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Research article

Can electrochemistry enhance the removal of organic pollutants by phytoremediation?

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ABSTRACT

An electrokinetic-assisted phytoremediation test using maize (*Zea mays* L.) was conducted in order to assess the role of the electric field on the enhancement of plant uptake and degradation of the moderate polar pesticide atrazine in spiked soils. Twelve different treatments, including two different initial atrazine soil doses (5 and 10 mg kg^{-1}) and two different values of the electric field applied (2 and 4 V cm^{-1}), together with the corresponding control treatments without plants and/or without electric current, were tested. The application of an electric field during a period of 4 h a day and with periodical polarity inversion (each 2 h) did not caused significant changes in soil pH; moreover, maize plants increased the buffering capacity of the soil. The application of an electric field of 2 V cm^{-1} led to a slight decrease on maize biomass while the accumulation of atrazine and its main metabolites in plant tissues was significantly enhanced. On the overall, the yield of atrazine removal by electrokinetic-assisted phytoremediation with maize was increased up to 36.5% with respect to the phytoremediation process without electricity. On our knowledge, this work is the first one specifically focused on the removal of organic pollutants from soils by using the combination of phytoremediation and electrokinetic remediation.

1. Introduction

Hazardous organic pollutants, as pesticides, represent a threat to human, animal and environmental health (Rodrigo et al., 2014). Changes in agricultural practices have led to the widespread use of pesticides and the succeeding increase in their concentrations in the environment (Kang, 2014). Consequently, soil remediation is becoming a key area of study for the development of novel and efficient treatment systems (such as the electrokinetic-assisted technologies) in order to reduce the hazards of pesticides and other pollutants in the environment (Vieira dos Santos et al., 2016).

The coupling of phytoremediation and the electrokinetic (EK) remediation (electrokinetic-assisted phytoremediation, EK-phytoremediation) has been proposed to overcome the current disadvantages of the individual technologies, such as the difficulties for pollutant mobilization towards the plant roots observed in phytoremediation and the long-term accumulation of contaminants in distant electrodic wells, which occurs in some EK remediation practical cases (Hodko et al., 2000; Lobo et al., 2009). EK-phytoremediation has already shown very promising results for metals and semimetals (O'Connor et al., 2003; Lim et al., 2004; Zhou et al., 2007; Bi et al., 2011; Cang et al., 2011, 2012; Kubiak et al., 2012; Putra et al., 2013). To date, the combination of phytoremediation and electrokinetic remediation has not been deeply assessed in soils polluted by organic compounds. To our knowledge, there are only two recent papers reporting the remediation of a soil contaminated by a mixture of metals and organic pollutants (PAHs), but without conclusive results (Chirakkara et al., 2015; Acosta-Santoyo et al., 2017). The cited works were mainly focused on soils polluted by metals while the aspects regarding the organic pollutants, such as the influence of electric current on the its bioavailability, the effect on its degradation and/or accumulation in plant tissues, and the changes in soil microbial activities, were not deeply addressed.

Another important point that must be considered is the selection of the plant species, which should be studied in combination with the specific operating conditions. Only a reduced group of plants species have been tested in the EK-phytoremediation tests, i.e. *Brassica juncea*

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(Indian mustard) and *Brassica napus* (rapeseed), *Nicotiana tabacum* (tobacco), *Avena sativa* (oat), *Poa pratensis* (Kentucky bluegrass), *Lolium perenne* (ryegrass) and *Helianthus annuus* (sunflower). As a clear pattern in the choice of plant species has not yet been found, to date, it has been preferred to conduct EK-phytoremediation using plant species with a successful performance on phytoremediation tests.

This work constitutes the first attempt to check if the application of an electric field really improves the phytodegradation of organic contaminants in soils. We report the results obtained in a pot experiment using a combination of maize (*Zea mays*) and an electric field to decontaminate a low permeability soil spiked with atrazine. Maize was selected based on its good efficiency for atrazine degradation (Sánchez et al., 2017). Atrazine was selected because it is a moderately polar herbicide, whose octanol partition coefficient below 3 (log K_{ow} = 2.68) and its water solubility of 33 mg.L^{-1} (Amadori et al., 2016) should be enough for it to be transported by electromigration and/or electroosmosis under the application of an electric current to the soil. The interest of studying this herbicide is also motivated because, in spite it was banned in the European Union since 2004, it remains being one of the most plentiful pesticide contained in waterways in Europe (Weber et al., 2018). Moreover, the results obtained here could be extrapolated to other moderately polar or polar organic pesticides. The specific goals of this work were: (i) to study the changes caused by the electric current in soil pH during the electrokinetic assisted phytoremediation (EK-phytoremediation); (ii) to investigate how this innovative technology influence the uptake of atrazine by maize and the soil-plant degradation processes; (iii) to assess if EK-phytoremediation is capable to increase the effectiveness of atrazine removal from soil with respect to the phytoremediation by maize.

