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MINTEQA2; soil remediation

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Abstract: The sorption/desorption characteristics of heavy metals onto/from soil particle surfaces are the primary factor controlling the success of the remediation of heavy-metal contaminated soils. These characteristics are pH-dependent, chemical-specific, and reversible; and can be modified by enhancement agents such as chelates and surfactants. In this study, batch experiments were conducted to evaluate the feasibility of using citric acid industrial wastewater (CAIW) to desorb cadmium from a natural clay from Shanghai, China at different soil mixture pHs. It can be observed from the results that the proportion of cadmium desorbed from the soil using synthesized CAIW is generally satisfactory, i.e., > 60%, when the soil mixture pH is lower than 6. However, the proportion of desorbed cadmium decreases significantly with increase in soil mixture pH. The dominant cadmium desorption mechanism using CAIW is the complexion of cadmium with citric acid and acetic acid in CAIW. It is concluded that CAIW can be a promising enhancement agent for the remediation of cadmium-contaminated natural soils when the environmental conditions are favorable. As a result, CAIW, a waste product itself, can be put into productive use in soil remediation.

Desorption of Cadmium from a Natural Shanghai Clay Using Citric Acid Industrial Wastewater

Ying-Ying Gu¹ and Albert T. Yeung^{2,*}

Novelty Statement

The paper presents the results of an investigation on the potential use of citric acid industrial wastewater (CAIW) as an enhancement agent in electrokinetic remediation of cadmium contaminated high acid/base buffer capacity natural soil. The desorption characteristics of cadmium of a natural clay from Shanghai for a range of soil mixture pH values were evaluated experimentally. The information is vital for the use of CAIW as an enhancement agent for electrokinetic remediation, as the soil pH changes throughout the remediation process. Moreover, it establishes the viability of a productive use of a waste material to remediate cadmium contaminated high buffer capacity natural soil. The paper should be published in the Journal of Hazardous Materials as many readers of the journal are interested in soil remediation technologies.

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Desorption of Cadmium from a Natural Shanghai Clay Using Citric Acid Industrial Wastewater

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Highlights

- CAIW is very effective in desorbing cadmium from soil particle surfaces at soil mixture pHs of lower than 5.
- The cadmium desorption efficiency of CAIW also depends on the initial sorbed concentration of cadmium on the soil particle surface.
- Complexion of cadmium with citric acid and acetic acid are the dominant mechanisms for cadmium desorption in the soil mixture pH range of 4 to 8.
- CAIW may be a promising enhancement agent for the remediation of heavy metalcontaminated soils.

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KEYWORDS: Electrokinetic remediation; sorption; desorption; citric acid industrial wastewater (CAIW); MINTEQA2; soil remediation

1. Introduction

Cadmium contamination of soil and groundwater is a worldwide environmental problem, posing threats on both public health and the environment. For example, vegetable cropland, paddy, and natural soils of many sites in Shanghai, China are contaminated by cadmium [1, 2]. The natural concentration of cadmium in soil is between 0.1-1.0 mg Cd/kg soil and a cadmium concentration of higher than 10 mg Cd/kg soil can be toxic for plants [3]. Cadmium is a significant metal contaminant in the environment due to its high water solubility and toxicity [4], and its ability to cause *itai-itai* disease [5, 6].

When cadmium is sorbed on soil particle surfaces or precipitated, it is immobile and thus difficult to be extracted by most soil remediation technologies [7, 8]. Therefore, an effective soil remediation technology must be able to transform and maintain cadmium in a mobile state to facilitate its removal from soil. Electrokinetic remediation of fine-grained soils has many advantages over many existing remediation technologies because an electrical gradient is a much more effective driving force in transporting fluid and chemical flows through fine-grained soils than a hydraulic gradient [7]. It applies a direct-current electric

 field across the contaminated soil through electrodes inserted into the contaminated soil. Contaminants are transported by electroosmosis, electromigration, and/or electrophoresis. Meanwhile, the fluids at the anode and cathode undergo electrolytic decomposition. An acidic environment is developed at the anode, favoring the solubilization of metal ions from soil particle surfaces. At the cathode, an alkaline environment is formed which enhances sorption of metals onto soil particle surfaces and precipitation of metallic oxides. Therefore, there is a need for an effective and economical technology to control the sorption/desorption characteristics of soil particle surfaces, so as to make the contaminant mobile to enhance the effectiveness of the remediation technology.

