Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine. Experimental and modeling

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Abstract

The atrazine behaviour in soils when submitted to an electric field was studied and the applicability of the electrokinetic process in atrazine soil remediation was evaluated. Two polluted soils were used, respectively with and without atrazine residues, being the last one spiked. Four electrokinetic experiments were carried out at a laboratory scale. Determination of atrazine residues were performed by enzyme-linked immunosorbent assay (ELISA). The results show that the electrokinetic process is able to remove efficiently atrazine in soil solution, mainly towards the anode compartment: Estimations show that 30–50% of its initial amount is removed from the soil within the first 24 h. A one-dimensional model is developed for simulating the electrokinetic treatment of a saturated soil containing atrazine. The movement of atrazine is modeled taking into account the diffusion transport resulting from atrazine concentration gradients and the reversed electro-osmotic flow at acidic soil pH.

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1. Introduction

The contamination of soils, groundwater, and surface waters by chemicals used in agriculture is currently a significant concern. Many of these agrochemical compounds are considered a threat both to the environment and to human health. Atrazine (2-chloro-4-ethyl-amino-6-isopropylamino-s-triazine) is a selective herbicide worldwide used to control broadleaf and grassy weeds in agriculture and in conifer reforestation plantings. Atrazine, due to its persistence and mobility characteristics (moderate solubility), is a chemical which causes environmental concern, particularly in hydrogeological vulnerable areas, with agricultural uses, where when submitted to leaching in the non-saturated zone can reach groundwaters. As consequence atrazine is one of the most frequently detected contaminants in the waterbodies in Europe (Gascón et al., 1997; Carabias-Martínez et al., 2002). Additionally, atrazine has been reported as a potential endocrine disruptor (Renner,
The determination of atrazine is usually performed by gas chromatography (GC) coupled with nitrogen phosphorous detector and hyphenated with mass spectrometry (GC–MS) (USEPA, 1991, 1995), high performance liquid chromatography (HPLC) (Karlaganis et al., 1991; Carabias-Martínez et al., 2002) and more recently enzyme linked immunosorben assays (ELISA) (Cerejeira et al., 1997; Gascón et al., 1997; USEPA, 1998).

The electrokinetic remediation technique uses a low-level direct current, as the cleaning agent, to transport the pollutants out of the soil towards one of the electrode compartments, from where they can be removed. Several authors have critically reviewed its state of knowledge (Pamukcu and Wittle, 1992; Acar et al., 1995; Ottosen, 1995; Yeung and Datla, 1995; Page and Page, 2002; Virkutyte et al., 2002).

The present study reports results from the application of the electrokinetic process to atrazine contaminated soils. The main goals are: (i) to assess the behaviour of atrazine in soils when submitted to an electric field; (ii) to evaluate the applicability of the technique to remove atrazine from soils and (iii) to model the movement of atrazine in soils, taking into account the diffusion transport resulting from atrazine concentration gradients and the reversed electro-osmotic flow at acidic soil pH. A one-dimensional model is developed for simulating the electrokinetic treatment of a saturated soil containing atrazine.

2. Experimental section

2.1. Reagents and chemicals

The ELISA kits, Atrazine RaPID Assay® (A00071) and the Magnetic Separation Rack (A00004) were obtained from Strategic Diagnostics, Inc. (USA). All triazine standards, atrazine, simazine and propazine, were PESTANAL grade and obtained from Riedel-de Haen (Germany). All organic solvents used were HPLC-grade and purchased from Merck (Darmstadt, Germany). The Supeleclean ENVI™ 18 Disks, with a 47 mm diameter, for solid phase extraction, were purchased from Supelco (Bellefonte, USA).

2.2. Atrazine analysis

Atrazine analysis were performed by ELISA, in soils and electrolyte solutions, according to the procedures stated on the Technical Notes 0003 and A00071 from Strategic Diagnostics, Inc. (USA). The absorbance measurements were performed on a spectrophotometer UNICAM Helios x v2.03 at 450 nm. The detection limit achieved for atrazine was 0.05 μg l⁻¹.

