

Electrokinetic removal of 2,6-dichlorophenol and diuron from kaolinite and humic acid-clay system

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Abstract

This paper presents the results of a study on the electrokinetic treatment of kaolinite and humic acid kaolinite complexes spiked with 2,6-dichlorophenol or 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron). In particular, the attention was paid to the interaction between solid surface and dissolved organics: the effects of contaminant sorption as well as the physicochemical reactions on the efficiency of electrokinetic remediation were investigated. Using a 3 V/cm voltage gradient, approximately 90% of diuron was removed from kaolinite after one water pore volume was collected in the cathode reservoir, but much lower efficiency was obtained in the electrokinetic removal of this compound from humic acid-coated kaolinite. The results also showed that partial degradation of the contaminant occurred during electrokinetic treatment of kaolinite clay spiked with 2,6-dichlorophenol: the contamination in the clay could be remediated by the combination of electrokinetic extraction and electrochemical reactions.

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Keywords: Electrokinetic remediation; Sorption; Kaolinite; 2,6-Dichlorophenol; Diuron

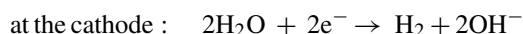
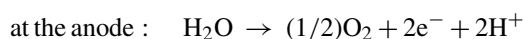
1. Introduction

Contamination of fine-grained soils by toxic organic chemicals is a dangerous source of pollution since dissolved contaminants can slowly diffuse into adjacent high permeability zones, thus affecting the quality of groundwaters.

In situ remediation technologies are in most cases not effective in cleanup of clayey soils because of their low hydraulic permeability. Electrokinetics is a well-known technology with applications in structural engineering and for soil stabilization: in recent years, a number of laboratory-scale and field-scale studies have shown the technical feasibility of electrokinetic processes in removing various contaminants from fine-grained soils [1,2].

This technique employs electrodes placed in the ground with a direct current passed between them using an external power supply. When electrokinetics is used to process soil, ionic migration, electroosmotic flow and chemical diffusion are considered to be important mass transfer mechanisms. Electrolysis reactions

at the electrodes result in the following water splitting reaction:



As a result of these reactions, an acid front and a basic front are created at the anode and cathode, respectively. The migrating front of low pH water has been the focus of several papers on electrokinetic remediation of heavy metal contaminated soils: the acidic front exchanges with adsorbed cations in the electrical double layer of the particles and causes the movement of the pollutant (mainly migration) toward the cathode. Aside from its use in treating heavy metal contamination, electrokinetic soil processing has also been employed for treating some organic contaminants. In particular, laboratory investigations have shown that electrokinetics can be successfully used for the remediation of benzene, toluene, phenol, chlorophenol, polycyclic aromatic hydrocarbon and atrazine [3–8]. If the pollutant is non-ionic, it can be removed by the electroosmotic flux. For fine-grained soils, in which the low hydraulic permeability does not allow an effective pump and treat techniques, the electrokinetic remediation may be the only useful process to remove of organic pollutants: Cherepy and Wildenschild [9]

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obtained an effective hydraulic velocity of 4×10^{-7} m/s during electrokinetic treatment at 4 V/cm in a soil sample characterized by a hydraulic permeability of 5×10^{-10} m/s, which may be considered essentially impermeable to mechanical pumping.

However, electrokinetic extraction is effective in removing only contaminants present as solutes in the pore fluid or weakly sorbed onto the soil surface; the adverse effect of a strong sorption on contaminant removal is very significant in fine-grained soils because of the large and active specific surface area. The aim of the present work is to investigate the influence of sorption on electrokinetic removal for different contaminant clay systems. Equilibrium isotherms and electrokinetic experiments were carried out with clays spiked by model contaminants: 2,6-dichlorophenol (DCP) and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron). Chlorophenols are an important class of environmental contaminants which are used in antiseptics, in pesticides for wood, leather and glue preservation and in anti-mildew treatment. Diuron is commonly used to control a large number of weed species in a variety of crops and is known to be toxic and persistent. Moreover, the selected contaminants have different chemical properties, which may result in a different behaviour during electrokinetic treatment: DCP is a monoprotic weak acid and diuron a neutral hydrophobic compound.

Kaolinite was adopted as model clay; since organic matter is considered the major component affecting the sorption of organic contaminants, humic acid-coated kaolinite was also used in the experiments. Humic acid-clay complexes have previously been used in sorption studies by other authors as a model for clayey soils [10–12]. A first observation to note is that soil behaves as a dual sorbent, in which the soil organic matter acts as a partitioning medium and the mineral fractions as conventional adsorbents. However, for moderately and strongly polar functional group-containing compounds, including many pesticides, multiple sorption mechanisms may occur. The relevant mechanisms include specific interactions with mineral components such as clays, as well as solute partitioning into the soil organic matter.

2. Materials and methods

2.1. Sorbates

3-(3,4-Dichlorophenyl)-1,1-dimethylurea (diuron, purity of >98%) was supplied by Aldrich and 99% pure 2,6-dichlorophenol was supplied by Carlo Erba.

