



Assessment of combined electro–nanoremediation of molinate contaminated soil



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HIGHLIGHTS

- Molinate is degraded in soil by zero valent iron nanoparticles (nZVI).
- Higher contact time of nZVI with soil facilitates molinate degradation.
- Soil type was the most significant factor influencing iron and molinate transport.
- When using nZVI and EK molinate is not only transported to catholyte, but also degraded.

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ABSTRACT

Molinate is a pesticide widely used, both in space and time, for weed control in rice paddies. Due to its water solubility and affinity to organic matter, it is a contaminant of concern in ground and surface waters, soils and sediments. Previous works have showed that molinate can be removed from soils through electrokinetic (EK) remediation.

In this work, molinate degradation by zero valent iron nanoparticles (nZVI) was tested in soils for the first time. Soil is a highly complex matrix, and pollutant partitioning between soil and water and its degradation rates in different matrices is quite challenging. A system combining nZVI and EK was also set up in order to study the nanoparticles and molinate transport, as well as molinate degradation.

Results showed that molinate could be degraded by nZVI in soils, even though the process is more time demanding and degradation percentages are lower than in an aqueous solution. This shows the importance of testing contaminant degradation, not only in aqueous solutions, but also in the soil-sorbed fraction. It was also found that soil type was the most significant factor influencing iron and molinate transport. The main advantage of the simultaneous use of both methods is the molinate degradation instead of its accumulation in the catholyte.

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1. Introduction

The widespread use of pesticides in intensive agriculture leads to soil and groundwater contamination. One of the pesticides that causes environmental concern is molinate (S-ethyl N,N-hexamethylene-1-carbamate), often applied annually to flooded fields during rice seeding to control the overgrowth of weeds (Castro et al., 2005). In 2013, there were 165.5 million hectares of rice paddies worldwide (FAO, 2013). Molinate can be found in natural surface and ground waters and also in wastewaters (Köck-Schulmeyer et al., 2013) due

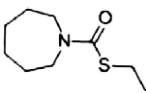
to its high water solubility (Table 1), as well as in soils and sediments near rice paddies (Castro et al., 2005; Cerejeira et al., 2003; Hildebrandt et al., 2007).

Zero valent iron nanoparticles (nZVI) degraded different pesticides in aqueous solutions, such as atrazine (Bezbaruah et al., 2009; Joo and Zhao, 2008; Satapanajaru et al., 2008), lindane (Elliott et al., 2009; Joo and Zhao, 2008), chloroacetanilide (Alachlor) (Bezbaruah et al., 2009) and molinate (Feitz et al., 2005), and remediated soils contaminated with pesticides such as malathion (Singhal et al., 2012), dinoseb (Satapanajaru et al., 2009), and chlorpyrifos (Reddy et al., 2013). Most of the research with iron nanoparticles analyzed the contaminant degradation in aqueous media, showing high degradation rates, including molinate degradation by nZVI through an oxidative process (Feitz et al., 2005; Joo et al., 2004). However, only a limited number of studies have assessed nanoparticle performance for soil-sorbed contaminants

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Table 1
Chemical and physical properties of molinate.
Mabury et al., 1996

Chemical name	Molinate
CAS No.	2212-67-1
Structure	
Molecular formula	C ₉ H ₁₇ NOS
Boiling point	202 °C (10 mm Hg)
Density	1.06
Water solubility	800–912 mg L ⁻¹
Half-life	21 days
K _{oc}	190 mL g ⁻¹ OC
log K _{ow}	3.21

(Singh et al., 2012; Zhang et al., 2011), and as far as our knowledge concerns, no previous study was done for soil-sorbed molinate.

The combination of electrokinetic remediation (EK) and nZVI allows the enhancement of the transport of iron nanoparticles in low permeability fine-grain soils (Chowdhury et al., 2012; Gomes et al., 2013; Gomes et al., 2014; Jones et al., 2010; Pamukcu et al., 2008; Rosales et al., 2014) and degradation of organic contaminants (Fan et al., 2013; Reddy et al., 2011; Yang and Chang, 2011; Yuan et al., 2012). With the simultaneous use of both remediation techniques (EK and nZVI), the contaminant is not only removed from soil (traditional outcome in EK), but also it is additionally degraded by nZVI, whose transport can also be enhanced by electric direct current. Electrokinetics can successfully remove molinate from soils to the catholyte due to electroosmotic transport as showed by Ribeiro et al. (2011), both by experimental work and modeling.

This work studies for the first time the degradation of molinate in soil using nZVI. It also assesses the integration of nZVI and electrokinetics to enhance the nanoparticles and molinate transport and degradation in two different soils.

2. Materials and methods

2.1. Soils

We used two different soils: S1 (sandy), sampled near a sanitary landfill at Valadares, Vale de Milhaço, Portugal, and S2 (sandy loam with higher organic matter content), sampled in an industrial park, in central Portugal. Table 2 presents some of their physical and chemical characteristics.

