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Research paper

Removal of paraquat from water by an Algerian bentonite

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ABSTRACT

The sorption–desorption of the cationic pesticide 1,1′-dimethyl-4,4′-bipyridinium dichloride (paraquat) on a bentonite from Maghnia (Algeria) desiccated at 110 °C (M), and calcined at 400 °C (M400) and 600 °C (M600) from aqueous solution at 25 °C has been studied using batch experiments. A complete characterization of the natural and heat activated bentonite samples has been carried out through the following techniques: X-ray fluorescence spectroscopy, FTIR, X-ray diffraction, thermogravimetric and differential thermogravimetric analysis and surface analysis. In order to have a better understanding of the variables affecting the sorption of this herbicide, factors such as the working temperature or the ionic strength of the solution have been investigated. The sorption experimental data have been fitted to the Langmuir equation in order to calculate the maximum sorption capacities (X_m) of the samples. The results show that the sorption capacity of the calcined samples greatly decreased with heat treatment. On the other hand, the sorption process is hardly affected by the working temperature, whereas the higher electrolyte concentration, the lower sorption of this pesticide. In addition to batch experiments, a decontamination continuous process (DCP) was designed by the authors using the natural clay to evaluate the potential application of this adsorbent for removing paraquat from water.

1. Introduction

The use of pesticides has become a prerequisite aspect of agriculture and public health. Versatile use of pesticides had resulted in contamination of all basic necessities of life, i.e. air, water and food. Amongst various pesticides, paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) along with glyphosate, is one of the most widely used herbicides in the world (Péguy Nanseu-Njiki et al., 2010). This compound is a non-selective contact herbicide which destroys plants by inhibiting photosynthesis (Péguy Nanseu-Njiki et al., 2010; Tsai et al., 2005). Unfortunately, paraquat is known to display some harmful effects such as pulmonary fibrosis, which results from the transformation by paraquat of the oxygen available in the lungs into free radicals. Once paraquat enters the soil environment, it is rapidly and strongly bound to clay minerals and organic matter and becomes biologically inactive (Ricketts, 1999). The risk of contamination by paraquat is enhanced by its high water solubility (620 g/L) (Tomlin, 2009), having been detected in surface and drinking waters (Hadi et al., 2005; Zhou et al., 2009). For European standards, the maximum permissible concentration for individual pesticides (including paraquat) in drinking water is 0.1 $\mu g \cdot L^{-1}$ and 1–3 $\mu g \cdot L^{-1}$ for surface waters (Mojović et al., 2009). Thus, the necessity to reduce the concentration of paraquat in water is a worldwide challenge as far as water pollution is concerned. In this sense, the sorption/desorption phenomena of pesticides in soils are of great importance from the environmental point of view, as pesticide sorption affects other processes like transport, degradation, volatilization and bioaccumulation of these compounds in the soil (Kumar and Philip, 2006). Furthermore, other authors have reported the strong relationship between the desorption process and the potential mobility of pesticides in soil (Haung and Weber, 1998).

Different materials have been investigated for this purpose, such as diatomite, phillipsite–faujasite tuff (faujasite), zeolite covered with alkylsilane, and methacrylic acid-modified rice husk (Hadi et al., 2005; Khalil and Haneen, 2009; Shih-Tong and Ting-Chung, 2007; Tsai et al., 2005), the majority being the results of the synthesis or transformation of natural products.

Clay minerals are good adsorbents owing to their high cation exchange capacity and high specific surface areas associated with their small particle sizes, and have the advantage of being abundant and inexpensive. Thus, their surface reactions have strong biochemical and ecological effects in soils and waters, and these materials are being used for decontamination and remediation treatments (Quintelas et al., 2011; Sánchez-Jiménez et al., 2011). For this study, we have used a natural Algerian bentonite, which has been widely used in catalysis, sorption of dyes, pesticides, metals and drilling of oil wells for its rheological properties (Abollino et al., 2003; Cheng-Cai et al., 2004; Sankarasubbier and Kiranmayi, 2000; Wang and Wang, 2008). A review of relevant

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literature reveals that there are no complete studies of the physico-chemical characterization of this clay, therefore, this aspect has been considered as part of this study and is detailed in this paper.

On the other hand, given that sorption capacity may be enhanced by thermal or chemical modifications, the present study was aimed at investigating the behavior of the Algerian bentonite as adsorbent after thermal treatment.

In addition, interactions involving divalent organic pesticides, such as paraquat, and clays, depend on environmental conditions such as ionic strength or temperature so, taking into account the above stated; the aims of the present study were therefore: (1) to carry out a complete characterization of the Algerian bentonite, (2) to analyze the effect of calcination temperatures in the sorption capacity of the activated samples, (3) to quantify the sorption/desorption of paraquat on the Algerian bentonite by using batch experiments in an aqueous and saline medium with different values of ionic strength at 25 °C, (4) to evaluate the effect of the working temperature in the sorption process and (5) application of a continuous dynamic system which permits a total removal of paraquat in potential contaminated waters with this herbicide by using a single process.

2. Materials and methods

2.1. Materials

A montmorillonite-rich material originating from the Hammam Boughrara deposit (Maghnia, Algeria), and industrially treated with sodium carbonate, was supplied by ENOF Ltd. (Algeria). The material was not ground because it was already in an adequate grain size (<60 μm) and was only air dried first and then at 110 °C. This bentonite will be designated M in the following.