Additional confirmation of atrazine detection (positive ELISA) was conducted using a Merck-Hitachi HPLC system with an UV detector. The analytical separation was performed on a Lichroshpher RP-18 (125 mm × 4.6 mm, 5 μm) from Merck (Darmstadt, Germany). The UV wavelength was setup to 220 nm. The analysis was performed in isocratic mode using water-methanol (65:35) with a flow rate of 1.0 ml min⁻¹.

When the atrazine content in an electrolyte sample was below the detection limit of the ELISA method, a solid-phase extraction step was used to concentrate the samples. The used procedure was based on the Technical Note T00020, from Strategic Diagnostics, Inc. and Supelco Application Note 59.

Initial and final detection and quantification of atrazine in soils, for each experiment, was carried out extracting 5 g of soil with twice 20 ml of methanol by sonication, using a Bandelin Sonarex Super RK 102 H, for 10 min. Both extracts were collected in conjunction and concentrated to 10 ml, under a nitrogen flux. When the atrazine content was smaller than the detection limit of the ELISA method, the extracts were concentrated to 1 ml.

2.3. Soils

Two types of soil were used. The first, sampled at Valadares (Vale de Milhãço, Portugal), corresponds to an Eutric Regossol (FAO/UNESCO soil classification). An average sample was collected at 0–15 cm depth, it has a sandy texture, and its characteristics are shown in Table 1 (soil 1). More details related to its physical, chemical and mineralogical properties can be found in Ribeiro (1992). Initially free of atrazine residues, this soil was spiked with atrazine without residue aging. The second soil, collected from the rice crop fields of the Ebro Delta area (Tarragona, Spain), where the pesticides are currently applied, was “naturally” contaminated, with aged residues corresponding to the last atrazine application, carried out 40 d ago. Characteristics of this soil are shown in Table 1 (soil 2), and more details are available at Durand et al. (1989).

<table>
<thead>
<tr>
<th>Characteristics of the soils used in the experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical determination</td>
</tr>
<tr>
<td>Sand (%)</td>
</tr>
<tr>
<td>Silt (%)</td>
</tr>
<tr>
<td>Clay (%)</td>
</tr>
<tr>
<td>Organic matter (%)</td>
</tr>
<tr>
<td>pHH₂O</td>
</tr>
<tr>
<td>Cation exchange capacity (cmolₖg⁻¹)</td>
</tr>
</tbody>
</table>

* Depth = 0–20 cm.
2.4. Electrokinetic laboratory cell

The electrokinetic experiments were carried out in a laboratorial cell. The cell is divided into three compartments, consisting of two electrode compartments \( (L = 7.46 \text{ cm}, \text{internal diameter} = 8 \text{ cm}) \) and a central one \( (L = 3 \text{ cm}, \text{internal diameter} = 8 \text{ cm}) \), in which the soil, saturated with deionised water, is placed (Fig. 1). Passive membranes assured the separation between the electrode compartments and the central one (cellulose, corresponding to five Bio & Bernsen filter paper, in each side). A power supply (Hewlett Packard E3612A) was used to maintain a constant dc current and the voltage drop was monitored (Kiotto KT 1000H multimeter). The electrodes were platinized titanium bars, with a diameter of 3 mm and a length of 5 cm (Bergsøe Anti Corrosion A/S, Denmark). The fresh electrolyte was a \( 10^{-2} \text{ M NaNO}_3 \) solution with pH 7, but the catholyte was periodically adjusted to an acid value, pH \( \approx 3 \), with HNO_3 solution, whereas anolyte evolves freely during the experiment.

2.5. Electrokinetic experimental conditions

The polluted soils (spiked and natural) were submitted to the electrokinetic process for about 9 d, with a constant current density of \( 0.2 \text{ mA cm}^{-2} \) and the flow to each electrode compartment was \( 1.4 \text{ ml min}^{-1} \). This is, during the experiments, the incoming flows to the electrode compartments were maintained constant in this value, meanwhile the outlet flows depend on the value of the electro-osmotic flow too.

