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Adsorption of paraquat herbicide on deposits from drinking water networks

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HIGHLIGHTS

- Interaction between paraquat (PQ) and typical pipe deposits is studied.
- Good adherence between experimental data and both kinetic and equilibrium models.
- In case of a contamination event, it is unlikely that PQ may adsorb on deposits.
- Brown and tubercle deposits are good alternative adsorbents for water treatment.

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ABSTRACT

Although forbidden in Europe, paraquat is still largely used worldwide as herbicide. Therefore, the hypothesis of an accidental or deliberate contamination of drinking water distribution systems (DWDSs) may be posed. The interactions between paraquat and three typical deposits (S2, S3 and S4 deposits) from DWDS were investigated in order to understand the fate of this chemical in such systems in case of contamination. Additionally, these materials can be valorized as adsorbents in wastewater treatment applications. The effect of stirring speed, adsorbent dose, initial paraquat concentration and temperature on the adsorption kinetics was evaluated. Good adherence was observed between experimental data and both kinetic (pseudo-second order) and equilibrium (Langmuir) models. The interaction between paraquat and the deposits is extremely weak when compared to those established in the paraquat-clay system, where irreversible sorption was observed. It was found that S2 and S3 may represent potential adsorbents regarding the treatment of paraquat-contaminated waters.

1. Introduction

Paraquat is the most widely used herbicide in the world, although forbidden in Europe. Its popularity is related to its quick and non-selective action to kill green plant tissue upon contact. Additionally, some studies proved that this compound is one of the few herbicides capable of controlling the growth of weeds that became resistant as a result of over-use of non-selective glyphosate herbicides [1,2]. Due to the intensive use of this and other pesticides on agriculture, and because the interaction between such compounds with soils determines their biological activity, mobility and degradation, the sorption of pesticides on soil has been subject of numerous studies [3–11]. Indeed, the inaccessibility of micropores to microbes, the surface stabilization against desorption of the pesticide and the reduction of aqueous-phase concentrations to levels below those necessary for microbial utilization compromise the microbial attack of the compounds that are sorbed to inorganic/organic surfaces [12]. In the particular case of paraquat, the interaction with clays, which are the main components of the mineral fraction of soils, and organic matter, is very rapid and strong [9,13,14]. In some cases, this non-selective herbicide is inactivated by irreversible adsorption on clays [15,16]. Although this fact may induce the conclusion that paraquat could be considered as safe for many agricultural uses, it has been detected in waters. Watercourse contamination may result from a vertical transport through the soil profile promoted by the dissolved colloids such as dissolved organic matter and dispersed colloidal clay [4]. Fernández et al. analyzed water samples from irrigation channels, rivers and lagoons taken from three different marsh areas of the Valencian community (Spain) and a paraquat concentration of 3.95 μg/L was detected [17]. More recently (2006), paraquat concentrations between 1.5 and 18.9 μg/L and 9.3 and 87.0 μg/L were found in ground and surface water of Thailand, respectively [11]. Even at very low doses, this herbicide can pass some treatment steps and reach the water distribution systems, posing a threat to human

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health. Thus, effective treatments are required, like oxidation [18,19] or adsorption, for which low-cost adsorbents are required.

Beyond the natural occurrence of paraquat in drinking water due to its large usage in some countries [20,21], its presence may be the result of a deliberate or accidental contamination. The present work is part of a European project (SecurEau) whose main objective is to launch an appropriate response for rapidly restoring the use of drinking water networks after a deliberate contamination event [22]. In those circumstances, the paraquat concentration in water could be very high, partially due to its high solubility in water.

Most water distribution networks have a buildup of particles in the walls – deposits. Depending on the material used in the network construction and several water quality parameters, deposits with different properties and characteristics may be formed [23,24]. In spite of this large heterogeneity, typically they are classified in three main representative groups: brown, tubercle and white deposits [25]. According to Echeverría et al. [25], brown deposits are constituted by aluminosilicates and humic acids, tubercle deposits are mostly mixtures of magnetite, goethite and in some cases lepidocrocite, and white deposits are formed by calcite, aluminosilicates and quartz. The study of pesticides adsorption on such deposits is thus of paramount importance. In fact, there are several studies about paraquat adsorption on clays and soils (Table 1 – [3–11,13,14,26–32]) but, up to the author's knowledge, there are no studies regarding the sorption of paraquat on deposits typically found in DWDS. Although often compared to soils, deposits found in drinking water networks may be very distinct. The main objective of this work is to evaluate the interaction between paraquat and the deposits found in a DWDS, which is of crucial importance to understand the behavior and fate of paraquat in aquatic systems. Besides, it would allow exploring the use of such materials, often discarded upon pipes cleaning/maintenance operations, as low-cost adsorbents in, at least, a first and quick decontamination treatment approach of paraquat contaminated waters. For that, three real deposits, representative of drinking water networks, were collected from an old water distribution system in Germany and the Netherlands.