2.2. Sorbents

The main properties of kaolinite clay (used directly as supplied by Carlo Erba) are reported in Table 1. The humic acid-coated kaolinite was prepared according to the procedures described by Li [11]: 1 g of humic acid was dissolved in 1 l of distilled water, followed by mixing with 10 g of pure kaolinite for 1 week. The humic acid-coated kaolinite obtained by centrifugation was washed repeatedly with de-ionised water until

Table 1
Selected parameters of kaolinite and compacted kaolinite column

Properties of kaolinite	
Mineralogy	Kaolinite 100%
Particle size distribution	
Sand (%)	2.0
Silt (%)	34.4
Clay (%)	63.6
CEC (cmol/kg)	9.6
pH	6.1
Specific gravity (ASTM 854) (kg/dm ³)	2.3
Parameters of the compacted clay column	
Void ratio, ϵ	0.33
Pore water volume, V_p (cm ³)	33.6
Humidity (%)	26
Bulk density, ρ_d (kg/dm ³)	1.4
Tortuosity factor, τ	0.4

neither light brown-colored humic substances in supernatants nor humic acid particulates accumulating on the top of the clay after centrifugation were visible. The organic content for humic acid-coated kaolinite prepared following this procedure amounted to 2%.

2.3. Sorption isotherms

Sorption experiments were conducted using a batch equilibration method: kaolinite and humic acid-coated kaolinite were weighed in a glass centrifuge tube (5–20 g), and 50 ml of initial solution of contaminants at different concentrations was added. The tubes were then shaken end over end for 4 days at room temperature (20 ± 2 °C). The pH of the slurries was monitored and, depending on the runs, adjusted to pre-fixed values by adding proper amounts of HNO₃ or NaOH. The samples were centrifuged at 5000 rpm for 30 min and decanted to separate liquid and solid phases. An aliquot of supernatant was transferred to a clean vial for HPLC analysis in order to determine the equilibrium concentrations. Each run was performed in triplicate.

2.4. Electrokinetic experiments

Electrokinetic experiments at constant potential were carried out using an experimental apparatus for the electrokinetic tests that consisted of three main parts: soil cells, electrode compartments and power supply.

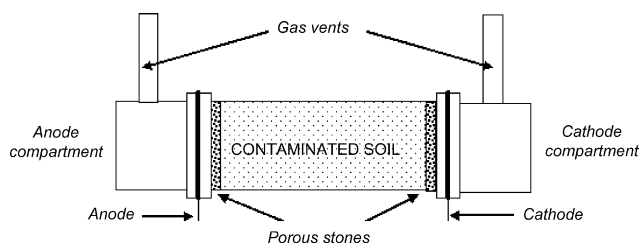


Fig. 1. Experimental apparatus.

The cell (Fig. 1) measured 10 cm in length and 3.6 cm in inner diameter. The soil in the cell was separated from the electrode compartment by two porous stones. The anode was a titanium sheet covered with RuO₂ whereas the cathode was made from a stainless steel sheet.

The electrode compartments containing 400 cm³ of electrolyte solution, were equipped with vents for discharging the oxygen and hydrogen produced by the electrolysis of water at both electrodes.

The polluted soil specimen was prepared by equilibrating for a period of 4 days 500 g of clay with 100 ml of aqueous solutions containing 100 mg/dm³ of 2,6-dichlorophenol or 40 mg/dm³ of diuron. The slurry was then placed in the cell and compacted for 120 h at 2 kg/cm² before starting the electrokinetic run: the weight of the specimen was 200 ± 10 g.

The main parameters for the compacted specimen are reported in Table 1.

The tortuosity of the specimen was obtained by breakthrough curves of Cl⁻ ions, following the procedure suggested by Alshawabkeh and Acar [13].

Electrokinetic tests were performed at a constant potential gradient of 3 V/cm in which both electrolyte compartments initially contained 0.001 M Na₂SO₄. The electrical current was measured during the tests and an average value of 5 mA was obtained. The pH of catholyte and anolyte were monitored during testing and samples were withdrawn and analyzed for organic concentration.

At the end of each experiment the soil sample was extracted from the cell and divided into 10 layers, which were then divided in two samples to obtain the pH value and pollutant concentration. The pH was obtained by suspending the soil samples in de-ionised water (1:2.5, w/w). Acetonitrile was used to extract the pesticides from the soil samples as follows: 1 g of soil sample was placed in a glass vial and 10 ml of extractant was added; the vial was then stirred for 1 day. After centrifugation (5000 rpm for 30 min) 4 ml of supernatant was filtered through a 0.45 μm Teflon membrane and was then analyzed by HPLC. The extractions and the analyses of each layer were performed in triplicate.

2.5. Analytical techniques

Analyses of pesticide concentrations in supernatants were performed by Waters High Performance Liquid Chromatograph equipped with a UV–vis detector. In order to determine DCP concentrations, the analytical conditions required were: λ = 278 nm, column Chrompack Chromosphere 5 C8, mobile phase: CH₃OH + 0.1% H₃PO₄ and 0.05 M KH₂PO₄ + 0.1% H₃PO₄ = 50:50; flow rate, 1.7 cm³ min⁻¹; column temperature, 25 °C. Diuron concentrations were determined using the following analytic conditions: λ = 254 nm, column Purospher STAR RP-18 encapped (5 μm), mobile phase: acetonitrile/3.46 mM phosphate buffer pH 5.0, 30/70 (v/v); flow rate, 1.4 cm³ min⁻¹; column temperature, 25 °C. Identification of chromatographic peaks was performed by comparison with pure standards.