Four different laboratory experiments A, B, C and D were carried out. The first three ones (A–C) were performed with soil 1, spiked with atrazine solutions in diethyl ether (concentrations given later in the text). The aim of each experiment was the following:

Experiment A: To verify if atrazine in soil solution was mobilized by the action of an electric field. For that, the central cell compartment of the electrokinetic cell was filled with soil 1 (spiked). The atrazine concentration after spiking was 19.03 \( \mu \text{g g}^{-1} \), without residue aging.

Experiments B and C: To study that the electric field mobilized atrazine in soil solution and identify if there was a predominant sense towards which atrazine flows (if towards the direction of anode or towards the cathode compartment), and not only diffusion. For that, the central cell compartment of the electrokinetic cell was filled with three slices of soil 1, in which only the middle one was previously spiked (Fig. 1). The atrazine concentration after spiking was 13.17 \( \mu \text{g g}^{-1} \), without residue aging. Experiment C was a replicate of experiment B.

Experiment D: To study if the electric field mobilized aged residues of atrazine in the soil; to verify if the predominant flow of atrazine was similar to the one obtained with previous experiments, as well as to test the viability of the electrokinetic process in removing atrazine out of real contaminated soil. For that, the central cell compartment of the electrokinetic cell was filled with soil 2, “naturally” contaminated, with aged residues, with a concentration of 0.02 \( \mu \text{g of atrazine per g of soil} \).

The detection and quantification of the initial atrazine in soil 2 (and the proof of its non-existence in soil 1) was carried out before all experiments.

Electrolyte samples (catholyte and anolyte) were collected, during the experiments, for further quantification of atrazine, and the pH and respective volume registered.

At the end of each experiment the total soil in the cell was sectionated into five “slices” (samples 1–5, specified in Table 2) and their respective masses determined. Subsamples were collected to pH in \( \text{H}_2\text{O} \) (1:2.5) and humidity measurements. The rest of the known mass of each “slice” was submitted to extraction, by sonication, for further analysis of atrazine. For determination of atrazine adsorption to the passive membranes, those were put in 100 ml methanol and submitted to sonication, for 10 min. The resultant extracts were concentrated to 10 ml and filtrated by Acrodisc Gelman filters (0.45 \( \mu \text{m of diameter} \), before being submitted to analysis by ELISA.

3. Model description

A one-dimensional model is developed for simulating the electrokinetic process. The principal objective of this model is to supply a qualitative and quantitative description of the behavior of the selected pollutant–soil systems, but also to become an useful tool of prediction.
In future applications of electrokinetics to remove other uncharged organics.

The electrokinetic process takes place in a domain as the one shown in Fig. 2, which is the soil containing atrazine initially, the anode and cathode compartments and the inlet and outlet of these compartments. To model the soil, it was divided in 15 volume elements, high enough number to allow the study of the electrical transport and diffusion effects in the soil with low numerical dispersion (Wilson et al., 1995; Rodríguez-Maroto et al., 1998) and two additional ones, at either end of the system compartments (anode on the left and cathode on the right).

The model operates in two steps: first simulates the process by integrating forward in time \((\Delta t = 60 \text{ s})\) one-dimensional kinetic equations and, after that, re-establishes the water equilibrium before next step of integration, because this extremely rapid reaction can be considered instantaneous, when compared with the transport phenomena.

The total transport for \(i\)th species \((i = 1–5; \text{H}^+, \text{OH}^-, \text{Na}^+, \text{NO}_3^-, \text{and atrazine})\) in a \(j\)th volume element, is described by the mass conservation equation:

\[
\frac{d m_i}{dr} = (N_{ij-1} + N_{ij+1})A + R_i V_j
\]

where, \(m_i\) is the mass of \(i\)th species in the \(j\)th volume element, \(N_{ij-1}\) and \(N_{ij+1}\) total mass flux of \(i\)th species from \((j-1)\)th and \((j + 1)\)th element volume into \(j\)th volume element, \(A\) the cross-sectional area of column, \(V_j\) the vol-

