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Ying-Ying Gu[a]; Albert T. Yeung[a]; Albert Koenig[a]; Hong-Jiang Li[b]
[a] Department of Civil Engineering, University of Hong Kong, Pokfulam Road, Hong Kong [b] State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai, China

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Effects of Chelating Agents on Zeta Potential of Cadmium-Contaminated Natural Clay

Ying-Ying Gu,[1] Albert T. Yeung,[1] Albert Koenig,[1] and Hong-Jiang Li[2]
[1]Department of Civil Engineering, University of Hong Kong,
Pokfulam Road, Hong Kong
[2]State Key Laboratory of Pollution Control and Resource Reuse,
Tongji University, Shanghai, China

Abstract: The effects of pH, ionic strength, cadmium concentration, and chelating agents on the zeta potential of a natural clay of high acid/base buffer capacity from Shanghai, China were investigated in this study, with a view to enhancing the efficiency of electrokinetic remediation of the cadmium-contaminated clay. An increase in the ionic strength of the background solution or cadmium concentration increases the zeta potential on soil particle surfaces, i.e., less negative. CAIW increases the zeta potential slightly but the effects are not pronounced. EDTA and phosphonates decrease the zeta potentials of soil particle surfaces, thus enhancing forward electroosmotic flow.

Keywords: Acid/base buffer capacity, cadmium, citric acid industrial wastewater, EDTA, electrokinetic remediation, natural clay, phosphonates, zeta potential

INTRODUCTION

Electrokinetic remediation of heavy metal-polluted soils is a promising in-situ hazardous waste site remediation technology because of its high removal efficiency of metallic contaminants from soils of low hydraulic conductivity when the environmental conditions are favorable (1–4). The soil remediation technology utilizes a direct-current (dc) electric field

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Address correspondence to Albert T. Yeung, Department of Civil Engineering, University of Hong Kong, Pokfulam Road, Hong Kong. Tel.: +852 28598018; Fax: +852 25595337. E-mail: yeungat@hku.hk

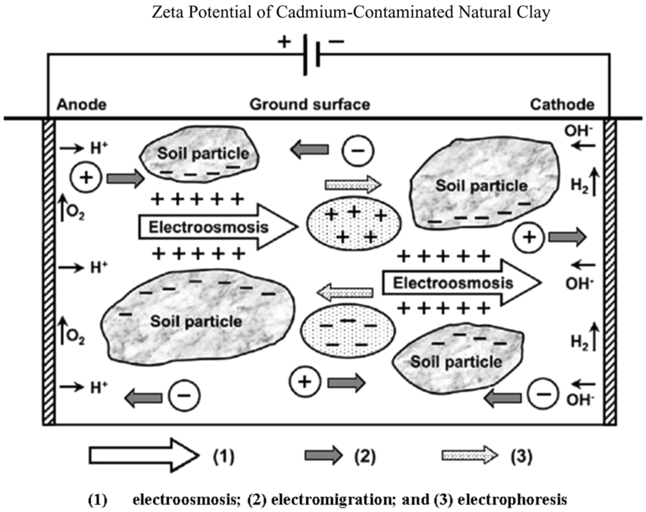

Figure 1. Concept of electrokinetic extraction of contaminants from soil (3).

to transport contaminants through the soil matrix towards either the anode or the cathode before extracting them from the subsurface for further treatment as shown in Fig. 1. The migration direction of contaminants depends on the polarity of the charges of the contaminant and the direction of electroosmotic pore fluid flow. During the electrokinetic remediation process, the electroosmotic flow of soil pore fluid is usually from the anode towards the cathode while ionic species and charged colloids move towards the electrodes of opposite charges by electromigration and electrophoresis, respectively (2–5). Therefore, electroosmosis, electromigration, and electrophoresis are the three major mechanisms responsible for contaminant removal from soil during the electrokinetic remediation process.

Although the electroosmotic flow rate is approximately an order of magnitude less than that of electromigration (3), the direction of electroosmotic flow still plays an important role during the electrokinetic remediation process as it can accelerate or retard the ionic migration of heavy metal species or electrophoresis of charged colloids and facilitate the injection of enhancement agents. The zeta potential at the soil particle-pore fluid interface is a dominating factor controlling the direction and magnitude of electroosmotic flow during the process. However, it is dependent on many environmental factors such as pH, ionic strength, contaminant concentration, presence of chelating agent, etc. Moreover, the success of electrokinetic remediation of polluted soils depends on many geochemical processes that occur simultaneously (4). Therefore, the study reported in this paper was performed to develop a better understanding of these factors and the geochemical processes involved, so as to improve the efficiency of electrokinetic remediation of cadmium-contaminated natural clay of high acid-base buffer capacity.

