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Enhancement of the Electrokinetic Remediation Method of Fine-Dispersed Clay Soils

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Abstract—The possibility of application of the modified electrokinetic treatment method to removal both inorganic and organic contaminants from clay soils has been demonstrated. The proposed improvements include the adjustment of pH of the soil pore solution, as this parameter is one of the major factors determining the treatment efficacy. The modification consists in replacement of the conventional acidic or alkaline reagents with neutral ones, thus enhancing the ecological compatibility of the detoxification process.

Keywords: electrokinetic remediation, clay soil, pH of pore solution, electromigration, electroosmosis, inorganic contamination, organic contamination

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INTRODUCTION

Accumulation of toxic compounds in soil as a result of anthropogenic activities has become an important environmental problem. Such toxic compounds include heavy metals, radioactive nuclides, and organic compounds including chlorinated as well as polycyclic aromatic ones, and pesticides. Sorption of the toxic compounds with soil components significantly complicates the contaminations removal as compared with detoxication of water or air; on the other hand, the toxic components are continuously leached becoming additional sources of surface and ground waters pollution.

No universal method of efficient and ecologically compatible removal of wide range of the contaminants from various soil types has been proposed so far. The following detoxication methods have been recognized as the most promising: soil washing with special solutions [1, 2], bioremediation [3, 4], vapor extraction [5, 6], thermal desorption [7, 8], and electrokinetic remediation [9, 10].

The decontaminating soil type is among the major factors determining the efficacy of this or that detoxication method. The fine-dispersed clay soil is the most challenging object for decontamination, due to the two reasons. The first one is the large surface area of the soil particles and its specific properties leading to strong interactions between the soil and the contaminants. The second factor is high hydro- and aerodynamic resistance excluding the possibility of efficient surfactant washing or vapor extraction. The two mentioned factors are operative in the cases of virtually all the contaminants: ionic (heavy metals and radioactive nuclides) as well as nonionic (organic) compounds.

Electrokinetic remediation is a procedure allowing efficient removal of any types of contaminants from clay soils. This method has been recently studied in detail [9–12]. However, it is not free of certain drawbacks. This work aimed to develop this promising method in order to enhance its ecological compatibility and manufacturability while preserving its efficacy.

Elecrokinetic Remediation Fundamentals

Electrokinetic remediation is based on the soil treatment with external electric field. A set of processes occurs in the soil pore solution upon the treatment [13], electromigration and electroosmosis being the most important for decontamination. Electromigration plays a crucial part in removal of heavy metals and radioactive nuclides, while electroosmosis allows for removal of organic compounds. One of the major factors determining the efficacy of the both processes is pH of the soil pore solution.

In the case of heavy metals and radioactive nuclides removal, the pH value determines the degree of the contaminants desorption into the pore solution as well as the possibility of the contaminants precipitation in the form of hydroxo compounds; i.e. the electromigration efficiency of the contaminants. Generally, low pH values allow for high electromigration mobility.

As far as removal of non-charged organic compounds is concerned, pH of the pore solution affects the decontamination efficiency via the change of electrokinetic potential, as the pH value along with the electric field intensity determines the electroosmosis flow value [14]. For most of clay soils, the electrokinetic potential increases with pH. For example, in the case of kaolin ξ-potential is of +0.7 mV at pH 2 and of –54 mV at pH 10 [9].

Hence, in any particular case a certain pH value should be used in order to enhance the transport process and ensure its stability leading to the highest decontamination efficacy. However, the soil treatment is complicated by the electrode reactions occurring upon the electric field application: generation of hydroxyl ions at the cathode and of protons at the anode. As a result, the initial pH value of the pore solution is changed, and the non-uniform pH profile is formed, with increased pH at the cathode and lowered pH at the anode [12].

Such change of the pH value in the course of decontamination leads to concentration of the major part of heavy metals and radioactive nuclides near the cathode, since they form insoluble hydroxo compounds at the increased pH range. In the case of organic compounds removal, the negative effect of non-uniform pH field is due to the resulting non-uniform electrokinetic potential and thus the non-uniform electroosmosis flow, stronger at the cathode side and weaker at the anode side. This can result in drying out of the cathode part of the cell and complete shutdown of the electroosmosis transport.