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experiment A</th>
<th>Experiment B</th>
<th>Experiment C</th>
<th>Experiment D</th>
<th>Observations</th>
<th>Schematic representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(0.050 \times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>Close to cathode</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(0.080 \times 10^{-3})</td>
<td>0.063 (\times 10^{-3})</td>
<td>0.090 (\times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>Middle vertical section</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(0.070 \times 10^{-3})</td>
<td>0.086 (\times 10^{-3})</td>
<td>0.100 (\times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>Middle horizontal section</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(0.080 \times 10^{-3})</td>
<td>0.024 (\times 10^{-3})</td>
<td>0.040 (\times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>Middle, in cross*</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(0.040 \times 10^{-3})</td>
<td>0.040 (\times 10^{-3})</td>
<td>0.030 (\times 10^{-3})</td>
<td>&lt;(0.005 \times 10^{-3})</td>
<td>Close to anode</td>
<td></td>
</tr>
<tr>
<td>Total (mg g(^{-1}))</td>
<td>(0.310 \times 10^{-3})</td>
<td>0.210 (\times 10^{-3})</td>
<td>0.260 (\times 10^{-3})</td>
<td>&lt;(0.003 \times 10^{-3})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Removal % | 98 | 98 | 98 | 89

* In experiment A, the analyzed soil corresponds to the shaded part, whereas in experiments B–D corresponds to the parts represented in white.

Fig. 2. Domain in which the electrokinetic process takes place—schematic view. EORF = Electro-osmotic reverse flow.
ume of water in soil jth cell and \( R_n \), the reaction rate for species.

Four transport phenomena are considered in the system: electromigration, electro-osmotic transport, diffusive transport and advection, and two kinds of reactions, electrochemical and chemicals.

The electromigration includes the movement of ions from the electrolyte and of the protons and the hydroxyl ions. The electromigration of atrazine is not included because this one, being a weak base (pK_a = 1.7), is practically not ionized (uncharged) at soil acidic pH. The electro-osmotic transport is considered, both for the ions and for atrazine. Diffusion is included only for atrazine, because in the case of ions its value is usually negligible if compared to the other transport phenomena (Acar and Alshawabkeh, 1993). Advection transport is present specifically in the electrode compartments supplying fresh electrolyte to the system and removing the contaminant, but movement of fluid resulting from head differences is not inside the soil, because the experimental cells were carefully placed in order to avoid hydraulic gradients.

3.1. Electrochemical and chemical reactions

It is assumed that the only electrochemical reactions to take into account are the reduction and oxidation of water on the electrodes.

The half-reaction at the cathode is:

\[
\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- (\text{aq}) + \text{H}_2(\text{gas}) \quad E^0 = -0.828 \text{ V}
\]

And the anode half-reaction is:

\[
\text{H}_2\text{O} \rightarrow 4\text{H}^+ (\text{aq}) + \text{O}_2(\text{gas}) + 4e^- \quad E^0 = -1.229 \text{ V}
\]

Then the electrochemical reactions must be included in the mass balance equations of anode and cathode compartments (Park et al., 2003).

\[
V_0 \left( \frac{d\mathbf{c}_i}{dt} \right)_{\text{ER}} = V_{N+1} \left( \frac{d\mathbf{c}_{N+1}}{dt} \right)_{\text{ER}} = \frac{I}{F} \eta
\]

where \( V_0 \) and \( V_{N+1} \) are the volumes of electrolyte in the electrode compartments, \( c_{10} \) and \( c_{2N+1} \), \( \text{H}^+ \) and \( \text{OH}^- \) concentrations generated there by electrochemical reactions, \( I \) is the current intensity, \( F \), the Faraday constant and \( \eta \) the Faradic efficiency.

On the other hand, the only chemical reaction here is the consumption of atrazine. This one, in different soil conditions (e.g. pH, oxidants and reducing media, humidity, temperature), is well documented and the final products of these reactions have been identified (Jones et al., 1982).

The problem to model emerges because the rate of atrazine dissipation is highly dependent on environmental conditions and type and amount of constituents contained in the media (Grambell and Patrick, 1988; DeLaune et al., 1997). So half-lives ranging from 0.2 to 742 d have been reported, depending on the experimental conditions (Solomon et al., 1996). Furthermore, reduction–oxidation reactions also can be stimulated in soils as consequence of presence of electrical field (Pamukcu et al., 2004).