ZETA POTENTIAL OF CLAY PARTICLE SURFACES

The Helmholtz-Smoluchowski theory is the most widely accepted model describing the electroosmotic flow in soil (1–3). The electroosmotic fluid flow rate is related to the electrokinetic properties of soil, flow properties of pore fluid, and operational parameters by

$$V_{eo} = k_e \nabla(-E) = -\frac{\varepsilon \zeta n}{\eta} \nabla(-E) \tag{1}$$

where V_{eo} = average electroosmotic flow velocity (m/s); k_e = coefficient of electroosmotic conductivity of soil (m^2/V-s); $\nabla(-E)$ = dc electric field applied across the soil (V/m); ε = permittivity of pore fluid (F/m); ζ = zeta potential of the soil particle surface (V); n = porosity of soil; and η = viscosity of pore fluid (N-s/m^2). Detailed derivation of Eq. (1) is given by Yeung (1). All parameters in Eq. (1) are practically constant during the electrokinetic remediation process except the zeta potential.

The zeta potential is the electrical potential developed at the soil particle-pore fluid interface (6). However, the zeta potential of soil particle surfaces is determined experimentally by measurement of electrophoretic mobility of the soil particles. Therefore, assumptions made in the determination of zeta potential of soil particle surfaces include:

1. soil particles are solid spheres; and
2. electric charges are uniformly distributed on the soil particle surfaces.

It should be noted that these assumptions are not strictly applicable to clay particles in suspension. The zeta potential is determined from the electrophoretic mobility measured using the equation,

$$u_E = \frac{2\varepsilon\zeta}{3\eta} \times f(\kappa r) \tag{2}$$

where u_E = electrophoretic mobility of solid particles (m^2/V-s); $f(\kappa r)$ = a function depends on the shape of the particle; κ = reciprocal of the thickness of the diffuse double layer (1/m); and r = radius of particle (m) (1,7). Therefore, the absolute value of the zeta potential so determined also depends on the function f(κr) chosen. However, valuable semi-quantitative information can still be obtained on the soil-contaminant interactions by measuring the zeta potential of clay particles under specific environmental conditions.

The pH value that generates zero electrical charge on the soil particle surface is defined as the point of zero charge (PZC) (8). At this pH, there is no net charge contributed by the ions in the diffuse ion swarm, indicating the absence of freely-moving ions and the enhancement of inter-particle forces that produce flocculation of soil particles (9). When the soil pH is higher than the PZC, soil particle surfaces carry negative charges and the zeta potential is negative, resulting in a forward electroosmotic flow from the anode towards the cathode as illustrated by Eq. (1). Therefore, the migration of cationic contaminants, such as metal ions, is accelerated by the electroosmotic flow towards the cathode. On the other hand, when the soil pH is lower than the PZC, soil particle surfaces carry positive charges and the zeta potential is positive, resulting in a reverse electroosmotic flow from the cathode towards the anode, retarding the migration of metal ions towards the cathode (1). However, a reverse electroosmotic flow accelerates the migration of anionic contaminants towards the anode. Furthermore, surface charges of soil particles influence the sorption/desorption characteristics of heavy metals onto/from soil particle surfaces, thus affecting the removal efficiency by electrokinetic remediation of metal-contaminated soil. It can also be observed in Eq. (2) that the electrophoretic mobility of soil particles at the PZC is zero. Therefore, the zeta potential of soil particle surfaces vanishes at the PZC.

During the electrokinetic remediation process, the zeta potential of soil particle surfaces varies as a function of pH which can range from 2 at the anode to 12 at the cathode as a result of electrolytic decomposition of water at the electrodes (4). Moreover, the zeta potential of soil particle surfaces is also affected by pore fluid chemistry. The type and concentration of ions present in the pore fluid have profound influence on the surface charges of soils (10). Enhancement agents have been utilized in recent studies in electrokinetic remediation to desorb metals from soil particle surfaces and to solubilize them in the pore fluid so as to enhance the removal efficiency of metal species from soil (3,4,11,12). These agents do not only enhance the removal efficiency by forming chalets/complexes and increasing the solubility of metals, they also change the pore fluid chemistry and therefore have direct influence on the zeta potential of soil particle surfaces (10,13–18). A systematic study of these inter-related factors was conducted and results are reported in this paper.

MATERIALS

Soil

The clayey soil used in this study was collected at depths of 0.5–1.0 m in Nanhui District, Shanghai, China where soil contamination by metals, such as cadmium, is a serious environmental problem (19–21). The soil was stored in polyethylene bags for transfer to the laboratory where it was air-dried at room temperature, pulverized, sieved through a 2-mm sieve, homogenized, and saved for later use.