The total organic content of the humic acid-coated kaolinite was determined by using TOC-5000(A) carbon

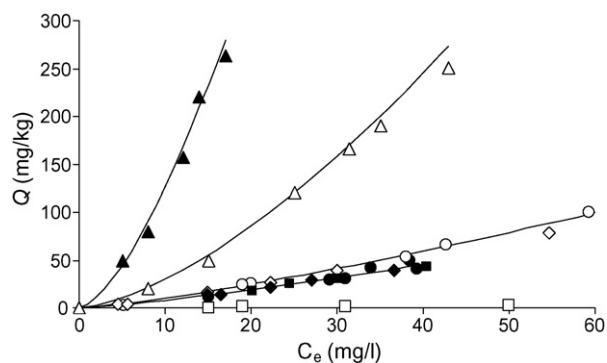


Fig. 2. Sorption isotherms of diuron (full symbols) and 2,6-dichlorophenol (empty symbols): (▲, △) humic acid-coated kaolinite pH 6.1; (○, ●) kaolinite pH 6.1; (◇, ◆) kaolinite pH 4.5; (■, □) kaolinite pH 7.8.

analyzer (Shimadzu) equipped with SSM-5000 Solid Sample Module.

3. Results and discussion

3.1. Sorption isotherms

The sorption isotherms of diuron and DCP obtained in this work are shown in Fig. 2.

The solid phase concentrations Q (mg/kg) were calculated from the mass balance for the solute:

$$Q = \frac{V}{m}[C_0 - C_e] \quad (1)$$

where V (dm³) is the volume of the solution with an initial concentration C_0 (mg/dm³) equilibrated with the clay, m (kg) the weight of the clay and C_e is the equilibrium concentration.

The Freundlich equation was adopted to interpret the experimental data:

$$Q = K_F C_e^N \quad (2)$$

where K_F (mg^{N-1} l^N kg⁻¹) is the Freundlich sorption coefficient and N (dimensionless) is a descriptor of the isotherm curvature. Eq. (2) was linearized in the form:

$$\ln Q = \ln K_F + N \ln C_e \quad (3)$$

to obtain the isotherm parameters. Table 2 reports the fitted values (95% confidence limits) from linear regression of log-transformed data obtained in the different runs. Analysis of linear regression was performed using Systat statistical software (SPSS Inc., Chicago, IL). F values (i.e. the ratio between-groups variance and within-groups variance) were in all cases greater than tabulated F statistics, so that the model was adequate to interpret the experimental data.

It can be noticed that values of the parameter N greater than 1 were determined for both compounds since the isotherms are convex to the abscissa (upward curvature). This isotherm shape is generally attributed to weak adsorbent–adsorbate forces at low concentration, followed by cooperative adsorbate–adsorbate interactions that promote adsorption [14]. It was also suggested that, when the sorption occurs primarily in clay interlayers, the

Table 2
Freundlich parameters for the sorption of 2,6-dichlorophenol and diuron on kaolinite and humic acid-coated kaolinite

	2,6-Dichlorophenol				Diuron			
	K_F^a ($\text{mg}^{N-1} \text{ l}^N \text{ kg}^{-1}$)	N^a	R^2	F^b	K_F^a ($\text{mg}^{N-1} \text{ l}^N \text{ kg}^{-1}$)	N^a	R^2	F^b
Kaolinite pH 6.1	0.45 (0.41–0.51)	1.31 (1.27–1.34)	0.995	704	0.43 (0.33–0.55)	1.25 (1.20–1.33)	0.985	201
pH 4.5	0.48 (0.44–0.54)	1.28 (1.25–1.32)	0.997	848	0.39 (0.35–0.42)	1.25 (1.21–1.32)	0.997	922
pH 7.8	0.015 (0.006–0.038)	1.31 (1.15–1.45)	0.928	72	0.45 (0.41–0.51)	1.23 (1.20–1.22)	0.998	1367
Humic coated kaolinite	0.82 (0.75–0.91)	1.53 (1.50–1.56)	0.998	1254	3.81 (3.21–4.42)	1.5 (1.42–1.58)	0.992	411

^a Fitted value [95% confidence limits], from linear regression of log-transformed data.

^b At 95% confidence level. F statistic values: $F_{3,4} = 6.55$; $F_{2,5} = 5.79$.

initial intercalation of small amounts of sorbate may enhance further adsorption [11]. In the sorption experiments on kaolinite at pH 6.1 both compound showed similar behaviour, as it results from the fitted K_F values, which are encompassed in the 95% confidence interval. As the pH increases, DCP and diuron exhibit a different behaviour: the K_F values for diuron fall between 0.33 and 0.55 $\text{mg}^{N-1} \text{ l}^N \text{ kg}^{-1}$, and the 95% confidence intervals encompass all these values (Table 2), whereas values of K_F decreasing with pH and statistically distinct are determined for the sorption of DCP (see Table 2).

