model.

2. Materials and methods

2.1. Chemicals, soil and raw materials

Chlorsulfuron analytical standard was obtained from Dr. Ehrenstorfer GmbH (Germany). The stock solution (1000 mg L^{-1}) of chlorsulfuron molecules was prepared in hexane, while working solutions (1–100 mg L^{-1}) were diluted with ultrapure water and stored at 4 °C. All chemicals (hexane, methanol) were of high performance liquid chromatography grade (Merk, Germany). The water used was purified using a Milli – Q water – purification system (Millipore, USA). 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 soil and straw materials (wheat and corn type) used in the experiments were sampled from Ezareni – the Experimental Farm of the Agricultural University Iasi Romania (47°07′ N - 27°30′ E). The soil is a cambic chernozem (SRTS, 2012) (haplic chernozem WRB-SR, 2006), with a clay – loamy texture, 6.96 pH, 3.06% humus content and 21.22 me/100 g soil cationic exchange capacity (Cara et al., 2017). Texture (38.8% sand, 35.% clay) was determined by sedimentation using the pipette method, while total organic carbon content (1.39% C_{org}) was determined by dichromate oxidation.

The elemental composition and some physical-chemical characteristics of raw materials have been presented in previous studies (Cara et al., 2015).

Before the alkaline treatment, the raw straws were washed several time with ultrapure water and dried at 70 °C in oven, grounded and then sieved to obtain particles of 140–160 μm.

The alkaline treatment was done by treating the raw samples with an aqueous solution of 4 M KOH. Thus, 2.0 g of wheat and corn straw were boiled for 2 h (t = 100 °C) in a 4 M potassium hydroxide (KOH) solution, 1:1 mixture ratio. The samples were cooled at room temperature and washed with ultrapure water, dried at 105 °C and stored in desiccators for further use.

The concentration of the alkali and the temperature used during the treatments were based on previous results obtained for the treatment of other materials – rice, soybean straw (Chang et al., 2014; Liu et al., 2015; Martelli-Tosi et al., 2017).

2.2. Characterization of straw

The surface morphology of each material was examined using a FEI (Field Electron and Ion Company) scanning electron microscopy (SEM) at an accelerating voltage of 5 KV.

The treated and untreated straw were analyzed by Fourier Transform Infrared (FTIR) Spectroscopy to identify the functional groups and any chemical changes that may have occurred after alkaline treatment. All the spectra were the average of 100 scans recorded at a resolution of 4 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1}.

2.3. Kinetic study

2.3.1. Equilibrium time

The adsorption experiments were performed by batch technique according to the Organization for Economic Development guideline no. 106 for the testing of chemicals. (OECD, 2000).

Each experiment was performed by mixing 2 g of soil and 0.01 g of treated samples with 20 mL of chlorsulfuron solution (1–100 mg L^{-1} concentrations). The solutions were shaked on an orbital shaker at 350 rpm, at room temperature. The concentrations of the chlorsulfuron were determined by LC-MS at given time intervals: 2, 5, 10 15, 20 and 25 h.

The amount of chlorsulfuron molecules adsorbed at the considered time t, q_t (mg adsorbate/g adsorbent), was calculated using the following Eq. (1):