Physicochemical properties of the soil are tabulated in Table 1. In accordance with the Unified Soil Classification System, the soil is classified as CL. Soil pH was measured in soil mixtures of soil: deionized water ratio of 1:1 by weight. The soil is a slightly alkaline clay of low plasticity, and its properties are typical of soils in the alluvial plain of the Yangtze Delta. The background concentration of cadmium in the natural soil is negligible relative to the cadmium concentration to be spiked into the soil in this study.

Enhancement Agents

Enhancement agents used in the study include simulated citric acid industrial wastewater (CAIW), ethylenediaminetetraacetic acid (EDTA), and four phosphonates including ethylene diamine tetramethylene phosphonic acid (EDTMP), amino trimethylene phosphonic acid (ATMP), diethylenetriamine-penta-methylene phosphonic acid (DTPMP), and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP).

Table 1. Physicochemical properties of the soil used in this study

Property	Result
Specific gravity	2.73
Liquid limit (%)	36
Plastic limit (%)	19
Plasticity index (%)	17
pH (1:1)	8.29
Organic content (%)	0.18%
Electrical conductivity (dS/cm)	0.339
Cd concentration (mg/kg)	1.6

CAIW has yet to be studied in detail as a potential cost-effective enhancement agent for electrokinetic remediation of metal-contaminated soils. EDTA and phosphonates are metal chelates with strong ability to increase metal solubility in the pore fluid in a wide range of pH values. Their viability in the removal of metals from soils of high acid/base buffer capacity by electrokinetics has been established experimentally (11–12,17,22). However, available data on the effects of these chelating agents on the zeta potential of natural clay soils are very limited. Therefore, one of the objectives of this study is to investigate the influence of enhancement agents including simulated CAIW, EDTA, and phosphonates (EDTMP, ATMP, DTPMP, and HEDP) on the zeta potential of a natural clay soil experimentally. Details of the enhancement agents are given in the following sections.

Simulated Citric Acid Industrial Wastewater (CAIW)

Citric acid industrial wastewater (CAIW) is a waste liquid of low pH containing large quantities of citric acid, acetic acid, and other impurities (23). Being weak acids and metal chelates, citric acid and acetic acid have been demonstrated to be efficient in enhancing metal extraction from soils by many researchers (24–26). The wastewater may be used as a chelating agent in lieu of commercially available citric acid to enhance the electrokinetic remediation process for economic reasons. It may form anionic complexes with cadmium to enhance desorption of cadmium from soil particle surfaces and transportation of them to the anode. As CAIW is a recalcitrant wastewater, successful application of CAIW as an enhancing agent in the electrokinetic remediation process will put a waste product into productive use. The CAIW used in this study was synthesized in the laboratory according to the solution chemistry of typical CAIW. The chemical properties of the simulated CAIW are summarized in Table 2.

EDTA and Phosphonates

Five strong chelating agents including ethylenediaminetetraacetic acid (EDTA) and four phosphonates were used in this study. The four phosphonates were ethylene diamine tetramethylene phosphonic acid (EDTMP), amino trimethylene phosphonic acid (ATMP), diethylenetriamine-penta-methylene phosphonic acid (DTPMP), and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP). They are all strong chelating agents widely used in water treatment and cleaning applications (27).

Table 2. Chemical properties of simulated CAIW

Property	Value
pH	3.87
Citric acid (mg/L)	3000
Acetic acid (mg/L)	5500
SO_4^{2-} (mg/L)	2001.1
Ca^{2+} (mg/L)	504.5
Cl^- (mg/L)	984.4
NH_4^+ (mg/L)	45.1
Na^+ (mg/L)	958.9

These agents were obtained from Sigma-Aldrich Chemical Company of St. Louis, Missouri, U.S.A.

EDTA is a polyprotic acid containing four carboxylic acid groups and two amine groups each with a lone pair of electrons. It is a novel molecule for complexing metal ions. EDTMP is a structure analogue of EDTA but has a higher chelating capacity for metal ions. The complexation constant of EDTMP with Cu is the largest among all chelating agents. It is an innocuous high-pure grade reagent and has many industrial applications. It can be used as detergent in preparing semiconductor chips for manufacturing of integrated circuits, as carrying agent for radioelement in medical industry, and as agent for inspection and therapy. ATMP is commonly used in industrial circulating cool water system and oilfield water pipeline to decrease scale formation and to inhibit corrosion of metallic equipment and pipeline. It can also be used as a chelating agent in woven and dyeing industries and as a surface treatment agent for metals. ATMP is a structure analogue of another well known chelating agent nitrilotriacetic acid (NTA). DTPMP can be used as a scale and corrosion inhibitor in circulating cool water system and boiler water, and especially in alkali circulating cool water system without additional pH regulation. It can also be used in oilfield refill water, cool water, and boiler water with high concentration of barium carbonate. A structure analogue of DTPMP is diethylene triamine pentaacetic acid (DTPA). HEDP is an organophosphoric acid and a corrosion inhibitor. It can chelate with Fe, Cu, and Zn ions to form stable chelating compounds, and it can dissolve the oxidized materials on the surfaces of these metals. The solid state of HEDP is crystal powder, suitable for usage in freezing environments. Because of its high purity, it can be used as a cleaning agent in electronic fields and as additives in daily chemicals. The structures of these strong chelating agents and their corresponding structure analogues are presented in Fig. 2.