The different effect of pH on the adsorption of diuron and DCP can be seen in Fig. 3 in which the amount of compound sorbed on kaolinite is depicted as a function of pH, values of initial concentration being the same: the sorption of diuron, which is a neutral molecule, shows little dependence on pH, whereas DCP is no longer sorbed when the pH value is equal to 7.8. The different chemical properties of the selected adsorbates may be considered in order to explain the dependence of the sorption on the pH. Both the dissociation of the ionisable solutes and the de-protonation of the superficial sites of the clay are affected by pH. DCP may dissociate in different degrees and when pH is greater than $\text{p}K_a$ (6.78) most of the DCP in solution is expected to exist as phenate anion, which is rejected from the superficial sites of the clay since at these pH values, they are negatively charged (de-protonated).

The sorption of both DCP and diuron was impacted strongly by the presence of humic acid associated with clay. The sorption process on this substrate may arise from both hydrophobic interactions with organic matter and the adsorption on the mineral

fraction: previous studies suggest that multiple retention mechanisms may be operative in sorption of organic contaminants including solute partitioning the organic matter of in soil as well as specific interactions with clay surface sites [15]. It was found that minerals in soils, including those with organic coating, may play an important role in the retention of certain pesticides [16,17].

It is worth to observe that whereas the values sorption constants for both compounds on kaolinite at natural pH (pH 6.1) are encompassed in the same confidence interval, on humic acid-clay system they are significantly distinct (Table 2). Humic acid modification enhances diuron sorption more than it does for DCP indicating that the organic matter is the main sorption domain for diuron, whereas the mineral fraction considerably contributes to the sorption of DCP containing polar functional groups.

3.2. Electrokinetic remediation

The experimental results of electrokinetic tests carried out at 3 V/cm, without the use of enhancing reagents and without pH control in the electrodic compartments, indicate that the lower is the sorption of contaminant in clay the higher is the effectiveness of remediation which can be achieved by electrokinetic treatment. If the contaminant is diuron, a 90% removal efficiency rate using unmodified kaolinite is achieved after 50 h when a total cumulative flow equal to 35 cm^3 (1.04 pore volume V_p) was collected in the cathode reservoir. If the kaolinite is coated by humic acid the removal rate of diuron is considerably lower, only 35% of the contaminant is removed after 160 h of treatment with a cumulative fluid quantity equal to 3 V_p .

In the electrokinetic removal of DCP the effect of the organic matter on the clay surface is lower; the removal efficiency of DCP from pure kaolinite reaches 90% after 110 h of treatment, while from kaolinite modified by humic acid the contaminant removal rate reaches 80% after 160 h. Moreover, the experimental results showed that DCP is partially oxidised during the treatment: the chemical analyses of both the catholyte and the samples obtained by extraction from the clay after the treatment evidenced the presence of benzoquinone, which is a typical product of DCP oxidation. A small amount of organic acids, such as oxalic acid, formic acid, maleic acid as well as others was also detected although was difficult to quantify.

Table 3 shows the mass balances for the electrokinetic test performed on kaolinite and kaolinite modified by humic acid. The balances compare the mass of contaminant present in the

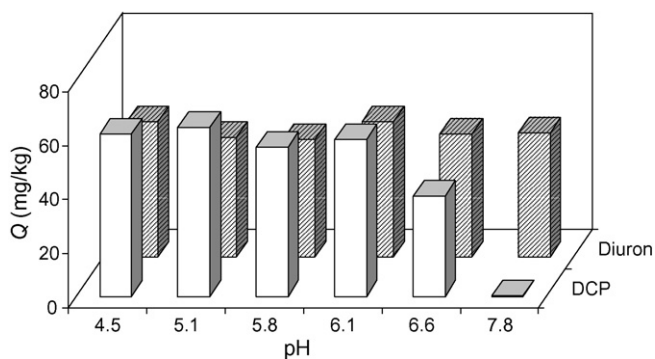


Fig. 3. Solid phase concentrations of adsorbed diuron and 2,6-dichlorophenol on kaolinite as a function of pH. Initial concentration: 40 ppm. Clay/solution ratio = 0.1 g/cm^3 .

Table 3
Mass balance analysis

Clay type	Pollutant	Treatment time (h)	Initial contaminant mass in the clay (mg)	Residual contaminant mass in the clay (mg)	Contaminant removed at the cathode reservoir (mg)	% contaminant removed from the clay sample	% mass balance
Kaolinite	Diuron	20	2.19	1.49	0.67	31.3	98.6
Kaolinite		35	2.05	0.79	1.30	61.4	102.0
Kaolinite		50	2.20	0.29	1.87	86.7	98.3
Humic coated kaolinite		50	2.40	2.28	0.11	5.0	99.6
Humic coated kaolinite		160	2.35	1.52	0.7	35.2	94.6
Kaolinite	DCP	110	1.49	0.068 ^a , 0.076 ^b	0.55 ^a , 0.64 ^b	90	89.5
Humic coated kaolinite		60	1.2	0.64 ^a , 0.15 ^b	0.27 ^a , 0.12 ^b	34.2	98.3
Humic coated kaolinite		160	1.25	0.04 ^a , 0.21 ^b	0.4 ^a , 0.5 ^b	80	92.0

^a Milligram of DCP that were not degraded during the treatment.