The sorption/desorption characteristics of soil particle surfaces are dynamic, pH-dependent, and reversible. In general, keeping a low pH environment in soil enhances the extractability of heavy metals. However, achieving an acidic environment may be difficult for natural soils of high acid buffer capacity [9, 10]. Nonetheless, the sorption/desorption characteristics of soil particle surfaces can be modified by the use of enhancement agents including chelates, surfactants, organic acids, etc. [6, 9, 11-13]. Among these enhancement agents, EDTA has been demonstrated to be one of the most effective in desorbing heavy metals from soils of high buffer capacity [6, 9, 11, 14]. The injection of EDTA into contaminated Milwhite kaolinite effectively desorbs lead and cadmium from soil particle surfaces and mobilizes them during electrokinetic extraction [6, 11, 13, 15]. However, the high cost and non-selective nature of EDTA have limited its use in the remediation of metal-contaminated sites [16, 17]. Moreover, EDTA resists biodegradation and can be sorbed on soil particle surfaces. As a result, soils remediated by EDTA or similar chelating agents may not be suitable for future agricultural use [18, 19].

In this study, citric acid industrial wastewater (CAIW) was studied as a potential cost-effective enhancement agent for electrokinetic remediation of metal-contaminated soils,

so as to put a waste product into effective and economical use. However, the pH of the contaminated soil may be changed by the electrokinetic remediation process as a function of time and space. Therefore, a comprehensive study of the performance of CAIW at different soil mixture pHs was conducted in this study.

CAIW is a recalcitrant dark-colored wastewater of low pH containing large quantities of citric acid, acetic acid, and other impurities. Although many techniques have been developed for the treatment of CAIW [20-22], effective and economical disposal of the large quantity of CAIW being produced routinely remains a challenge. As weak organic acids and heavy metal chelates, citric acid and acetic acid have been used successfully to promote efficient removal of heavy metals from soils [14, 18, 19, 23-25]. CAIW was also used as the chelating agent in the phytoremediation of heavy metal contaminated soils by Chen *et al.* [26]. Their results indicate that CAIW is effective in improving the availability of different forms of copper in the contaminated soil for the plant, although it is still less efficient than EDTA. However, the potential application of CAIW in electrokinetic remediation technology as an enhancement agent has yet to be studied. Therefore, the study presented in this paper was conducted.

CAIW may be a cost-effective chelating agent source in lieu of commercial citric acid and acetic acid so as to put a waste product to a productive use. As weak organic acids, they would not lower the soil pH to a level detrimental to the environment [27]. Moreover, a very low soil pH may reverse the electroosmotic flow direction, thus reducing the efficiency of electrokinetic remediation of metal-contaminated soils [6]. Therefore, CAIW may serve as an efficient and economical enhancement agent in electrokinetic remediation of cadmium-contaminated fine-grained soil.

In this study, batch experiments were conducted to extract cadmium from a natural clay soil from Shanghai, China. Effects of soil mixture pH, initial sorbed concentration of

cadmium on the soil particle surface, and CAIW concentration on cadmium desorption from clay particle surfaces were studied. Moreover, desorption tests using different individual constituents of CAIW were carried out to evaluate their individual contribution towards the desorption ability of CAIW.

2. MATERIALS AND METHODS

2.1 **Materials**

2.1.1 Soil

The soil used in this study is a natural clay soil collected at depths of 0.5-1.0 m in Nanhui District, Shanghai, China. The soil was air-dried, pulverized, screened through a 2-mm opening sieve, homogenized, autoclaved for 120 minutes, and then stored for later use. The soil was autoclaved to remove the microorganisms in the soil to eliminate possible biodegradation of any chemical in the system, so as to avoid misinterpretation of the results. The soil is classified as CL, i.e., inorganic clays of low to medium plasticity, in accordance with the Unified Soil Classification System [28]. In fact, it is a slightly alkaline clay soil of low plasticity. The background concentration of cadmium in the soil is negligible relative to the cadmium concentration to be spiked into the soil in this study. Physicochemical properties of the soil are tabulated in Table 1 and more details are given in Gu et al. [9].