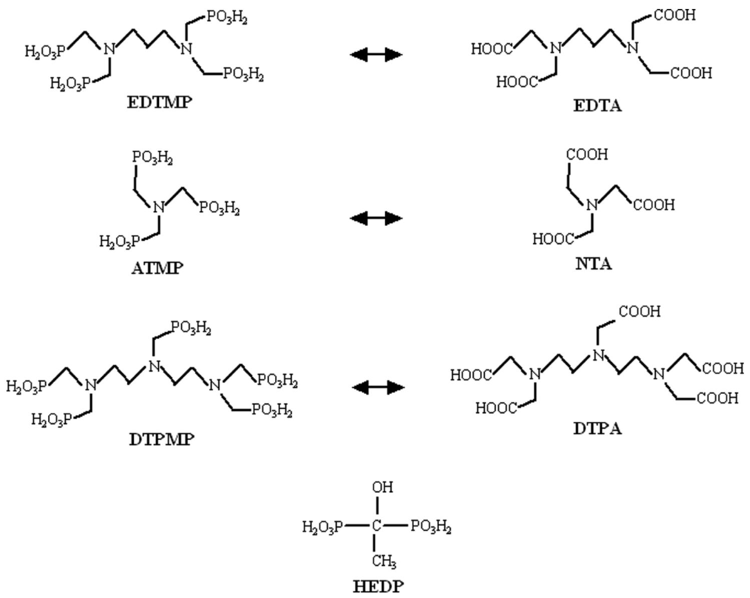

Figure 2. Structures of phosphonates in comparison with aminopolycarboxylates.

EXPERIMENTAL PROCEDURE

Four series of experiments were conducted to study the effects of pH on the zeta potential of soil particle surfaces using:

1. background solutions of different ionic strengths, i.e., KCl solutions of 0.001 M, 0.01 M, and 0.1 M;
2. different cadmium concentrations, i.e., 0.01 mM, 0.1 mM, and 1.0 mM;
3. different enhancement agents including 10 dilution and 100 dilution of simulated CAIW, 0.1 mM EDTA, and 0.1 mM phosphonates; and
4. combinations of different cadmium concentrations and types of enhancement agents.

The experimental operating parameters and objective of each series of the tests are tabulated in Table 3.

In all these tests, each sample was prepared using 0.1 g of soil (passing a 63 μm sieve) and a total of 1.0 L of solution. Background solution was added first and cadmium was then added to the soil suspension. The added cadmium was allowed to sorb on the soil particle surfaces

Table 3. Details of electrophoresis experiments

Test series	pH	Ionic strength (M KCl)	Cadmium conc. (mM)	Enhancement agent	Objective
I	2–11	0.001	–	–	To study the effects of ionic strength of background solutions on zeta potential at different pHs
		0.01	–	–	
		0.1	–	–	
II	2–11	0.01	0.01	–	To study the effects of cadmium concentration on zeta potential at different pHs
			0.1	–	
			1.0	–	
III	2–11	0.01	–	CAIW (100 X)	To study the effects of simulated CAIW on zeta potential at different pHs
			–	CAIW (10 X)	
			0.1	CAIW (100 X)	
IV	2–11	0.01	–	0.1 mM EDTA, 0.1 mM phosphonates	To study the effects of EDTA and phosphonates on zeta potential at different pHs
			0.1	0.1 mM EDTA, 0.1 mM phosphonates	

overnight to simulate a cadmium contamination. The enhancement solution was then added afterwards and the soil suspension was allowed to equilibrate. The pH of the suspension was measured using an Orion pH electrode. The soil suspension was adjusted to the required pH value by drop-wise addition of 0.1 M or 1 M HNO_3/NaOH solution. The soil suspension was stirred using a magnetic stirrer until the pH value was stabilized.

The zeta potential of each soil suspension sample was measured at 25°C using a Delsa 440x microelectrophoresis instrument equipped with a microprocessor. The electrophoretic mobility measured is automatically converted to a zeta potential value by a built-in microprocessor. The zeta potential of each soil suspension sample was measured twice using positive and negative polarities to ensure precision and repeatability of test results. The average of three measurements using each polarity was used to calculate the mean value of the zeta potential of the soil particle surface. Standard deviations of the calculated zeta potentials were also calculated by the instrument, which was typically less than 2 mV in this study.

