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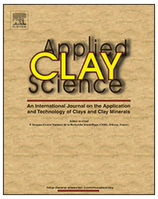

Research paper

Adsorption of linuron by an Algerian palygorskite modified with magnetic iron

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ABSTRACT

Three types of palygorskite nanoparticles for the retention of the herbicide linuron in water were tested: purified palygorskite (Pur Pal), palygorskite modified by magnetic iron oxides (FeO Pal_1) and this one synthesized by hydrothermal treatment (FeO Pal_2). The adsorbents were characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR), electron microscopy (TEM) and chemical analysis (XRF). XRD patterns indicate the presence of a magnetic Fe_2O_3 compound, and TEM images evidence how these crystals cover the palygorskite fibers' surface with different crystallite sizes (7–15 nm in FeO Pal_1 and 30-50 nm in FeO Pal_2). The adsorbent mass, the contact time, the initial adsorbate concentration and the effect of temperature were evaluated for linuron retention. Adsorption kinetics revealed that adsorption followed a pseudo-second order equation. Adsorption isotherms were better fitted to the Freundlich than to the Langmuir equation. Removed linuron amounts were ranged as FeO Pal_2 (83%) > FeO Pal_1 (55%) > Pur Pal (27%). The adsorbents could be used as a cheap alternative for pesticide removal in environmentally-contaminated waters.

1. Introduction

Since the industrial revolution, the land devoted to agriculture has increased at the exponential growth rate of the world population. The mechanization and modernization of techniques have encouraged increased production to meet growing demands. Accordingly, pesticides have been used worldwide in intensive agriculture in considerable quantities for over half a century. Algeria is a major consumer of pesticides with 30,000 tons “land applied” every year, with > 432 registered pesticides, from which the most frequently used are pyrethroids, organophosphorus, carbamates and substituted ureas (Moussaoui et al., 2002; Ministère de l'Agriculture, du Développement Rural et de la Pêche, 2015).

The increasing use of pesticides causes real environmental problems associated with the mobility of these compounds in the environment, particularly those related to drinking water quality (Gonzalez et al., 2013; Mekonen et al., 2016). According to Pimentel (1995) and Carriger et al. (2006), only a minor fraction of the applied pesticide actually reaches its targets, while the rest is distributed in the environment and submitted to different processes which can lead to its transport to aquatic ecosystems (Arias-Estévez et al., 2008; Gonzalez et al., 2013).

Among these substances, linuron, a selective substituted phenylurea herbicide, is a systemic herbicide used in the pre- and post-emergence control of annual grass and broad-leaved weeds, such as soybean, cotton, potato, corn, bean, pea, winter wheat, asparagus, carrot, and fruit crops. It is also used on crops stored in warehouses and storerooms (Malenčić et al., 2008). According to the Pesticide Properties Database (Footprint, 2015) this compound can be considered as slightly mobile and is classified as a transient leacher. Leaching experiments using disturbed or undisturbed soil lysimeters have shown that phenylurea mobility is highly dependent on pesticides' chemical structure, being linuron of intermediate mobility. It has been shown that up to 7% of applied linuron could be measured in the leachates (El Imache et al., 2008; Langeron et al., 2014). For all these reasons, and although the use of this herbicide was not approved in the EU after 2009, it is not surprising that linuron has been frequently detected in water bodies, either in Spain and Portugal, both in rivers and groundwater (Carabias-Martínez et al., 2003; Sánchez-González et al., 2013), in a French estuarine (Caquet et al., 2013) or in a Turkish delta (Yurtkuran and Saygi, 2013). In fact, under environmental conditions and depending on temperature and pH, phenylureas can persist at the $mg\,L^{-1}$ level in

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groundwater (Leon-Gonzalez and Townshend, 1991) for a number of days or weeks.

Furthermore, it has been reported that this herbicide acts as an antiandrogenic chemical altering sex differentiation in male rats (Lambright et al., 2000; McIntyre et al., 2002). Linuron has been classified as toxic to reproduction (category 2) and carcinogenic (category 2), whose target organs are liver and red blood cells and with the capability of inducing malformations, infertility or cell tumours (Marx-Stoelting et al., 2014).

Therefore, the removal of linuron from environmental samples is advisable. However, treatment of contaminated water is usually complicated, time-consuming, expensive and often not feasible. Consequently, the development of new materials and methods for water decontamination has become a current research topic. The retention of linuron from aqueous solutions has been approached using different adsorbents: surfactant-modified clays (Sánchez-Martín et al., 2006; Katsumata et al., 2007; Chaara et al., 2012), wood residues (Rodríguez-Cruz et al., 2007), plant extracts (Khalfaoui et al., 2015) or other modified clays (Pavlovic et al., 2013).

Natural or modified clay minerals have often been used in different industrial and technological processes. Over the past few decades, much emphasis has been placed on studies that explore their possible application as barriers in the immobilization of toxic organic pollutants, and, recently, their use has been extended to the immobilization of pesticides from point-sources of contamination (Sánchez-Martín et al., 2006; Ouali et al., 2015; Rodríguez-Liébana et al., 2016).

Palygorskite (Pal), a fibrous clay mineral, is a crystalline hydrated magnesium aluminum silicate consisting of two bands of silica tetrahedral linked by magnesium ions in an octahedral configuration, which are connected by a continuous plane of tetrahedral basal oxygen atoms, resulting in a relatively high surface area, moderate cation exchange capacity (CEC) and high sorption capacities (Zandonadi and Skitnevski, 1986; Fan et al., 2009). In addition, some isomorphic substitutions in the tetrahedral and octahedral layers develop negatively charged sorption sites that can adsorb cations through electrostatic attraction.