The electrode reactions therefore may seem side processes and should be avoided. However, the task is not as simple as mere preservation of the initial solution pH, but it should be regarded as formation and maintaining the pH profile optimal in view of the fastest transport of the contaminants. The electrode reactions can serve as sources of hydroxyl or hydroxonium ions to achieve the goal.

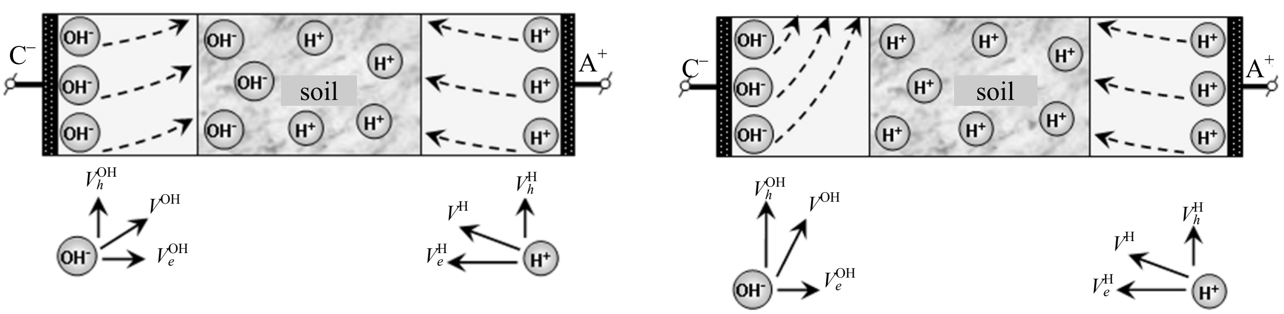
In order to achieve the required pH conditions, it is essential that certain ions (for instance, hydroxyl ions during removal of heavy metals) generated at the cathode do not come into the treated soil, allowing for transport of the protons generated at the anode. This will result in the required pH conditions without using any additional reagents.

Several methods to avoid the transport of ions deteriorating the decontamination into the treated system are known: using ion-exchange materials, special constructions of the electrodes, and introduction of the reagents neutralizing certain ions to the electrode chambers [15–18]. The latter approach has been recently recognized as the most promising; in particular, acidic solution is introduced into the cathode chamber, and alkaline solution is fed into the anode chamber. However, this implied application of aggressive liquids making the process less manufacturable and requiring special anti-corrosive properties of the equipment.

Excluding the aggressive reagents from the process would decrease its cost and make it more safe and environmentally friendly. The electrokinetic remediation can be improved by replacement of the acidic and alkaline solutions with neutral solution of inorganic salt [19]. Theoretical analysis of the transport in the electrode chambers has revealed that such a method can be advantageous due to the removal of undesired ions from the electrode chambers before they come into the treated soil.

Let us consider the processes occurring in the electrode chambers upon application of the electric current and pumping the solution through the chambers. In this case, movement of the ions generated at the cathode and the anode is a superposition of the electromigration and the hydrodynamic parts, being determined by their ratio (Fig. 1).

The rate of electromigration movement depends on the local strength of the electric field and on the electromigration mobility of the ions (being twice higher for protons as compared with hydroxyl ions). Hydrodynamic movement depends on the rate of the liquid pumping through the electrode chamber. At constant intensity of the electric field, the ions path will change in response to the varied rate of the electrolyte solution pumping. At low pumping rate, the



(a) (b)

Fig. 1. Scheme of protons and hydroxyl ions movements in the electrode chambers without (a) and with (b) regulating of pH.