RESULTS AND DISCUSSION

The inter-relating effects of pH, ionic strength of background solution, cadmium concentration, and enhancement agents on the zeta potential of the soil particle surfaces are elaborated in detail in the following sections.

Effects of pH and Ionic Strength

The variations of zeta potential of the soil particle surfaces in background solutions of different ionic strengths as a function of pH are presented in Fig. 3. In the pH range of 2 to 11, values of zeta potential of the soil are in the normal range of most clayey soils, i.e., −50 to 50 mV (1, 28) and are in good agreement with the results of many other experimental studies (16). However, there was no charge reversal within the pH range. Therefore, the point of zero charge (PZC) could not be determined. The negative charges in soil constituents are derived from isomorphous substitution within the structures of layered silicate minerals, broken

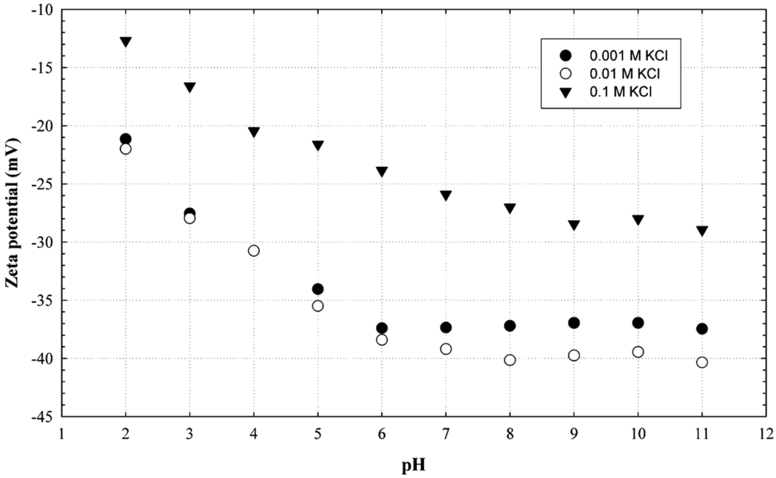

Figure 3. Effects of pH and ion strength on zeta potential of the soil particle surface.

bonds at mineral edges and external surfaces, dissociation of acidic functional groups in organic compounds, and permanent sorption of certain ions on soil particle surfaces (9).

In general, the variations of the zeta potential of the soil particle surfaces in background solutions of different concentrations of KCl follow a similar decreasing trend with increase in pH. As the pH of the soil suspension increases from 2 to 11, the zeta potential becomes more negative and decreases for 16–18 mV. The initial pH of the soil suspension is approximately 6.5. It can be observed in Fig. 3 that the addition of HNO_3 to the soil suspension reduces the net negative charges on the soil particle surfaces. The addition of acid leads to the replacement of cations sorbed on the soil particle surfaces by hydrogen ions H^+. The hydrogen ions on the soil particle surfaces can also slowly penetrate into the lattice of soil minerals (29), decomposing the clay minerals and releasing cations such as Al^{3+}. Speciation of aluminum in an acidic soil environment includes AlL (71%), AlF^{2+} (11%), Al^{3+} (11%), $Al(OH)^{2+}$ (5%), and $Al(OH)_2^+$ (2%), with the ligand "L" being the average organic ligand (9). The inner sphere complexation of these cations with clay surfaces reduces the net negative charges on the surfaces (30). Similarly, the addition of NaOH to the soil suspension slightly decreases the zeta potential of the soil particle surfaces. The addition of hydroxide ions OH^- onto the soil particle surfaces results in an increase in the thickness of the diffuse double layer (31). However, the effect on the zeta potential of the soil particle surface caused by the addition of NaOH is much less significant than that by the addition of HNO_3. In fact, the change in zeta potential with the addition of NaOH is minimal for soil suspensions with 0.001 M and 0.01 M KCl as background solutions. The phenomenon observed is not unexpected as the exchangeable cations on the soil particle surfaces include both Na^+ and Ca^{2+}. It has been reported by Chorom and Rengasamy (30) that the behavior of zeta potential of Na-clay is opposite to that of Ca-clay when the soil pH is higher than approximately 6.5–7. The zeta potential of Na-clay decreases (becomes more negative) with increase in pH from 2.5 to 9. However, the zeta potential of Ca-clay decreases with increase in pH in the range of 2.5–7 and then increases (becomes less negative) with the addition of OH^- to pH 9 due to the formation of $CaCO_3$ on the soil particle surfaces. In this study, the change in the zeta potential of the soil particle surfaces at pH higher than 6.5 is minimal, which may be due to the sum of the opposite effects of sorption of OH^- onto the soil particle surfaces and formation of $CaCO_3$.

The zeta potential of the soil particle surfaces increases (becomes less negative) with increase in the ionic strength of the background solution. The increase in ionic strength of the background solution reduces the thickness of the diffuse double layer (32), resulting in an increase in zeta potential following the principle of electrostatics (30,33).