Heat treatment of the natural bentonite was carried out by heating samples at 400 °C and 600 °C for 24 h. The products so obtained are labeled in the text as M400 and M600, respectively.

Analytical grade paraquat (1,1′-dimethyl-(4,4′-bipyridilium dichloride)), purchased from Sigma-Aldrich (Supelco, Spain) was used as adsorbate in this study.

2.2. Characterization

The cation exchange capacity (CEC) and the exchange acidity of the samples were determined by the $BaCl_2$-triethanolamine procedure and the carbonate content by using the Bernard calcimeter (Primo-Yúfera and Carrasco Dorrién, 1981).

Specific surface areas (S_{BET}) were obtained from N_2 sorption isotherms at 77.4 K, in a volumetric sorption system, Gemini II-2375 (Micromeritics). A value of 16.2 Å was adopted for the cross-sectional area per nitrogen molecule and the relative pressure interval used $0.02 < P/P_0 < 0.2$. The nitrogen used was 99.998% pure. The samples were degassed previously at 210 °C for 24 h.

The chemical composition of the natural and heat treated bentonite samples was determined by X-ray fluorescence spectroscopy with a MagiX PANalytical equipment.

XRD patterns of bentonite (before and after activation) were collected on a XPERT PRO DE PANALYTICAL diffractometer using graphite-monochromated Cu K_α radiation.

Thermal properties and stability of samples were analyzed using a TGA Q50 thermogravimetric analyzer (TA Instrument). The analyses were conducted at atmospheric pressure under an air flow (100 $mL \cdot min^{-1}$) with a heating rate of 10 $°C \cdot min^{-1}$ and a temperature limit of 900 °C.

The FTIR spectra of the clay samples were recorded using KBr pellets on an ATI Mattson spectrometer over a range of 4000–400 cm^{-1}.

FTIR spectrum of the natural clay saturated with paraquat was also obtained through the following procedure: an aqueous pesticide solution (25 mL) with a concentration corresponding to the maximum used in the sorption experiments was added under continuous stirring to 0.05 g of the adsorbent in 100 mL conical flasks. These flasks were shaken for the equilibrium time at 25 °C. Following the equilibration period, the samples were centrifuged and the supernatant concentration measured. Another 25 mL portion of the same pesticide solution was added and the process was repeated until the supernatant concentration was constant. The remaining solids were then air-dried without washing and pressed into potassium bromide pellets.

2.3. Sorption experiments

Sorption isotherms were determined by batch equilibration of 0.05 g of each clay sample with 25 mL of pure water solutions of paraquat of varied initial concentration (50 $mg \cdot L^{-1}$–300 $mg \cdot L^{-1}$). Experiments were carried out in a thermostatic shaker bath at 25 °C. Preliminary investigations on the sorption rate by using the clay adsorbent indicated that the process occurred rapidly. After a period of 45–60 min, a gradual approach to the sorption capacity was observed, so the sorption equilibrium time used in the experiments was 24 h.

After equilibration, the dispersions were centrifuged, filtered through 0.45 μm nylon filters and the pesticide concentration measured in the supernatant solution (C_e) by absorption at 257 nm (the wavelength corresponding to its maximum absorbance), using a Shimadzu UV-1700 spectrophotometer. The amount of paraquat adsorbed (X) was calculated from the difference in concentration between the initial (C_i) and final (C_e) solutions. Blanks containing no paraquat, and two replicates of each sorption point were used for each series of experiments.

The effect of ionic strength on the sorption capacity of the original clay was studied by using 0.01 and 0.1 M KCl solutions of paraquat of varied initial concentrations (30 $mg \cdot L^{-1}$–280 $mg \cdot L^{-1}$). In the same way, sorption experiments were carried out at 15 °C and 35 °C in order to study the influence of the working temperature in the sorption process.

2.4. Desorption experiments

Desorption experiments were carried out with the original clay as this sample showed the higher sorption capacity.

Once the sorption process had finished after 24 h, the volume of the liquid phase in each centrifuge tube corresponding to the higher concentration of paraquat used in the experiment, was removed and replaced with an identical volume of solution (water or 0.01/0.1 M KCl solutions) containing no herbicide and the solution was processed as described above, with the procedure being repeated until the amount of pesticide desorbed remained constant. Desorption data are given as percentages of the initial amounts adsorbed. All measurements were made in duplicate.

2.5. Dynamic sorption experiments

The dynamic sorption study was carried out by using a column system designed by the authors (Fig. 1). The column experiments were only carried out with the natural clay since, as will be seen below, the sorption capacity of this sample is higher than the other clay samples. The system was constructed using two glass columns of 15 mm inside diameter by 250 mm in length, with tap and frit filter. At the top and bottom of both columns, glass wool was placed to prevent the blockage of the column. Some glass marbles were used at the bottom of the columns to facilitate a better contact between the paraquat and clay solutions. The experiment was carried out as follows: a paraquat aqueous solution and a clay dispersion were each passed through the bottom of the first column at a fixed flow using a pump working with a steady flow. The use of a second column allows the prolonging of the contact time between the clay and the herbicide. The study was conducted using different flows (Q) for both solutions (0.75, 1.5 and 3 $mL \cdot min^{-1}$) and varying the concentration of the clay dispersion used (0.8, 1.4, 2.1 and 3.5 $g \cdot L^{-1}$).