^b Milligram of DCP corresponding to the mg of BQ detected in the samples.

clay prior to electrokinetic treatment to the mass of contaminant present in the clay after the test added to the mass that accumulated in the cathode reservoir. In the anodic reservoir the analyses did not reveal the presence of organic contaminants. As can be seen from Table 3, for all the tests carried out with diuron the mass balance is close to 100%. In the case of DCP the amount of organic acid with low molecular weight was not considered in the balances: this could be the cause of the lack of mass evidenced in these tests, although the mineralization of a small quantity of DCP during the treatment cannot be excluded.

In order to interpret the experimental results the different mechanisms involved in the transport of contaminants throughout the clay under electric field, such as diffusion, electromigration, and electroosmotic advection should be considered. Mass flux caused by the different mechanisms can be expressed as:

- diffusive mass flux

$$J_d = D^* \nabla(-C) \quad (4)$$

where D^* is the effective molecular diffusion coefficient in the porous medium, which is related to that in free water by:

$$D^* = D \varepsilon \tau \quad (5)$$

being ε is the volumetric moisture content and τ is the tortuosity coefficient. τ accounts for the ratio between the average length of the streamlines in a porous medium (L_e) and the straight-line length L ($\tau = L/L_e$)²

- electromigrative mass flux

$$J_{em} = u^* C \nabla(-\Phi) \quad (6)$$

where u^* is the effective ionic mobility in the porous medium and Φ is the electric potential.

- electroosmotic advective mass flux

$$J_{eo} = k_{eo} C \nabla(-\Phi) \quad (7)$$

where k_{eo} is the electroosmotic permeability coefficient.

For one-dimensional implementation, assuming near instantaneous adsorption–desorption reactions and a constant electric

field through the whole sample, the mass balance of the contaminant can be written as [18]:

$$R_d \frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} + (u^* + k_{eo}) \frac{\partial C}{\partial x} \frac{\Delta \Phi}{L} \quad (8)$$

The adsorption–desorption reactions in Eq. (8) are represented by the retardation factor R_d , which for linear sorption is defined as:

$$R_d = 1 + \frac{\rho_d}{\varepsilon} k_L \quad (9)$$

where ρ_d is the dry density of the clay specimen and k_L is the adsorption constant.

In order to model the experimental results of the electrokinetic remediation of kaolinite spiked by diuron the contribution of the electromigrative flux was assumed equal to zero since diuron is a non-ionic specie in the pH range examined. Constant electroosmotic permeability was assumed during the treatment because a stable anode-to-cathode flow rate Q was experimentally observed until a water volume equal to $1V_p$ was collected in the cathode reservoir: the value of $k_{eo} = 1.2 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ was calculated by the following equation:

$$k_{eo} = \frac{Q}{A} \frac{L}{\Delta \Phi} \quad (10)$$

where A and L are cross-sectional area and length of the specimen, respectively.

To carry out the calculation a value of D equal to $8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and a retardation factor (R_d) equal to 3.0 were utilised; this value was obtained by means equation (9) using the sample characteristic (Table 1) and the adsorption constant of diuron on kaolinite.

Eq. (8) was numerically solved with the initial conditions:

$$t = 0 \quad \forall x, \quad C = C_0 \quad (11)$$

and the following boundary conditions:

$$t > 0, \quad x = 0, \quad \frac{\partial C}{\partial x} = 0, \\ t > 0, \quad x = L, \quad \frac{\partial C}{\partial x} = C k_{eo} \frac{\partial \Phi}{\partial x} \quad (12)$$

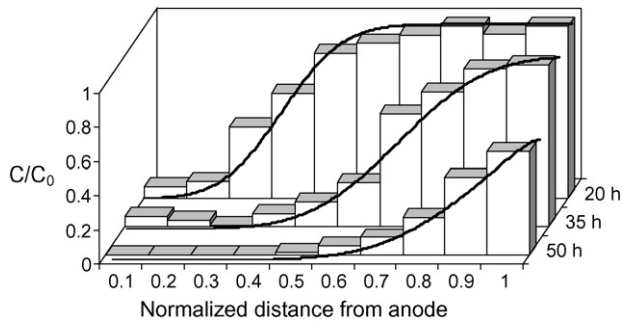


Fig. 4. Comparison between experimental and calculated profiles of diuron concentration into the kaolinite column at different treatment time.

The concentration profiles in the clay column calculated by Eq. (8) are presented in Fig. 4 and compared with the experimental data; as can be seen, a good agreement was achieved. Fig. 5 shows the experimental and calculated profiles of diuron concentration during electrokinetic treatment of kaolinite coated with humic acid. The strong adsorption of diuron on this substrate hinders the electrokinetic remediation, this results in a value of the equilibrium constant equal to 4.1 l/kg, which lead to a retardation factor $R_d = 17.1$. In this case after 50 h of electrokinetic treatment, when $1V_p$ is passed throughout the clay column, a 50% of pollutant removal in the column section near the anode was calculated by the model, which is in good agreement with the experimental results. However, only 5% of initial contaminant is removed from the whole specimen. At longer treatment time, the application of an electric field not only promotes the mass transport of contaminants, but it may also provoke a series of reactions [19] that lead to modifications of the clay characteristics. In these conditions the model previously utilised, based on constant k_{eo} and linear adsorption is not adequate. Fig. 5 also shows the experimental profile of diuron after passing the cumulative volume equal to $3V_p$: as can be seen the concentration of contaminant is reduced by 50% near the anode and is almost equal to the initial value in the cathodic zone. However, in order to obtain the passing of this water volume, 160 h of treatment are required, because a decrease in the electroosmotic flow was observed in the experiments after a volume greater than $1V_p$ passed through the sample.