Effects of Cadmium Concentration

It can be observed in Fig. 4 that cadmium ions have a strong influence on the zeta potential of the soil particle surfaces. When the pH of the soil suspension is low, the difference between the zeta potential of the soil particle surfaces with and without cadmium in the system is much smaller than that when the pH is high. The zeta potential of the soil particle surfaces increases (becomes less negative) with increase in cadmium concentration at all pHs. There is no charge reversal for cadmium concentrations of 0.01 mM and 0.1 mM. However, addition of cadmium of concentration of 1 mM produces a PZC at the pH of approximately 8.5, which is slightly below the pH of 8.67 at which precipitation of cadmium oxides occurs. Similar results for zeta potentials of montmorillonite with 0.1 mM and 10 mM $Pb(NO_3)_2$ solution were also reported by Kaya and Yukselen (31).

The PZC observed can be explained in terms of precipitation of hydrolysable cadmium ions on the soil particle surfaces. When the pH

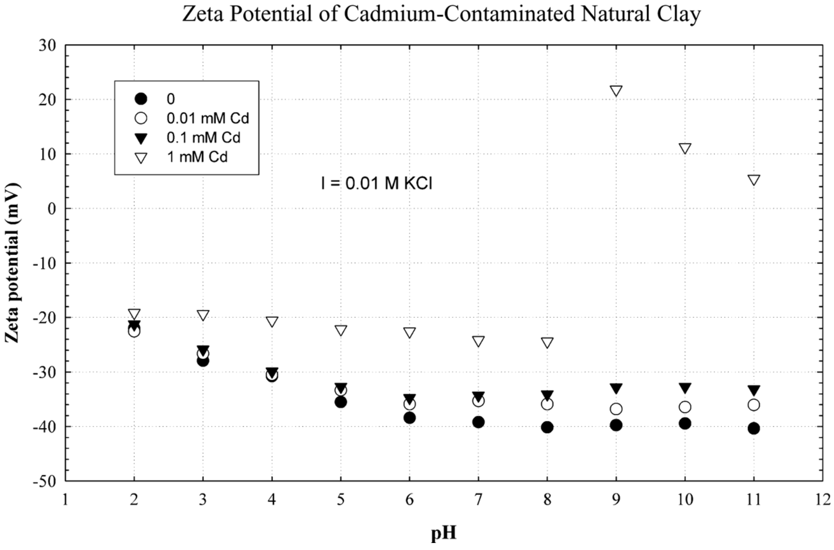

Figure 4. Effects of cadmium concentration on zeta potential of the soil particle surface.

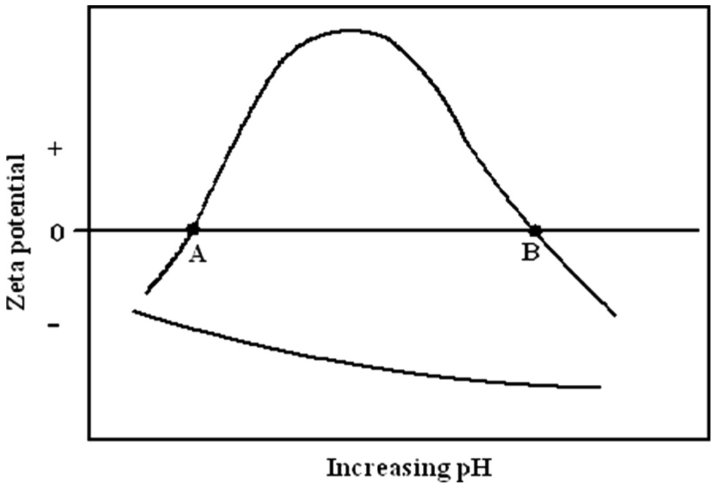

Figure 5. Schematic illustration of the behavior of zeta potential for soils in the presence and absence of hydrolysable metal ions [adapted from (34)].

was adjusted to above 8, white precipitation was observed in the soil suspension, and apparent changes in the color and size of soil particles were also observed. With the high concentration of cadmium in the suspension, i.e., 10 mmol/g soil, at high pH, the zeta potential measured are in fact the zeta potential of the precipitate rather than that of the soil particle surface. In a previous study on the zeta potential of clay minerals contaminated by heavy metals by Kaya and Yukselen (31), the hydrolysable metal ions, i.e., Cu^{2+}, Co^{2+}, Zn^{2+}, Al^{3+}, and Pb^{2+}, usually produce two PZCs as illustrated schematically in Fig. 5. In Fig. 5, Point A indicates occurrence of precipitation of metal hydroxide and Point B indicates complete coverage of soil particle surfaces by metal hydroxide. The line AB represents the increase in the concentration of hydrolysable metal ions. The lower curve represents a typical variation of zeta potential with pH in soils without hydrolysable metal ions. However, the second PZC could not be determined in this study. The phenomenon may be attributed to incomplete coverage of soil particle surfaces by cadmium as a hydrolysable cadmium oxide (31,34).