2.1.2 Citric Acid Industrial Wastewater (CAIW)

Citric acid industrial wastewater (CAIW) is a dark-colored waste liquid of low pH containing large quantities of organic acids and other impurities [29]. It is the wastewater generated by the manufacturing process of citric acid. The CAIW used in this study was synthesized in the laboratory and its properties are tabulated in Table 1. The CAIW was synthesized so that its chemical composition is representative of most real-life CAIW.

HoweverMoreover, the well-defined chemical composition of the synthesized CAIW can facilitate interpretation of the experimental results and repeatability of the study.

2.2 **Experimental Procedures**

Different series of batch experiments were conducted to evaluate the desorption characteristics of CAIW by systematically varying the experimental parameters and procedures as described.

2.2.1 Desorption Edge using CAIW

Desorption edge experiments were conducted following the method described by Torrens et al. [30]. One gram of soil specimen and 10 mL of 0.5, 1, 2, 3, 4, or 5 mM Cd(NO₃)₂ solution were added to a 50-mL centrifuge. The soil mixtures were shaken for 24 hours using a wrist action shaker at 25°C to allow cadmium to sorb on soil particle surfaces before they were centrifuged at 4,000 rpm for 15 minutes. The centrifuge tubes containing the mixtures were then weighed before and after the supernatants were decanted to determine the volume of cadmium solution retained in the soil. Cadmium concentration in the supernatant was diluted with 1% HNO₃ and measured using a Perkin Elmer Analyst 300 flame atomic absorption spectrometer. The sorbed concentration of cadmium on the soil particle surface was thus determined.

Afterwards, 10 mL of synthesized CAIW was added to each soil mixture to serve as the purging solution. A control test was also conducted using 10 mL of deionized water in lieu of CAIW. The pHs of the soil mixture pHs were adjusted to different values by adding 0.1 and/or 1 M HNO₃ or 0.1 and/or 1 M NaOH. The adjusted pH of the soil mixture was measured by a pH meter. The soil mixtures were shaken for 5 hours and then centrifuged. The supernatant was diluted with 1% HNO₃ and analyzed for cadmium concentration using

atomic absorption spectrometry to determine the quantity of cadmium desorbed. Each test was performed in duplicate to ensure repeatability of the experiments.

2.2.2 Effect of CAIW Concentration on Cadmium Desorption

Two milliliters of 2.5 mM Cd(NO₃)₂ solution was added to each 1-g dry soil specimen and the soil mixture was shaken for 24 hours to allow cadmium to sorb onto soil particle surfaces. Practically all the cadmium in the solution is sorbed on soil particle surfaces. Therefore, the initial sorbed concentration of cadmium on soil particle surfaces was 560 mg Cd/kg of soil in this series of experiments. Afterwards, 0, 0.5, 1.0, 2.0, 5.0, or 8.0 mL of synthesized CAIW was added to each soil mixture and diluted to 10 mL with deionized water. The pH of the soil mixture pH was adjusted to 5.3 by adding 1 M HNO₃. The soil mixtures were shaken for 5 hours and then centrifuged before the supernatants were analyzed for cadmium concentration.

Effects of Individual CAIW Constituents on Cadmium Desorption

CAIW contains large quantities of organic acids and other ions such as Cl⁻, SO₄²⁻, Ca²⁺, and NH₄⁺. These constituents may affect desorption of cadmium from soil particle surfaces differently. In this series of desorption experiments, purging solutions of deionized water, synthesized CAIW, or individual constituents of CAIW, including 2.96 g/L of Na₂SO₄, 1.4 g/L of CaCl₂, 0.134 g/L of NH₄Cl, 3 g/L of citric acid, and 5.5 g/L of acetic acid, were prepared to evaluate their individual effects on desorption of cadmium from the natural clay.