2. Materials and methods

2.1. Soil and plants

A natural soil with no antecedents of pollution coming from an agrarian area located in central Spain (Mora de Toledo, Toledo) was used in the experiment. After removing the surface layer of the soil (0–10 cm) and the vegetal cap, an enough amount of sample was collected from a depth of 10–100 cm. The soil was disaggregated, homogenised, air-dried and, finally, sieved to 2 mm prior to its use in the pot experiment. The soil has a pH (in water) of 9.42, a cation exchange capacity (CEC) of 23.42 $cmol_C.kg^{-1}$, a total organic carbon content of 0.60% and an electrical conductivity of 0.15 mS cm^{-1}. It was classified as a low plasticity clay (CL) soil according to the Unified Soil Classification System (USCS); the values for the liquid limit, the plastic limit and the plasticity index were 42, 24 and 18, respectively. Likewise, this soil can be considered as a low permeability soil for which electrokinetic technology is recommended.

A commercial variety of maize (*Zea mays* L., dent corn hybrid cultivar) was used in the EK-phytoremediation experiment. Seeds were pre-germinated in a growing medium (0.5 mM $CaSO_4$) and kept moist during three days at 28 °C. After the germination period, healthy seeds with uniform size were selected and carefully transplanted to the soil.

2.2. Experimental design

The EK-phytoremediation experiment was carried out using plastic pots (16 cm diameter and 18 cm depth) located in a growth chamber equipped with control of lighting, temperature and humidity. The experimental conditions were a photoperiod of 16-h, a relative humidity in air of 60–70% and day/night temperatures of 27/16 °C. Additional technical details of the growth chamber can be found in a previous paper (Sánchez et al., 2017).

The experiment was carried out using a completely randomized design with three replicates (individual pots) per treatment. Thus, twelve treatments were applied in this study; they resulted from the combination of planted and unplanted pots with initial soil atrazine concentrations of 5 and 10 mg kg^{-1} and the application (or not) of an electric field with voltage values corresponding to 2 and 4 V cm^{-1}. These values have been chosen taking into account the previous literature on EK-phytoremediation of metal-polluted soils (Cang et al., 2011, 2012; Cameselle et al., 2013) and our previous research on atrazine phytoremediation (Sánchez et al., 2017).

One kilogram of dry soil was placed in each individual pot forming a layer about 6 cm deep. The electric field was applied using a pair of graphite electrodes (15 cm in length and 6 mm in diameter) connected to a DC (direct current) power supply which worked in the range 0–120 V and 0–13 A (Delta Elektronica S.V., model SM120-13, The Netherlands). Graphite rods were used since graphite can be considered as an inert material which avoid the release of additional chemical species (different to H^+ and OH^-) to the soil (Virkutyte et al., 2002; they were vertically inserted into the soil at both sides of the pots (at a distance of 14 cm between them and 1 cm from the wall of the pot); metal clamps were used to connect the top part of the electrodes with the DC power supply. The pots were kept 7 days in the growth chamber; the soil moisture content was kept at 60–70% of its water holding capacity (by daily weighting) in order to ensure an optimum contact between soil and the graphite rods. Next, 14 pre-germinated maize seeds were planted in each pot. After 35 days of plant growth, the soils were spiked with the adequate volume of an aqueous solution of atrazine (prepared from a 250 mg.L^{-1} solution of atrazine in methanol; solid atrazine was supplied by Sigma-Aldrich, USA) in order to achieve initial concentrations of 5 and 10 mg of atrazine per kg of soil (corresponding to 23.18 and 46.36 μmol per pot, respectively). Atrazine was sprayed homogeneously on the soil surface, getting soil at water holding capacity (WHC) state. Electrical DC current (2 or 4 V cm^{-1}) was started to be applied the same day of atrazine addition with the following conditions: 4 h/day and switching the polarity every 2 h (in order to avoid extreme soil pH values). During the 14-day duration of the EK-phytoremediation experiment, the electrical intensity of each pot was recorded daily.

At the end of the experiment, soil and maize samples were collected from pots. The soil samples were air-dried and disaggregated and, later, analysed to determine soil pH (pH values were obtained of the homogenised soil) and the concentration of ATR and its metabolites (see Section 2.3). The maize shoots were harvested by cutting the stem 1 cm above the soil surface. The roots were harvested by separating the biomass from the soil and removing the external soil particles; next, they were thoroughly rinsed with deionized water. The plant samples (shoots and roots) were air dried at room temperature until constant weight and, finally, homogenised using a grinder (Retsch Model MM200, Germany). The dry matter biomass was recorded and the concentration of ATR and its metabolites was analysed (see Section 2.3).

2.3. Atrazine analysis

Atrazine and its main derivatives were quantified in soil and plant samples by HPLC analysis of the extracts obtained by using a shaking-centrifuging extraction procedure (Amadori et al., 2013). A sample of 2.0 g of soil or plant tissues (previously chopped, crushed and blended) was weighted in a glass flask, suspended in 3 mL of acetonitrile (Acetonitrile Chromasolv for HPLC, gradient grade, Sigma-Aldrich, USA) and shaken for 30 min and, finally, centrifuged for 15 min. This procedure was carried out three times and the respective supernatants phases were reserved and finally combined. The resulting extracts were filtered using 0.45 μm nylon syringe filters before HPLC determination.

The concentration of atrazine residues, i.e. atrazine (ATR) and its main metabolites (deethylatrazine, DEA, and deisopropylatrazine, DIA), were analysed in soil and plant extracts. Sample aliquots of 20 μL were injected into a HPLC system (Shimadzu Prominence UFLC XR, Japan) and analysed using a C18 reversed-phase column