2.2. Chemicals and solvents

Molinate standards were of Pestanal grade, obtained from Riedel-de Haën (Seelze, Germany). The technical molinate (95%) used in the

Table 2
Physical and chemical characteristics of the soils used.

Parameter	S1	S2
Textural classification	Sandy	Sandy loam
Organic matter (g kg ⁻¹)	4	128.3
pH (H ₂ O)	5.9	6.1
pH (KCl)	4.5	5.4
Exchangeable cations (cmol _(c) kg ⁻¹)		
Ca ²⁺	0.34	16.18
Mg ²⁺	0.05	3.98
K ⁺	0.05	0.70
Na ⁺	0.04	0.18
Sum of exchangeable cations (cmol _(c) kg ⁻¹)	0.48	21.04
Cation exchange capacity (cmol _(c) kg ⁻¹)	1.39	23.38
Saturation (%)	35	90

experiments was from Herbex (Sintra, Portugal). The solvents used in the present study were from Riedel-de Haën (Seelze, Germany), Panreac (Barcelona, Spain), Carlo Erba (Milan, Italy) and Merck (Darmstadt, Germany). Acetone was of Gradient Grade, hexane was of Pestanal grade, diethyl ether was of ACS grade, methanol was of HPLC grade and dichloromethane was of SupraSolv grade. The water was distilled and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). The iron nanoparticles were in a slurry-stabilized suspension (NANO FER 25S, NANO IRON, s.r.o., Rajhrad, Czech Republic) negatively charged due to the coating with polyacrylic acid (PAA), with an average particle size of 50 nm, an average surface area of 20–25 m² g⁻¹, a narrow particle size distribution of 20–100 nm and a high iron content in the range of 80–90 wt.%.

2.3. Degradation tests

Both soils were spiked with technical molinate to obtain a final concentration of 290 mg kg⁻¹. After air-drying, 1 g of soil and 25 mL of deionized water and 200 µL of nZVI slurry (final concentration 1.0 g L⁻¹ Fe) were placed in glass vials with a screw cap, in duplicate, under aerobic conditions, as the molinate degradation is an oxidative process (Joo et al., 2004). Blank samples were prepared as control, using the same spiked soil and without nZVI, for all the tested times. These soil suspensions were shaken in an orbital shaker (Bunsen AO 400) at 200 rpm at 25 ± 2 °C. After 24 h, the samples were centrifuged for 10 min at 7500 rpm (Sorvall RC5C Plus centrifuge). The supernatant was then removed and extracted through Solid Phase Extraction (SPE) using Strata X cartridges (200 mg/3 mL; Phenomenex Torrance, CA, USA) on a vacuum rack. The molinate in the soil was extracted by 10 mL hexane after 20 min sonication (Bandelin Sonorex Super RK 102H). The hexane extract was filtered through a 0.45 µm syringe Acrodisc PTFE filter (Pall Gelman Sciences, Ann Arbor, MI, USA) and concentrated under a gentle stream of nitrogen until 1.0 mL before analysis.

2.4. Electrokinetic experiments

2.4.1. Electrokinetic cell

The EK experiments were carried out in a laboratorial cell modified at the New University of Lisbon. The cell is divided into three compartments, consisting of two electrode compartments (L = 7.46 cm, internal diameter = 8 cm) and a central one (L = 4 cm, internal diameter = 8 cm), in which the soil, saturated with deionized water, is placed (Fig. 1). This central compartment, made of Plexiglas, was equipped

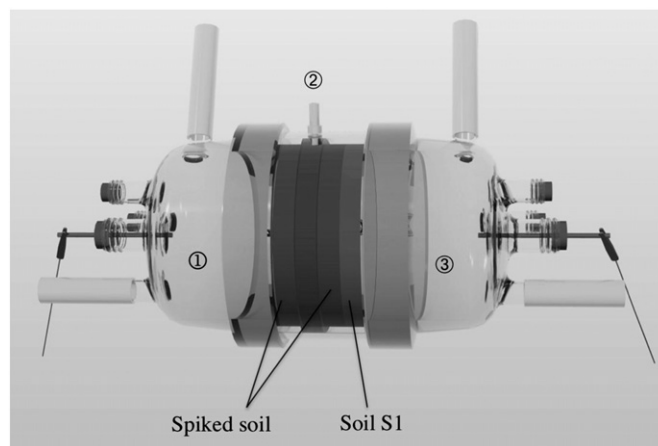


Fig. 1. Schematic representation of the laboratory cell. Legend: ① Anode compartment; ② reservoir for the iron nanoparticles injection; ③ cathode compartment. The separation between the soil and the compartments containing liquids was made through passive membranes (filter paper).

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