Two milliliters of 2.5 mM Cd(NO₃)₂ solution of was added to 1 g of soil placed in a 50-mL centrifuge tube and shaken for 24 hours to allow cadmium to sorb on soil particle surfaces. Afterwards, 8 mL of the purging solution was added to each mixture. The pHs of the soil mixture pHs were adjusted by addition of 0.1 and/or 1 M HNO₃ or 0.1 and/or 1 M NaOH and the adjusted pH was measured by a pH meter. After 5 hours of shaking, the soil mixtures were centrifuged and the supernatants were diluted with 1% HNO₃ for determination of cadmium concentration.

3. RESULTS AND DISCUSSION

Desorption Edge 3.1

The effects of CAIW on desorption of cadmium from soil at different soil mixture pH values are compared to those of deionized water in Figure 1. Ten milliliters of 0.5 mM Cd(NO₃)₂ solution was added to each 1-g soil specimen in this particular series of experiments, and tThe resulting initial sorbed concentration of cadmium on soil particle surfaces in this series of experiments was measured to be 530 mg Cd/kg soil. It can be observed that deionized water can desorb approximately 40% of cadmium from soil particle surfaces at soil mixture pH 5. When the soil mixture pH is increased to 7, desorption of cadmium from soil becomes less than 2%. However, with the addition of CAIW, the proportion of desorbed cadmium is increased to more than 85% at soil mixture pH 5. In the soil mixture pH range of 5 to 8, CAIW increases the proportions of desorbed cadmium by 20% to 45% more than those by deionized water at the same soil mixture pHs. Furthermore, the upper bound of soil mixture pH limit for cadmium desorption is extended from 7 to 10. The results indicate the ability of CAIW to solubilize the cadmium sorbed on soil particle surfaces is considerably better than that of deionized water.

Desorption curves of cadmium using CAIW of different initial sorbed concentrations are depicted in Figure 2. The drastic influence of soil mixture pH on desorption of cadmium from soil particle surfaces at all initial sorbed concentrations of cadmium on the soil particle surface is evidently demonstrated. At soil mixture pHs lower than 5, the proportion of cadmium desorbed from soil by CAIW is very high, i.e., > 85%. However, the proportion

 decreases significantly with increase in soil mixture pH when the soil mixture pH is greater than 5. However, the decrease in proportion of cadmium desorbed per unit increase in soil mixture pH is practically independent of the initial sorbed concentration. When the soil mixture pH is further increased to a threshold value in the range of 9.5 to 11.5, the proportion of cadmium desorbed becomes negligible. The threshold soil mixture pH depends on the initial sorbed concentration. The higher is the initial sorbed concentration, the higher is the threshold soil mixture pH.

It can also be observed that the proportion of cadmium desorbed increases with the initial sorbed concentration of cadmium on the soil particle surface. The phenomenon is more prominent when the soil mixture pH is higher than 5. When the initial sorbed cadmium concentration is low, cadmium ions are primarily sorbed onto high selectivity sorption sites. However, cadmium ions are getting sorbed onto low selectivity cation exchange sites when the initial sorbed cadmium concentration is increased. As a result, the increase in cadmium density on soil particle surfaces favors the cation exchange process by NH₄⁺, Ca²⁺, etc. in CAIW, thus increasing the proportion of cadmium desorbed. In a high pH environment, the surface charges on soil particles become more negative as indicated by the zeta potential of the soil particle surface, leading to an enhancement of specific sorption of heavy metals [9, 31]. Moreover, precipitation of insoluble cadmium hydroxides and cadmium carbonates makes desorption more difficult.

3.2 **Effect of CAIW Concentration on Cadmium Desorption**

The effect of CAIW concentration on cadmium desorption at pH 5 is shown in Figure 3. The relative concentration of CAIW is defined to be the diluted concentration of CAIW used in the experiment normalized by relative to the original concentration of the synthesized CAIW. Deionized water alone can only desorb 24.7% of cadmium sorbed on the soil particle

 surface at soil <u>mixture pH 5</u>. The addition of CAIW increases the proportion of cadmium desorbed. The higher is the relative concentration of CAIW, the higher is the proportion of cadmium desorbed from the soil. However, the increase in the proportion of cadmium desorbed per unit increase in relative concentration of CAIW decreases with increase in relative concentration of CAIW. Nonetheless, CAIW of relative concentration of 0.8 can desorb more than 80% of the sorbed cadmium from the soil, indicating the original concentration of CAIW is adequate to function as an enhancement agent to desorb cadmium from soil satisfactorily at soil <u>mixture pH 5</u>. Therefore, CAIW can be used as it is produced without much processing.