2. Experimental section

2.1. Pesticides and chemicals

Paraquat dichloride (PQ) PESTANAL® analytical standard (Fluka) was purchased from Sigma Aldrich (St. Louis, USA). Heptafluorobutyric acid (HFBA) was from Sigma Aldrich, and acetonitrile (HPLC grade) from Prolabo. Granular anhydrous calcium chloride and hydrochloric acid (37%) were obtained from Sigma Aldrich.

2.2. Deposits and other materials

The deposits samples (S2, S3 and S4) used in the adsorption studies were taken from a real DWDS. The deposits were removed from cast iron pipes that needed to be replaced. Deposits were submitted to drying in an oven (till no weight variation has been detected). Then, all deposits were sieved and were kept in dry conditions until the experiments. An extensive physico-chemical characterization of these deposits has been described previously [18] and, for that reason, the nomenclature used previously was maintained. In the same study, and according to the results obtained, it was possible to classify the S2, S3 and S4 samples as brown, tubercle and white deposits, respectively.

Clay was the other adsorbent used in this work. Its chemical composition was obtained from LNEG (Laboratório Nacional de Energia e Geologia, Portugal) and the particle size was determined by a Coulter Counter LS 230 with small volume model. The pHpzc (point of zero charge) was obtained as for deposits [18].

The organic matter content was determined in a TOC-VCSH apparatus with a solid sample module SSM-5000A. The total surface area was determined by mercury porosimetry.

The main properties of all adsorbents used are summarized in Table 2.

2.3. Adsorption experiments with suspended particles (clay, or from real "loose deposits")

A paraquat solution of 1 g/L was prepared by dissolving an appropriate amount of paraquat dichloride salt in distilled water. The adsorbent ("loose deposit" from drinking water pipes or clay particles) was first put in contact with 10 mL of distilled water to obtain stable conditions (for example constant pH). After that the contamination was done adding fixed volumes of 1 g/L paraquat solution. The experiments were performed at fixed stirring speed, temperature and pH. Stirring was ensured by a multi-positions magnetic stirrer from Velp Scientific (583 rpm – position 7 – unless otherwise stated). It is important to emphasize that all adsorption experiments with clay and deposits samples were performed at different pH values since they have different equilibrium pH in water. The aqueous phase of the contaminated samples was analyzed along time by high pressure liquid chromatography with diode array detector (HPLC-DAD) for determination of the paraquat dichloride concentration (kinetic experiments). In equilibrium experiments, the concentration of paraquat dichloride in the liquid phase was determined at the beginning ($t = 0$) and after equilibrium has been reached. All experiments were performed in duplicate and each sample was analyzed twice by HPLC-DAD, to guarantee the reproducibility of the results. A maximum coefficient of variation (CV%) of 15% was obtained for duplicates during the experiments.

2.4. Desorption experiments

Firstly, 0.5 g of S3 and S4 deposits were contaminated with 10 mL of a 50 mg/L paraquat solution during 24 h. After this time, even if the equilibrium stage has not been achieved, the solid and liquid phases were separated by centrifugation (4000 rpm; 10 min). Then, the liquid phase was analyzed by HPLC-DAD and the contaminated deposits were dried in a freeze-dry during 5 h. Afterwards, 10 mL of 0.01 M $CaCl_2$ was added to the contaminated samples and after 24 h the supernatant was analyzed in the HPLC-DAD. The process was repeated three times (total of four steps).

2.5. Analytical methods

Paraquat in aqueous phase was analyzed using HPLC-DAD (Hitachi Elite LaChrom System). The chromatographic separation was achieved by a Purospher® STAR LiChroCART® RP-18 endcapped (240 × 4 mm, 5 μm) reversed phase column supplied by VWR, using a mobile phase of 80% (v/v) of 10 mM HFBA in water and 20% (v/v) of acetonitrile, at isocratic conditions, with a flow rate of 1 mL/min. The calibration curve for paraquat dichloride in water was performed by direct injection of 9 standards, from 0.1 to 80 mg/L of PQ. The coefficient of determination obtained was 0.9999 and the linearity tests revealed an excellent fitness for the linearity. A detection limit of 0.01 mg/L was reached. Precision (expressed in terms of variation coefficient) was on average 8% and recovery of paraquat was 101% on average. The last parameter was determined by comparing the analytical responses obtained for PQ standards in distilled water and in spiked water after being in contact with each deposit.