Effects of CAIW

The variations of the zeta potential of the soil particle surfaces with pH and simulated CAIW of different dilutions are presented in Fig. 6. The

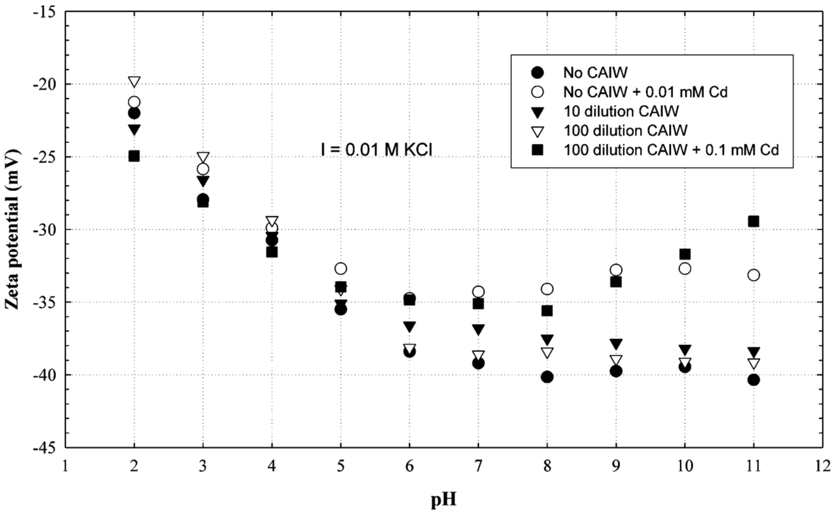

Figure 6. Effects of simulated CAIW on zeta potential of the soil particle surface.

change in the zeta potential of the soil particle surfaces caused by the addition of simulated CAIW is minimal. The system is very complicated as there are many components, organic and inorganic, in the simulated CAIW. Each component may have different effects on the zeta potential of the soil particle surfaces. For example, Ca^{2+} and Na^{+} can compress the thickness of the diffuse double layer, leading to an increase in zeta potential (31). On the other hand, sorption of citric acid on the soil particle surfaces can result in an increase in the thickness of the diffuse double layer and thus a higher zeta potential of the soil particle surfaces (31). However, it can be observed from Fig. 6 that the effects of cadmium on the zeta potential of the soil particle surfaces are much more pronounced than those of CAIW.

Effects of EDTA and Phosphonates

It is demonstrated by the data presented in Fig. 7 that a decrease in zeta potential of the soil particle surfaces was induced by the addition of EDTA and the phosphonates into the system. The results are in good agreement with those of previous results (14,16,18). Chelating agents, such as EDTA and HEDP, are capable of increasing the electroosmotic flow intensity during electrokinetic experiments by an order of magnitude (14). ATMP and EDTA were observed to decrease the zeta potential of

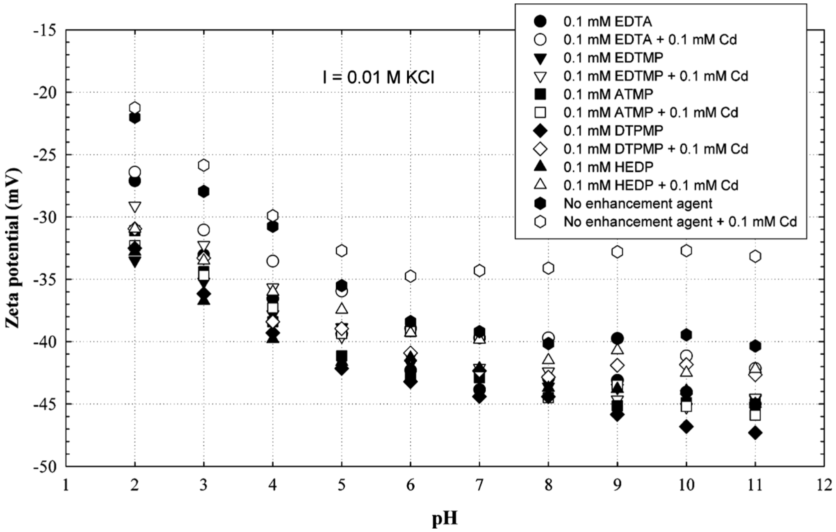

Figure 7. Effects of EDTA and phosphonates on zeta potential of the soil particle surface.

concrete by the formation of soluble complexes (18). The sorption of EDTA, phosphonates, and their metal complexes onto clay minerals has been studied by many researchers (27,35). Possible mechanisms may include:

1. sorption of the negative charged chelating agents on the clay particle surfaces;
2. dissolution of the amorphous hydroxide films from the surfaces of clay minerals, which can suppress the permanent negative charges of the clay particle surfaces; and
3. substitution of multivalent cations by univalent cations in the liquid phase including the outer Helmholtz plane of the diffuse double layer induced by complexion with chelating agents.