The trend of k_{eo} with the ratio V/V_p is shown in Fig. 6: it can be observed that a reduction of k_{eo} up to 75% occurred at long treatment time ($V/V_p > 3$).

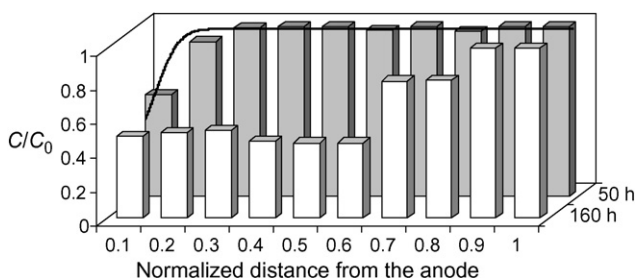


Fig. 5. Profile of normalized concentration of diuron in the humic acid-coated kaolinite specimen at different treatment time.

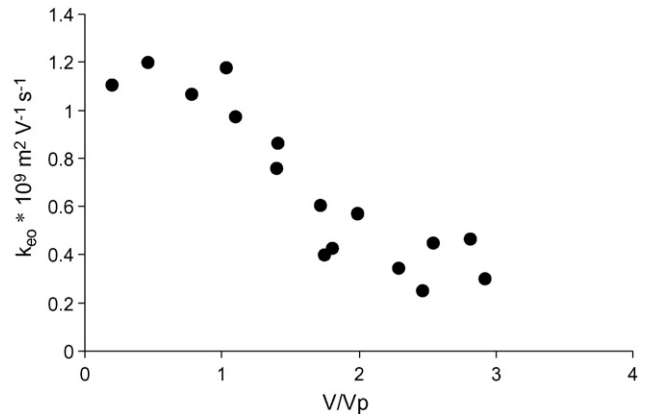


Fig. 6. Values of electrokinetic conductivity (k_{eo}) as a function of the ratio between cumulative volume and pore volume (V/V_p).

Previous works evidenced a decrease in electroosmotic conductivity when the electrokinetic process is performed without pH control in the electroodic compartments [20]. The loss of electroosmotic conductivity may be attributed to a combination of acidification in the anode zone and of the formation of a region of higher pH close to the cathode. The acid front mobilize metal ions such as calcium naturally present in the soil; these ions are transported to the cathode where low local permeability could occur due to the precipitation of carbonates at high pH. Moreover, acid conditions near the anode may lower or reverse the electroosmotic flow due to changes in the surface charge of the clay minerals. Change in the clay fabric to a more flocculated and stable form may also occur [21,22]. In this work, the pH of the clay was measured in the region near to the anode, in the central zone of the column and in the region near to the cathode during electrokinetic process: the results are shown in Fig. 7.

As can be seen from the figure, for low processing times, the acid front is rapidly drawn in to the core, toward the cathode and acid conditions are observed throughout the kaolinite column until the section near the cathode where the pH rises to 7. Since the mobility of OH^- is lower than that H^+ and the migration of OH^- toward the anode is hindered by the electroosmotic flow, only at longer processing times the pH in the zone closer to the cathode increase to 10 and reach an almost neutral value in the

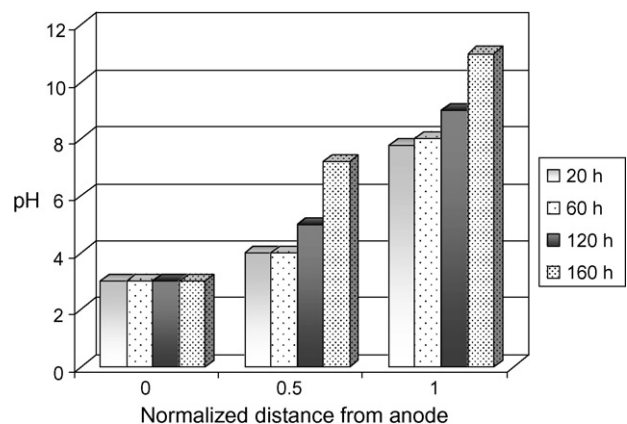


Fig. 7. pH profiles in humic acid-coated kaolinite specimens at different treatment times.

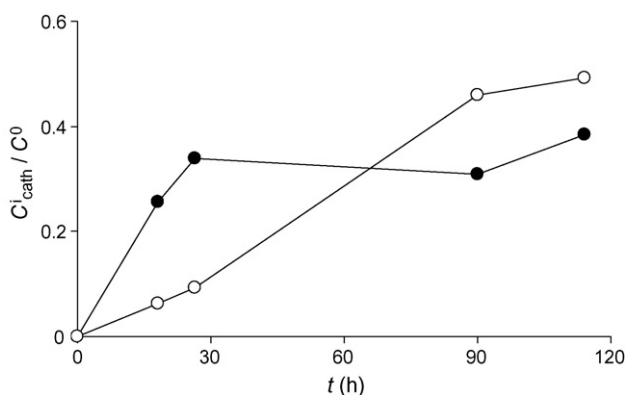


Fig. 8. Trend with time of 2,6-dichlorophenol (●) and benzoquinone (○) concentration, normalized with respect to the initial 2,6-dichlorophenol, in the catholyte during electrokinetic treatment of kaolinite.

central part of the column. Under these conditions the decrease observed in the electroosmotic flow may be mainly due to the precipitation of metal hydroxides when the mobilized cations meet the basic front.