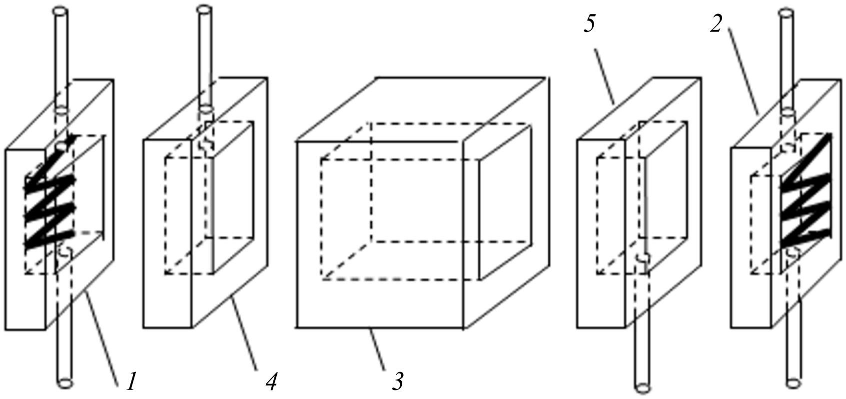


Fig. 2. Scheme of the electrochemical cell: (*1*) cathode chamber, (*2*) anode chamber, (*3*) central chamber, (*4*) chamber for withdrawal of the electroosmosis flow, and (*5*) chamber for input of the solution.

hydrodynamic part of the movement is low, the ions movement is majorly determined by the electromigration, and practically all the ions reach the treated soil, changing the pore solutions pH as described above (Fig. 1a).

With the increased pumping rate, the impact of the hydrodynamic term grows and changes the ions trajectory so that at certain critical pumping rate all the ions should be passed off the system not reaching the treated soil. If the pumping rate in the other chamber is low and the generated ions reach the treated soil, the overall process is as depicted in Fig. 1b.

Detailed analysis of the transport processes and the related theoretical simulation has been given elsewhere [20, 21]. The reported results confirm the possibility of pH regulation via alternation of the electrolyte pumping rate.

EXPERIMENTAL

The study of the proposed approach efficacy was performed using the electrochemical cell consisting of two electrode chambers (*1, 2*) equipped with vertical platinum electrodes and of the central chamber (*3*) filled with the treated soil (Fig. 2).

During the experiments under conditions of the major role of the electroosmosis the cell was additionally equipped with two chambers, for withdrawal of the electroosmosis flow from the system (*4*) and to introduction of the solution into the system (*5*) so that the electroosmotic loss of liquid is compensated for and the soil is continuously washed. Since the electrokinetic potential of clay soil is negative, the electroosmotic flow is directed from the anode to the cathode; therefore, the chamber (*4*) was placed at the cathode side and chamber (*5*) was

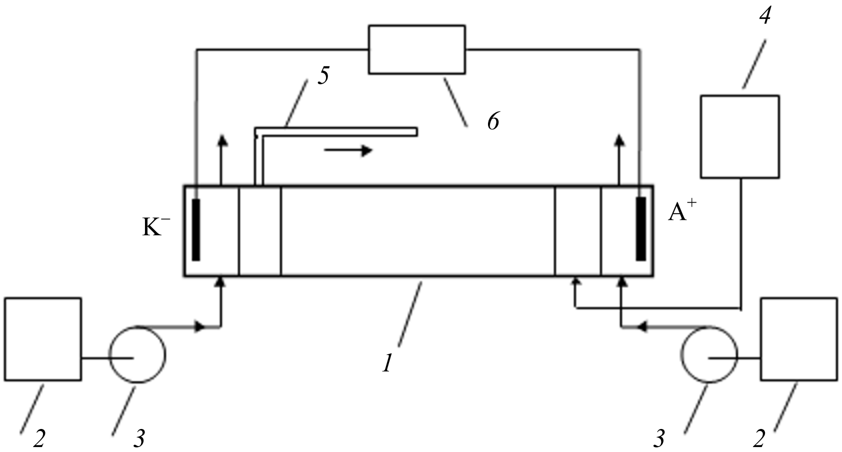


Fig. 3. The scheme of the experimental setup: (*1*) electrochemical cell, (*2*) electrolyte solution tank, (*3*) pump, (*4*) compensating tank, (*5*) microburet, and (*6*) power supply.

adjacent to the anode. The chambers were separated with polysulfone clothes.

Besides the electrochemical cell (*1*), the experimental setup (Fig. 3) included the two tanks (*2*) with the inorganic salt solution (0.1 mol/L $NaNO_3$), the two peristaltic pumps (*3*) allowing for its pumping through the electrode chambers, the compensating tank filled with the solution for electroosmosis soil washing (*4*), the microburet to estimate the electroosmosis velocity (*5*), and the power supply (*6*). In order to avoid the difference of the hydrostatic pressure, the solution level in the compensating tank was maintained at the level of the solution in the microburet. The experiments were performed in the potentiostatic mode at the average field intensity of 3 V/cm.