As reported by Wang et al. (2015), it is expected that palygorskite-based adsorbents will be stable, safe, low cost, and non-toxic. Furthermore they do not induce the risk of secondary pollution, like some organic adsorbents. However, the adsorption ability of natural palygorskite is usually limited, and therefore it should be treated to reach more satisfactory adsorption abilities before using it as an effective adsorbent. Therefore nanoparticles of palygorskite can be modified with magnetic iron oxide (FeO Pal) by a common co-precipitation method (Massart, 1981), adapted by different authors (Mornet et al., 2000; Daou et al., 2006; Liu et al., 2008; Ouali et al., 2015). Magnetic nanoparticles are being increasingly employed for the removal of contaminants, because they increase the retention capacity of clays through the formation of stable complexes between Fe ions and organic molecules. In addition, the retained pollutants can be easily removed by applying a magnetic field (Middea et al., 2015) and the adsorbents could be recovered and later regenerated for further reuse (Masoumi et al., 2016), making them a good option for removing organic and inorganic contaminants at low cost. In addition, a hydrothermal treatment may induce a performance enhancement by slightly changing the crystal structure, allowing the creation of new adsorption sites in the treated palygorskite and boost adsorption properties (Wang et al., 2015).

The objective of this study was to prepare new materials based on palygorskite which could display excellent properties to retain pollutants from contaminated water. With this aim three types of modified palygorskite [Pur Pal, FeO Pal_1 and FeO Pal_2] were evaluated for the adsorption of linuron, a model compound which may constitute a potential hazard for environmental waters in some countries where its use is still allowed. The operating conditions such as mass of adsorbent, concentration of adsorbate, time and adsorption temperature were studied.

2. Materials and methods

2.1. Chemicals and reagents

The fibrous clay mineral used is a palygorskite rich in dolomite obtained from tertiary sediments near the city of El Ghoufi, in East Algeria (Belaroui et al., 2014). Pur Pal was ground and sieved to 90 μm mesh size and was chemically treated according to the protocol of Dali Youcef (2012). Iron dichloride tetrahydrate ($FeCl_2.4H_2O$), iron chloride hexahydrate ($FeCl_3.6H_2O$), ammonium hydroxide (NH_4OH, 34% of ammonia), hydrochloric acid (HCl, 37%), nitric acid (HNO_3, 66%), acetone and HPLC grade acetonitrile were purchased from Prolabo® (France).

The substituted phenylurea herbicide linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] was used. A standard of linuron, a white crystalline solid of 99.5% purity (Dr Ehrenstorfer, Germany), was used without further purification. Linuron has an octanol-water partition coefficient (K_{ow}) of 3.0 and a water solubility of 63.8 mg L^{-1} at 20 °C (Footprint, 2015). A stock solution of linuron in acetone was prepared at 1 g L^{-1} and the required solutions were prepared by appropriate dilutions with high-quality MilliQ water (Millipore, USA).

2.2. Synthesis of FeO Pal nanoparticles

The nanoparticles modified with magnetic iron oxides were prepared by the co-precipitation method (Massart, 1981; Massart and Cabuil, 1987), which consists in mixing two iron precursors with ferric and ferrous chloride in 2:1 M ratio in an alkaline medium with 9 mL of NH_4OH at 34% with vigorous stirring during 15 min, as shown in Eq. (1):

$$2FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O \qquad (1)$$

The colloidal solution of Fe_3O_4 was washed with acetone, followed by deionized water. Two varieties of magnetic FeO Pal nanoparticles were prepared with the fibrous clay mineral. The first one, called FeO Pal_2, was prepared with a hydrothermal treatment at 200 °C for 48 h, by adding the colloidal solution of Fe_3O_4 to a 1% mass dispersion of purified palygorskite (Pur Pal), sieved at 90 μm mesh (Dali Youcef, 2012), under stirring for 2 h. The other one, called FeO Pal_1, did not suffer any hydrothermal treatment. Both samples were washed and dried at 80 °C.

2.3. Characterization of the nanoparticles

X-ray Powder Diffraction (XRPD) analysis was performed on a Panalytical X-Pert Pro diffractometer with Cu Kα radiation (45 kV, 40 mA), Ni filter, RTMS X'Celerator detector, 4°–70° scan range, 0.0084° step size, 10.150 s counting time, for a total of 7898 points and 11 min/sample.

The samples were analysed by infrared spectroscopy (FTIR) (Alpha-Bruker) in the range of 4000–400 cm^{-1}. The dried sample was ground with dried potassium bromide (KBr) powder and compressed into a disc before analysis.

Chemical sample analysis was performed with dispersive X-ray fluorescence (SpectraPLUS, S4 Pioneer, BRUKER) equipped with an Rh anode X-ray tube (60 kV, 150 mA).

Transmission electron microscopy (TEM) was used to obtain morphological and chemical information. Samples were suspended in ethanol, sonicated for 2 min and placed on a Cu grid. These samples were examined using a Phillips CM-20 electron microscope. Point-to-point resolution was 0.27 nm and beam sizes were 100 nm. Quantitative microanalyses were carried out in STEM mode using an EDAX-Genesis system equipped with a Si (Li) detector, using a 7-nm beam diameter and a 20 × 100 nm scanning area.

pH was measured in water at 1/2.5 ratio (w/v) (Cyberscan pH 2100, Eutech Instruments). Cation exchange capacity (CEC) was determined