Thus, atrazine degradation rates or half-lives are not available from literature for the specific conditions of a soil under electrokinetic treatment. However, it is well established that: (a) the degradation of atrazine is accelerated by the soil particles (Armstrong et al., 1967); (b) in the presence of organic matter and salt concentration, atrazine half-life decreases (Li and Feldback, 1972; Khan, 1978), and (c) the kinetic of the consumption for atrazine in soils is well represented by a first-order reaction (Widmer et al., 1993).

In these conditions, it is possible to take into account jointly all the chemical reactions of atrazine, and to represent its whole consumption by only one chemical first order reaction term:

\[
\frac{dm_{ij}}{dt} = R_j V_f = (-k_R c_j) V_f
\]

where \( k_R \) is the kinetic coefficient and \( c_j \) the atrazine concentration.

3.2. Electromigration transport of ions

The electromigration of ions into a general \( j \)th volume element through its left and right limits is analyzed. The cations are incoming in the cell from the \((j-1)\)th cell, and simultaneously anions are moving out to that volume element crossing this one. Assuming perfect mixing in the cell, no conductance through soil solids and using the transport number concept, this one results (Wilson et al., 1995) in:

\[
t_{i,j-1} = \frac{\lambda_i [c_{ij-1} S(z_i) S(c_{ij-1}) + c_{ij} S(-z_i) S(c_{ij})]}{\sum_{i=1}^{\lambda_i} [c_{ij-1} S(z_i) S(c_{ij-1}) + c_{ij} S(-z_i) S(c_{ij})]}
\]

where \( \lambda \) is molar conductivity and \( z_i \) charge number of \( i \)th ion, \( c_{ij} \) its concentration in the \( j \)th volume element and \( S(x) = 0 \), if \( x \leq 0 \), and \( S(x) = 1 \), if \( x > 0 \). The transport number through the right limit of \( j \)th volume element results:

\[
t_{i,j+1} = \frac{\lambda_i [c_{ij} S(z_i) S(c_{ij}) + c_{ij+1} S(-z_i) S(c_{ij+1})]}{\sum_{i=1}^{\lambda_i} [c_{ij} S(z_i) S(c_{ij}) + c_{ij+1} S(-z_i) S(c_{ij+1})]}
\]

Now, it is possible to calculate the electromigration movement of each ion \((i = 1-4)\) through the both walls inside of \( j \)th volume and, therefore, the electromigration mass balance for \( i \)th ion in \( V_f \) is given by:
where \( L \) is the length of soil column, \( \omega \), porosity of the soil, assumed saturated, and \( N \) number of volume elements into which the soil column is partitioned.

This expression is adequate for all of the volume elements in the soil column, but not for the anode and cathode compartments. In these cases, the equations change in order to satisfy their specific characteristics. Thus, in the anode \((j = 0)\) the mass balances give:

\[
V_0 \left( \frac{dc_{i0}}{dt} \right)_{EM} = (N_{i,1})_{EM}A = (t_{i,1}) \frac{I}{z_F} \tag{7}
\]

and, in the cathode:

\[
V_{N+1} \left( \frac{dc_{iN+1}}{dt} \right)_{EM} = (N_{i,N})A = (t_{i,N}) \frac{I}{z_F} \tag{8}
\]

3.3. Electro-osmotic transport

Generally, the electro-osmotic flow is from anode to the cathode, but here, the soil is enough acidic during the process to produce reversed electro-osmosis. Recently, direct and reversed electro-osmotic flows have been reported depending on soil pH during the electrokinetic remediation, but, adjusting the cathode pH, to control the system, all the electro-osmotic flow is towards anode (Zhou et al., 2004), as is also occurring in this case. Other authors also reported electro-osmotic flow towards anode during electrokinetic remediation as consequence of a soil pH under the point of zero charge (Yang and Lin, 1998; Kim et al., 2002).

The electro-osmotic mass balance for ions is:

\[
V_j \left( \frac{dc_{ij}}{dt} \right)_{EO} = \left( \frac{A \omega L}{N} \right) \left( \frac{dc_{ij}}{dt} \right)_{EO} = (N_{ij-1} + N_{ij+1})_{EO}A
\]

where \(Q_{EO} = \left( c_{ij+1} - c_{ij} \right)\)

\[
\tag{9}
\]

where \( Q_{EO} \) is the electro-osmotic flow rate.