The reduction of the electroosmotic coefficient has a negative effect on the removal of chemicals characterized by low mobility, in these conditions a proper management of the operative conditions is requested. In particular, according to previous works [9] the control of pH of anolyte (close to 7) and the catholyte (in acid conditions) can prevent the progressive decline in the electroosmotic flow rate.

When an electric field was applied to a column of kaolinite spiked by DCP, a complex behaviour was observed: the pollutant was moved mainly toward the cathode over the first 30 h of treatment, as it was evinced by the increasing concentration of the contaminant in the catholyte over this treatment time. Since the soil pH up to this point in time is less than the pK_a value (Fig. 7), DCP is transported in its neutral form toward the cathode by electroosmotic flow. After the soil pH is increased enough in the region near the cathode, the contaminant could be moved in its ionised form by electromigration toward the anode. So, as can be seen in Fig. 8, no further increase in concentration of DCP in the catholyte reservoir was observed. The analysis of the catholyte also shows the presence of benzoquinone and other by-products of oxidative degradation of phenols. The degradation of organic contaminants during electrokinetic remediation has previously been observed [23]. In particular, Cong et al. [24] noticed that a partial degradation of chlorophenols occurred close the electrodes: organic acids and benzoquinone were found to be intermediates of the anodic reaction.

After the water volume equal to $3V_p$ is passed throughout the kaolinite column and 90% of the organic contaminant (DCP or its degradation products) has been removed, the clay contains only small amounts of the original pollutant while appreciable concentrations of its degradation intermediates are found mainly in the region near the anode (Fig. 9).

When the kaolinite is modified by humic acid, similar phenomena are observed. As can be seen from Fig. 10, after 60 h of electrokinetic treatment, the DCP content in the regions near the anode and the cathode is reduced significantly while an

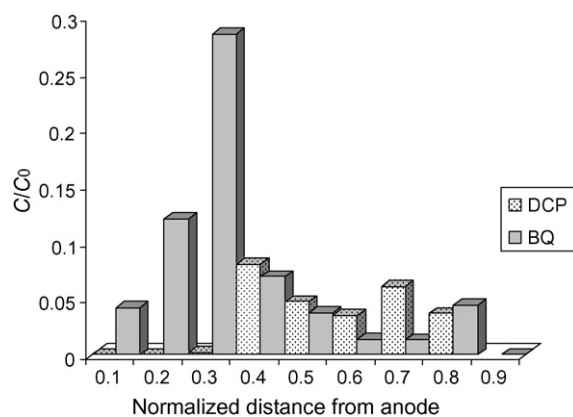


Fig. 9. Profile of normalized concentration of 2,6-dichlorophenol and benzoquinone in the kaolinite specimen after 110 h of treatment.

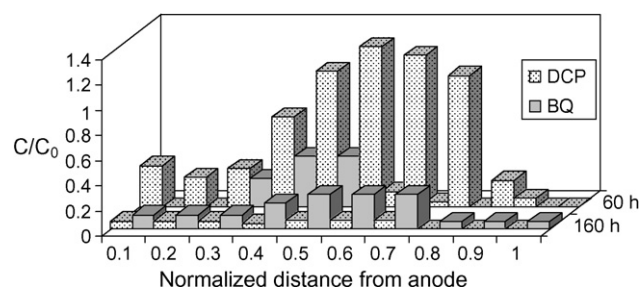


Fig. 10. Profiles of normalized concentration of 2,6-dichlorophenol and benzoquinone in the humic acid-coated kaolinite specimen at different treatment times.

accumulation of contaminant appears in the middle of the cell. This indicates that, also in this case, DCP is initially mobilized by electroosmotic flow toward the cathode and then toward the anode region by migration when the pH of the clay close to the cathode is high enough to favour the ionised form. The content of degradation intermediates in the clay is low at this time. After 160 h of treatment (Fig. 10) the clay contains only small amounts of degradation products and only traces of DCP are present, indicating that the intermediates could be moved by electroosmotic flow toward the electrodic compartments and degraded continuously in time. Thus, the contaminated clay could be remediated by the synergic effects of electrokinetic process and electrochemical reaction on the electrodes.

4. Conclusions

The effectiveness of electrokinetic techniques in removing the organic pollutants from kaolinitic clayey soils has been tested, by examining the effect of the different phenomena involved in the process. The results showed that:

- Non-ionisable and weakly sorbed compounds are removed from kaolinite by the electrokinetic flow, and accumulate in the catholyte.
- If the solid phase contains organic matter, such as humic acid-clay complexes, organic pollutants are strongly retained and the time required for the process increases. Moreover, with long processing times, modifications of the solid surface may

occur, mainly due to the interaction with H^+ and OH^- ions generated at the electrodes. These modifications may decrease the electrokinetic flux.