Kaolin was used as the soil model. The treated soil properties, its sorption parameters, the presence of buffer capacity, and initial pH of the pore solution were the factors determining the dynamics of pH profile establishment and decontamination. This work aimed to demonstrate the principal possibility of the modified method application to the clay soil detoxication, the model object was chosen in view of the neutral initial pH level of the used kaolin (pH = 6.37) and its low exchange capacity (1.3 meq/100 g) at practically absent buffer capacity.

Cadmium was chosen as a model ionic contaminant, its concentration being of 0.25 mg per 1 g of the kaolin; hydrophobic chlorobenzene at 4.5 mg per 1 g of the kaolin served as model nonionic organic contaminant.

Accounting for geometry parameters of the electrode chambers (height of 2.8 cm, width of 2.3 cm, and the electrodes-to-soil distance of 1.0 cm) and the electric field intensity, we calculated the critical rate of the inorganic salt solution pumping allowing for formation and maintaining of the required pH profile. As the electric conductance was changed in the course of decontamination, the total field intensity was redistributed, and the electromigration part of the ions movement was variable. Hence, the critical rate of the pumping was not constant with time. In order to avoid occasional overshoot of the non-desired ions into the treated soil, the highest calculated pumping rate was maintained in the course of the experiment. That pumping rate was of 85 mL/h for the cathode chamber and of 210 mL/h for the anode chamber.

RESULTS AND DISCUSSION

The study consisted of three sets of the experiments. Firstly, formation of the pH profile in the treated soil sample was studied as function of the electrolyte solution pumping rate. Then, the kaolin decontamination of cadmium and of chlorobenzene was performed at different setup of the electrode chambers washing.

The reference experiment was run without pH regulation, at the pumping rate much lower than the critical ones for the both chambers (Fig. 4, curve *1*). The result was in line with the conventionally observed pH distribution (increasing of pH at the cathode area and decreasing pH in the anode area).

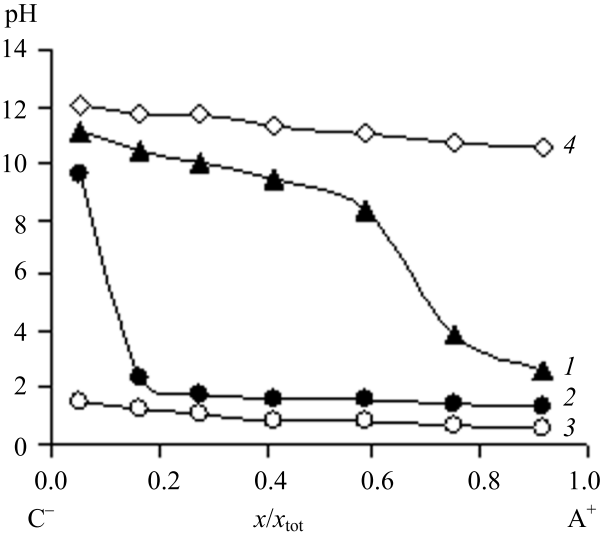


Fig. 4. pH profile over the normalized length of the loaded soil at different rates of pumping through the electrode chambers: (*1*) cathode chamber 20 mL/h and anode chamber 20 mL/h; (*2*) cathode chamber 75 mL/h and anode chamber 20 mL/h; (*3*) cathode chamber 115 mL/h and anode chamber 20 mL/h; and (*4*) cathode chamber 20 mL/h and anode chamber 250 mL/h. (C) cathode and (A) anode.