In the case of atrazine, a part of its mass in the soil is not in solution but as a solid, then the mass balance gives:

\[
\left( \frac{dm_{Sj}}{dt} \right)_{EO} = (N_{ij-1} + N_{ij+1})_{EO}A
\]

\[
\tag{10}
\]

3.4. Diffusive transport

The diffusive transport is calculated only for the atrazine. It is admitted that for the ionic species this transport is negligible, if compared with electromigration (Acar and Alshawabkeh, 1993). The mass balance equation for diffusive transport from \( j = 2 \) to \( N - 1 \) volume elements is (Gómez-Lahoz et al., 1996):

\[
\left( \frac{dm_{Sj}}{dt} \right)_{D} = (N_{S,j-1} + N_{S,j+1})_{D}A
\]

\[
\tag{14}
\]

where \( D_S \) is the effective diffusion coefficient of atrazine (cm\(^2\) s\(^{-1}\)).

However, for the cells close to the electrode compartments \((j = 1 \text{ and } j = N)\) it is:

\[
\left( \frac{dm_{S1}}{dt} \right)_{D} = (N_{S,0} + N_{S,2})_{D}A
\]

\[
\tag{15}
\]

\[
\left( \frac{dm_{SN}}{dt} \right)_{D} = (N_{S,N-1} + N_{S,N+1})_{D}A
\]

\[
\tag{16}
\]
and for anode and cathode:

\[
\begin{align*}
V_0 \left( \frac{d\psi}{dr} \right)_A &= (N_{5,1})_A/A = \frac{2D_j^2(c_{SN} - c_{SN+1})AN}{L} \\
V_{N+1} \left( \frac{d\psi}{dr} \right)_A &= (N_{5,N})_A/A = \frac{2D_j^2(c_{SN} - c_{SN+1})AN}{L}
\end{align*}
\]  

(17)

(18)

3.5. Advection in electrode compartments

The balance equations for input and output flows in the anode and cathode compartments are:

\[
\begin{align*}
V_0 \left( \frac{dc_i}{dr} \right)_A &= Q(c_i - c_{in}) \\
V_{N+1} \left( \frac{dc_i}{dr} \right)_A &= Q(c_i - c_{in+1})
\end{align*}
\]

(19)

(20)

where \( Q \) is inflow and outflow rate of electrolyte solution in the electrodes and \( c_i \) inlet concentration of \( i \)th species.

Cumulative collected volume output from anode and cathode compartments, \( V_{0Ac} \) and \( V_{N+1Ac} \), are calculated respectively from:

\[
\begin{align*}
dV_{0Ac} \left( \frac{dV}{dr} \right) &= (Q + Q_{EO}) \\
dV_{N+1Ac} \left( \frac{dV}{dr} \right) &= (Q - Q_{EO})
\end{align*}
\]

(21)

(22)

3.6. Chemical equilibrium of water

The extremely rapid reactions between protons and hydroxyls to form water and the reversed reaction in order to maintain the equilibrium conditions must also be taken into account because the acid and basic fronts generated at the electrodes are the principal agents to modify the value of pH in the soil.

\[ H^+ + OH^- \rightleftharpoons H_2O \]

The \( c_{1j} \) and \( c_{2j} \) concentrations are constrained by equilibrium constant:

\[ K_w = 10^{-20} \, \text{(mole/cm}^3\text{)}^2 = [c_{1j}][c_{2j}] \]

(23)

If \( c_a \) and \( c_b \) are the concentrations of \( H^+ \) and \( OH^- \) calculated in the \( j \)th volume element, after an increment of time during the integration of the total transport equations, new concentrations agree with equilibrium are obtained using these values \( (c_a \) and \( c_b) \), the reaction stoichiometry and chemical equilibrium constant for water.