The molecules of EDTA, EDTMP, ATMP, DTPMP, and HEDP in solution can be considered as negatively charged species in a wide range of pH values. H-bonds can develop between clay particles and molecules of the chelating agent. Moreover, cations such as Ca^{2+} and Fe^{3+} can establish electrostatic bridges between the anionic end of the molecules of the chelating agent and the clay particle surfaces, forming surface-bond complexes (16,36). As EDTA complexes have low retarding effect and high mobility, Mechanism (1) may not be dominating. However, the low mobility of phosphonates in soils favors Mechanism (1).

The addition of these ligand species as strong metal chelates can lead to the formation of negatively charged surface-bonded complexes with the hydroxide moieties. It was found in a previous study to investigate the effects of chelating agents such as EDTA and HEDP on the zeta potential of clay particle surfaces that the equilibrium content of background cations including Fe^{3+}, Ca^{2+}, and Mn^{2+} increases with the concentration of chelating agent, indicating the dissolution of hydroxide films from the surface of clay minerals (16).

EDTA and phosphonates have a unique masking ability and they are widely used as detergents. They are able to mask the multivalent cations in the solution and convert them into negatively charged complexes. Multivalent cations in the liquid phase will thus be substituted by univalent cations. As univalent cations have weaker ability to compress the diffuse double layer, there will be a decrease in the zeta potential of the soil particle surfaces.

The presence of cadmium in the soil-chelating agent system increases the zeta potential slightly. However, the addition of these chelating agents to cadmium-contaminated soil can still decrease the zeta potential of the soil particle surfaces by 5–10 mV as shown in Fig. 7, resulting in a higher electroosmotic flow rate of the pore fluid from the anode towards the cathode. As the direction of the electroosmotic flow is opposite to that of the transportation of the negatively charged metal-complexes, the increase of the electroosmotic flow rate will retard the extraction of negatively charged metal-complexes by electrokinetic remediation.

CONCLUSIONS

The following conclusions can be drawn from this experimental study on the effects of pH, ionic strength, cadmium concentration, and chelating agents on the zeta potential of a natural clay of high acid/base buffer capacity from Shanghai, China:

1. The relationships between the zeta potential of clay particle surfaces and the aqueous chemistry of pore fluid are extremely complex and inter-dependent.
2. The soil particle surfaces are negatively charged in the pH range of 2 to 11. The PZC does not exist for the soil in its natural state. The zeta potential decreases (more negative) with increase in pH. Theoretically, the electroosmotic fluid flow in this soil is always forward, i.e., from

the anode to the cathode, as described by the Helmholtz-Smoluchowski model. However, the zeta potential at the cathode is more negative than that at the anode, resulting in a higher value of the coefficient of electroosmotic conductivity at the cathode on the basis of Eq. (1). On the other hand, positive charges occur when a high concentration of cadmium is present and the pH is higher than approximately 8.5, which may lead to reverse electroosmotic flow from the cathode towards the anode. Therefore, the coefficient of electroosmotic conductivity becomes non-uniform between electrodes during electrokinetic remediation, resulting in other complications of the process.

3. The zeta potential of the soil particle surfaces increases with the ionic strength of the background solution.
4. The zeta potential of the soil particle surfaces increases with the cadmium concentration in the soil suspension. The effects are more pronounced in an alkaline environment than in an acidic environment. When the cadmium concentration is high, a PZC is observed probably due to precipitation of hydrolysable cadmium ions on the soil particle surfaces.
5. Addition of simulated citric acid industrial wastewater (CAIW) increases the zeta potential of the soil particle surfaces slightly. However, the effects are not pronounced.
6. Addition of chelating agents including ethylenediaminetetraacetic acid (EDTA), ethylene diamine tetramethylene phosphonic acid (EDTMP), amino trimethylene phosphonic acid (ATMP), diethylenetriamine-penta-methylene phosphonic acid (DTPMP), and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) of concentration of 0.1 mM decreases the zeta potential of the soil particle surfaces. Three mechanisms are viable: (1) sorption of the negative charged chelating agents on the clay particle surfaces; (2) dissolution of the amorphous hydroxide films from the surfaces of clay minerals; and (3) substitution of multivalent cations by univalent cations in the liquid phase.
7. The interactions between soil particles, pore fluid, and contaminant are complicated and site-specific during the electrokinetic remediation process, it is necessary to conduct experiments to study the behavior of zeta potential of the specific soils under specific environmental conditions.

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