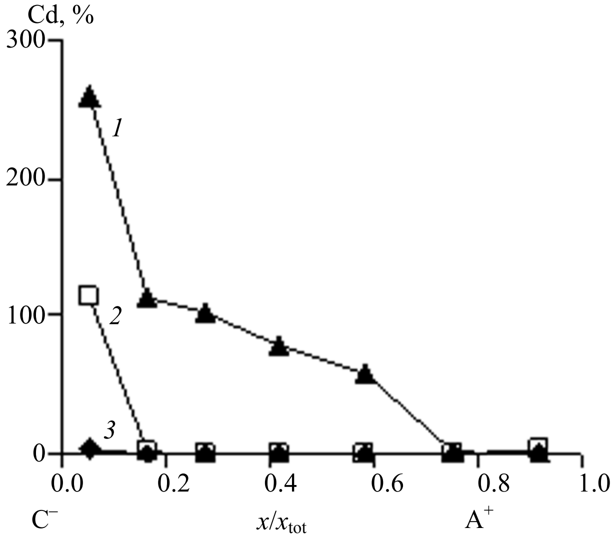


Fig. 5. Velocity of electroosmotic flow and distribution of residual Cd over the normalized length of the loaded soil at different rates of pumping through the electrode chambers and the treatment time: (*1*) cathode chamber 20 mL/h and anode chamber 20 mL/h, 18 h; (*2*) cathode chamber 110 mL/h and anode chamber 20 mL/h, 18 h; and (*3*) cathode chamber 110 mL/h and anode chamber 20 mL/h, 24 h. (C) cathode and (A) anode.

Further experiments aimed to achieve the uniform pH value over the whole sample. Curve *2* (Fig. 4) demonstrates the pH profile when the pumping rate through the cathode chamber was slightly below the critical value and the pumping rate of the anode chamber was well below the critical value (allowing all the protons generated to reach the treated soil). As the cathode chamber pumping rate allowed a part of hydroxyl ions to reach the soil sample, the thin layer close to cathode showed high pH value.

Increasing of the pumping rate above the critical one maintained the acidic pH over the whole volume of the treated soil (Fig. 4, curve *3*). Under the opposite pumping conditions (the low pumping rate in the cathode chamber and that in the anode chamber above the critical level), the pH profile was alkaline over the whole soil sample. Hence, the developed method indeed allowed formation of the required pH profile over the treated sample.

Distribution profiles of the residual cadmium content obtained in the second set of the experiments coincided with the pH profiles. In particular, under conditions of no pH regulation cadmium was completely removed from the regions with low pH and was concentrated at the increased pH (Figs. 4 and 5, curves *1*); the overall decontamination degree was of 27.4%.

Under conditions of low pH (Fig. 4, curve *3*), the 18 h treatment allowed removal of 85.8% of the total cadmium content, the residual 14.2% of cadmium being concentrated in the layer adjacent to the cathode (Fig. 5, curve *2*). However, such concentrating was not critical, as it could be due to the lower cadmium electromigration as compared to that of protons, leading to lag of cadmium removal with respect to pH profile development. If so, the longer treatment could afford practically complete removal of cadmium, as confirmed by the results of the longer experiment (Fig. 5, curve *3*). The residual cadmium content in the latter case was of less than 0.5 %.

The next set of experiments aimed to elucidate the efficacy of the developed method towards removal of uncharged organic compounds from the clay soil. In general, the task of toxic organic compounds removal is more complicated, because maintaining strong and stable electroosmotic flow is a necessary but not sufficient condition to do so. Indeed, most of the nonionic contaminants are hydrophobic, and surfactant should be applied for their solubilization. The choice of the surfactant and determination of its optimal