If \( c_a > c_b \) then: \( c_{1j} = c_a - c_b + x \) and \( c_{2j} = x \)  

(24)

If \( c_b > c_a \) then: \( c_{1j} = x \) and \( c_{2j} = c_b - c_a + x \)  

(25)

\[
\begin{align*}
x &= (1/2)\{-(c_a - c_b) - \sqrt{[c_a - c_b]^2 + 4K_w}\}
\end{align*}
\]

(26)

3.7. Atrazine equilibrium of solubility and sorption

An important fraction of atrazine in the studied spiked soil is present as a solid phase, because the spiking procedure permits the operation with an amount of atrazine over its solubility in water. Thus, the atrazine transport is highly influenced by its dissolution. Here, it is assumed local equilibrium between solid phase and aqueous solution. After an increment in time along the process, it is checked if solid phase atrazine is present in each element of volume in order to establish the value of the local concentration of atrazine in the aqueous phase.

\[
\begin{align*}
\text{If } \left( \frac{Nm_j}{A0L} \right) &\geq S \text{ then: } c_{5j} = S \\
\text{If } \left( \frac{Nm_j}{A0L} \right) &< S \text{ then: } c_{5j} = \left( \frac{Nm_j}{A0L} \right)
\end{align*}
\]

(27)

(28)

where \( S \) is the atrazine solubility.

In order to a better fitting and interpretation of experimental data, also the presence-absence of sorption effects using linear, Freundlich and Langmuir isotherm models has been checked, but the sorption on these soils is as low that results are practically indistinguishable.

3.8. Complete model

Finally, the complete model consists on: (a) the differential equations governing the total transport of the present ions and of atrazine through the soil; (b) the definitions of the fluxes due to different transport phenomena; (c) the electrochemical and chemical reaction rates, including the generation in the electrodes, and (d) the prescriptions for equilibrating the protons and hydroxyls concentration.

The periodical adjust of pH catholyte is taken into account in the model modifying the proton (hydroxyl) concentrations and increasing the nitrate concentration in solution corresponding to the quantity of nitric acid added in the cathode compartment. The cumulative quantities of atrazine collected in the effluent from anode, \( M_A \), and from cathode, \( M_C \), compartments were calculated by:

\[
\begin{align*}
\frac{dM_A}{dt} &= (Q + Q_{EO})c_{50} \\
\frac{dM_C}{dt} &= (Q - Q_{EO})c_{SN+1}
\end{align*}
\]

(29)

(30)

Along the calculations, it was continuously checked that the electrical neutrality condition was satisfied in each element of volume at all times, although, in fact,
the procedure used in electromigration calculation guarantees it (Wilson et al., 1995; Vereda-Alonso et al., 2004):

$$\sum_{i=1}^{n} z_i c_{ij} = 0$$  \hspace{1cm} (31)

4. Results and discussion

All the experiments presented similar values of voltage and current. In relation to pH, as it was expected, the catholyte of the four experiments presented predominantly an alkaline pH and the anolytes an acid pH which varied between 3 and 4.

The accumulated volumes of the catholyte and anolyte of the four experiments are shown in Fig. 3. All of them presented close values, because the electro-osmotic flow was low, but anolyte cumulative volumes are higher than catholyte ones. Experiment B was the one which registered a higher difference between the anolyte and catholyte volumes, and clearly indicates an electro-osmotic flow towards the anode (Fig. 3).

The atrazine quantities removed by the electrokinetic process for the cathode and the anode compartments of the cell showed that in experiments A, B and C, the highest amounts are in anolytes (Fig. 4). Furthermore, in these experiments, 30–50% of its initial amount is removed from the soils within the first 24 h. A similar behaviour was observed in experiment D, only differing at the order of magnitude, since the quantity of atrazine initially present in the soil was also much smaller (Fig. 4). In the same figure it can be seen that the model (solid lines) reproduces satisfactorily the experimental data of cumulative atrazine removed for the anode and the cathode compartments, and also it does with pH, and drop potential evolutions, and with volume collected along the time from outlet electrodes, as well as the final concentration in the soil (not represented). Modeling parameters are given in Table 3.

In experiment A, the quantity of atrazine in the catholyte is quite significant in relation to the ones of experiments B and C. This is due to the fact that in that experiment all the soil in contact with the membranes was spiked, allowing atrazine to pass in to the cathode compartment by diffusion.