- Surface reaction of OH^- and H^+ also affects the pH of the pore water, as well as the behaviour of ionisable compounds such as DCP; at high pH these compounds are present as anions and are then transported toward the anode by electromigration.
- In the case of easily oxidisable compounds, such as phenols, partial oxidation may occur when long processing times are long: the contaminated clay can be remediated by the synergic effects of electrokinetic processes and electrochemical reaction on the electrodes.

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References

- [1] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation—critical overview, *Sci. Total Environ.* 289 (2002) 97–121.
- [2] A.T. Yeung, Contaminant extractability by electrokinetics, *Environ. Eng. Sci.* 23 (2006) 202–224.
- [3] E.R. Saichek, K.R. Reddy, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, *Chemosphere* 51 (2003) 273–287.
- [4] Y.B. Acar, H. Li, R.J. Gale, Phenol removal from kaolin by electrokinetics, *J. Geotech. Eng.* 118 (1992) 1837–1852.
- [5] C.J. Bruell, B.A. Segall, M.T. Walsh, Electroosmotic removal of gasoline hydrocarbons and TCE from clay, *J. Environ. Eng.-ASCE* 118 (1992) 68–83.
- [6] A.P. Shapiro, R.F. Probst, Removal of contaminants from saturated clay by electroosmosis, *Environ. Sci. Technol.* 27 (1993) 283–291.
- [7] Q. Luo, X. Zhang, H. Wan, Y. Qian, Mobilization of phenol and dichlorophenol in unsaturated soils by non-uniform electrokinetics, *Chemosphere* 59 (2005) 1289–1298.
- [8] A.B. Ribeiro, J.M. Rodríguez-Maroto, E.P. Mateus, H. Gomes, Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine. Experimental and modeling, *Chemosphere* 59 (2005) 1229–1239.
- [9] N.J. Cherepy, D. Wildenschild, Electrolyte management for effective long-term electro-osmotic transport in low-permeability soils, *Environ. Sci. Technol.* 37 (2003) 3024–3030.
- [10] X.-P. Wang, X.-Q. Shan, L. Luo, S.-Z. Zhang, B. Wen, Sorption of 2,4,6-trichlorophenol in model humic acid-clay systems, *J. Agric. Food Chem.* 53 (2005) 3548–3555.
- [11] H. Li, G. Sheng, B.J. Teppen, C.T. Johnston, S.A. Boyd, Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes, *Soil Sci. Soc. Am. J.* 67 (2003) 122–131.
- [12] C.T. Chiou, T.D. Shoup, P.E. Porter, Mechanistic roles of soil humus and minerals in the sorption of nonionic organic compounds from aqueous and organic solutions, *Org. Geochem.* 8 (1985) 9–14.
- [13] A.N. Alshawabkeh, Y.B. Acar, Electrokinetic remediation. II. Theoretical model, *J. Geotech. Geoenviron. Eng.* 122 (1996) 186–196.
- [14] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, London, 1982.
- [15] B.N. Kimani Njoroge, W.P. Ball, R.S. Cherry, Sorption of 1,2,4-dichlorobenzene and tetrachloroethene within an authigenic soil profile: changes of Koc with soil depth, *J. Contam. Hydrol.* 29 (1998) 347–377.
- [16] S.A. Boyd, G. Sheng, B.J. Teppen, C.T. Johnston, Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays, *Environ. Sci. Technol.* 35 (2001) 4227–4234.
- [17] K.M. Spark, R.S. Swift, Effect of soil composition and dissolved organic matter on pesticide sorption, *Sci. Total Environ.* 298 (2002) 147–161.
- [18] S.-O. Kim, J.-J. Kim, S.-T. Yun, K.-W. Kim, Numerical and experimental studies on cadmium II transport in kaolinite clay under electrical fields, *Water Air Soil Pollut.* 150 (2003) 135–162.
- [19] A.T. Yeung, C.-N. Hsu, R.M. Menon, Physicochemical soil-contaminant interactions during electrokinetic extraction, *J. Hazard. Mater.* 55 (1997) 221–237.
- [20] T. Grundl, P. Michalsky, Electroosmotically driven water flow in sediments, *Water Res.* 30 (1996) 811–818.
- [21] G.C.C. Yang, S.-L. Lin, Removal of lead from a silt loam soil by electrokinetic remediation, *J. Hazard. Mater.* 58 (1998) 285–299.
- [22] T.J. Thomas, R.W. Lentz, Changes in soil plasticity and swell caused by electro-osmosis, in: *Physico-chemical Aspects of Soil and Related Material*, ASTM STP 1095, American Society for Testing and Materials, Philadelphia, 1990, pp. 108–117.
- [23] D. Rahner, G. Ludwig, J. Röhrs, Electrochemically induced reactions in soils—a new approach to the in-situ remediation of contaminated soils? Part 1: the microconductor principle, *Electrochim. Acta* 47 (2002) 1395–1403.
- [24] Y. Cong, Q. Ye, Z. Wu, Electrokinetic behaviour of chlorinated phenols in soil and their electrochemical degradation, *Trans. IChemE*, part B 83 (2005) 178–183.