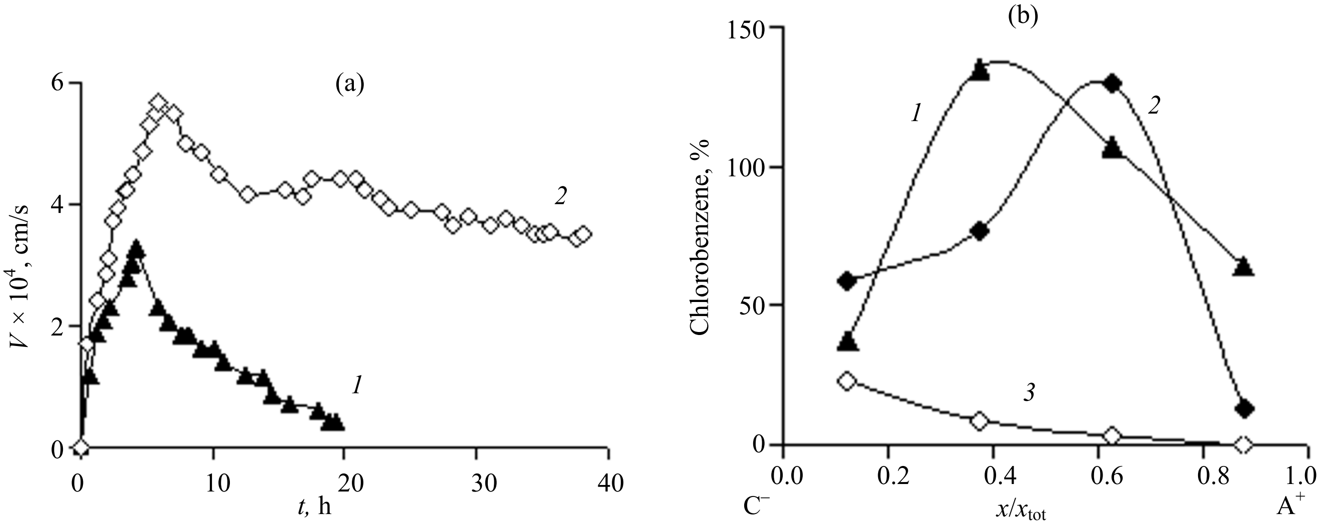


Fig. 6. Velocity of electroosmotic flow (a) and distribution of residual chlorobenzene over the normalized length of the loaded soil (b) at different rates of pumping through the electrode chambers and the treatment time: (*1*) cathode chamber 20 mL/h and anode chamber 20 mL/h, 19 h; (*2*) cathode chamber 20 mL/h and anode chamber 250 mL/h, 14 h; and (*3*) cathode chamber 20 mL/h and anode chamber 250 mL/h, 38 h. (C) cathode and (A) anode.

concentration is not trivial and should be analyzed separately [22, 23]. In this work we used 0.01 mol/L aqueous solutions of Triton X-100 to solubilize chlorobenzene.

Similarly to the case of cadmium removal, the first experiment with chlorobenzene was performed without any pH regulation, at the pumping rate below the critical values. The initial electroosmotic flow was enhanced (Fig. 6a, curve *1*) due to increase of the solution pH at the cathode side (Fig. 4, curve *1*) resulting in increase of the local electrokinetic potential.

However, the local electrokinetic potential near the anode was decreased due to the decreased pH of the pore solution; hence, the transfer of liquid from the anode chamber could not compensate for the liquid removal from the cathode chamber, and the electroosmosis velocity went down to zero in time. As a result, 19 h treatment allowed transfer of only 32 mL of the solution through the kaolin, and the decontamination degree was of 11.5%. The observed residual chlorobenzene distribution (Fig. 6b, curve *1*) corresponded to the discussed mechanism. The strong electroosmotic flow allowed removal of more than 60% of the initial chlorobenzene content form the cathode area, the highest residual value likely corresponding to the region of the osmosis flow break: chlorobenzene transferred from the anode region could not be further transported to the cathode region.

At the rate of the solution pumping from the anode chamber exceeding the critical value, the electroosmosis character was changed (Fig. 6a, curve *3*). Similarly to the above-discussed case, the initial rise was due to the increased electrokinetic potential due to the hydroxyl ions influx into the pore solution. The alkaline pH profile formed in time afforded the uniform electrokinetic potential conditions over the whole sample volume, and, hence, led to the stable electroosmotic flow. The slight decrease of the electroosmosis velocity could be due to the changes of the system electric conductivity leading to the local voltage drop.

The profile of residual chlorobenzene distribution after the 14 h treatment was similar to the previously discussed case (Fig. 6b, curves *1* and *2*), since the electroosmosis features showed similar regularities due to the local heterogeneities of the electrokinetic potential at the initial stage. However, the absolute values of the flow velocity were higher because the electrokinetic potential did not go down in the anode region; that resulted in the higher degree of decontamination: 40 mL and 28.2%. The longer treatment under conditions of the stable electroosmotic flow due to the alkaline pH of the pore solution allowed flow of 160 mL during 38 h and resulted in the decontamination degree of 91.3%. Practically all the residual chlorobenzene was located near the cathode (Fig. 6b, curve *3*), therefore, the further prolonged experiment run could allow enhancement of the detoxication degree.

CONCLUSIONS

We demonstrated that the proposed modified method of electrokinetic decontamination allowed control of pH of the pore solution during the soil treatment without application of aggressive solutions, thus improving the ecological compatibility and manufacturability of the process. The optimal pH conditions of the treated soil allowed for stable transport of the ionic as well as the nonionic contaminants thus enhancing their efficient removal from the fine-disperse clay soil.

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