In experiments B and C, where the spiked soil occupied the central zone of the soil cell compartment (Fig. 1), much lower quantities of atrazine were obtained in the catholytes, when compared with experiment A (Fig. 4). Once experiment C is a duplicate of experiment B, the obtained results are quite similar. The highest quantity removed in the anolyte of experiment B is in accordance with the highest volume obtained in comparison to the one of experiment C.

In experiments B and C, higher quantities of atrazine were registered in the soil near the anode than near the cathode (samples 1 and 5 in Table 2), corroborating the results previously obtained in the electrolytes (Fig. 4), confirming that under the action of an electric field, atrazine is mobilized towards the anode compartment, due to reverse electro-osmosis. In experiment A, the quantities of atrazine in the soil, near the cathode and near the anode, are similar (samples 1 and 5 in Table 2), probably due to the previously pointed out: passage of atrazine towards the cathode due to diffusion.

In the electrokinetic experiments carried out, the atrazine removal efficiencies in the soil solution were high, \( \geq 89\% \) (Table 2). No atrazine was found in the passive membranes.

Summing-up: This study has shown that atrazine is mobilized when submitted to the action of an electric field, essentially towards the anode compartment, due to reversed electro-osmosis. This behaviour was similar in all experiments (spiked and natural contaminated soils). The electrokinetic process was able to remove atrazine in the soil solution, and about 30–50% of its initial quantity was removed during the first 24 h. The results may be extended to other organic compounds with similar physic-chemical proprieties.

![Fig. 3. Cumulative electrolyte volumes in the four experiments (l).](image-url)
Acknowledgments

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Table 3
Parameters used in modeling

Common values in all the experiments
Current intensity I: 0.01 A
Initial and influent concentration of the electrolyte (NaNO₃) c₅ and c₆: 10⁻² M
Initial soil pH: 6
Electrode compartment volume, V₀ and Vₙ₊₁: 375 cm³
(H⁺) z₁: +1  λ₁: 349.8 Ω⁻¹ mol⁻¹ cm²
(OH⁻) z₂: -1  λ₂: 198.5 Ω⁻¹ mol⁻¹ cm²
(Na⁺) z₃: +1  λ₃: 50.1 Ω⁻¹ mol⁻¹ cm²
(NO₃⁻) z₄: -1  λ₄: 71.4 Ω⁻¹ mol⁻¹ cm²
S, atrazine solubility: 33 mg l⁻¹
η, Faradic efficiency: 1
kₘ: ≈5×10⁻⁵ cm² V⁻¹ s⁻¹ (from Casagrande, 1948; Schultz, 1997; Pomes et al., 2002)
D₅ atrazine diffusion coefficient in free solution at infinite dilution: 5.39×10⁻⁶ cm² s⁻¹ (from Scholtz et al., 1999)

Values changing in each experiment

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Initial mass of atrazine in the soil (µg)</th>
<th>Initial weight of contaminated soil (g)</th>
<th>D₅ × 10⁶ (cm² s⁻¹)</th>
<th>Electro-osmotic flow Qₑₒ (ml d⁻¹)</th>
<th>kₑ (s⁻¹)</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>6500</td>
<td>341.65</td>
<td>2.16</td>
<td>180</td>
<td>1.25×10⁻⁵</td>
</tr>
<tr>
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<td>341.65</td>
<td>2.16</td>
<td>160</td>
<td>3.60×10⁻⁵</td>
</tr>
<tr>
<td>C</td>
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<td>341.65</td>
<td>2.16</td>
<td>216</td>
<td>3.30×10⁻⁵</td>
</tr>
<tr>
<td>D</td>
<td>33</td>
<td>213.65</td>
<td>2.96</td>
<td>216</td>
<td>3.60×10⁻⁵</td>
</tr>
</tbody>
</table>
References


Technical Note A00071, User guide-RaPID assay atrazine, Strategic Diagnostics, Inc.

Technical Note T0003, Detection of atrazine, alachlor, cyanazine and metalochlor in soil, Strategic Diagnostics, Inc.

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