3.3 Contributions of Individual Constituents of CAIW to Cadmium Desorption

The results of cadmium desorption using individual constituents of CAIW at different soil mixture pHs are depicted in Figure 4. It can be observed that citric acid is the most efficient purging solution followed by acetic acid, indicating desorption of cadmium from soil by CAIW can be mostly attributed to the presence of citric acid and acetic acid. Citric acid is a weak triprotic acid which can form mononuclear, binuclear, or polynuclear and bi-, tri-, and multidentate complexes with heavy metals, depending on the type of metallic ion [32]. Acetic acid is a low-weight organic acid which can form soluble monodentate complexes with heavy metals. The higher stability of citrate-cadmium complexes leads to the higher efficiency of citric acid in desorbing cadmium from soils than acetic acid, as observed in the tabulated stability constants of cadmium complexes in Table 2.

The enhancing effects of weak organic acids on desorption of heavy metal have been studied by many researchers [14, 17, 33-37]. However, most of these studies use these low molecular weight organic acids as a conditioning solution to lower the soil <u>mixture pH</u> but do not investigate in detail the effects of soil <u>mixture pH</u> on the desorption efficiency of heavy

 metals from soil.

Other ionic species in CAIW also enhance the extraction of cadmium from the soil. NH₄⁺, SO₄^{2□}, and Cl[□] have a slight ability to desorb cadmium from soil by forming complexes with cadmium, such as Cd(NH₃)₄²⁺, CdSO₄, CdCl⁺ and CdCl₂. Cations such as Ca²⁺ and Na⁺ can enhance the solubilization of cadmium at lower soil mixture pHs by competing for sorption sites on soil particle surfaces with cadmium ions [38].

Cadmium desorption by different constituents of CAIW is pH-dependent. Cadmium extractability from soil decreases when the soil mixture pH is increased from 5 to 9. The results are in good agreement with those of many previous studies. Naidu and Harter [39] reported that desorption of cadmium using organic ligands including acetate and citrate decreased with increase in soil mixturethe pH of the ligand solution. Yuan et al. [37] observed that desorption of cadmium by citric acid decreased sharply with increase in soil mixture pH. Mustafa et al. [37] demonstrated experimentally that an increase in equilibrium soil mixture pH from 5.5 to 6.0 can reduce cadmium desorption from goethite using Ca(NO₃)₂ significantly.

However, opposite results revealed by some other studies indicate that metal desorption by citric acid decreased at low soil mixture pHs [40, 41]. The difference can be easily explained by the different physicochemical properties of soils used for the experiments. The soils used by these researchers carry positive surface charges at low soil mixture pHs, causing the sorption of negatively charged complexes on soil particle surfaces. However, the natural soil used in this study has no point of zero charge (PZC) and always carries negative surface charges [9]. Negatively charged complexes are thus repelled by negatively charged soil particle surfaces into the solution phase.

When the soil mixture pH increases from 5 to 7, the proportion of cadmium desorbed from soil particle surfaces using citric acid is much higher than those using other constituents

 of CAIW, probably due to complexion of cadmium with citric acid. As the pK_a values of citric acid are 3.13, 4.76, and 6.40, the ratio of [Citrate]³⁻ increases significantly and dominates at <u>soil mixture</u> pHs of higher than 7.0, accounting for the high desorption rate of cadmium from soil particle surfaces. However, the logarithmic stability constant of $Cd[Citrate]^{-}$, i.e., 11.3, is less than the solubility of $Cd(OH)_2$ ($pK_{sp} = 13.6$), resulting in precipitation of cadmium with OH^{-} with increase in <u>soil mixture</u> pH [37].

The interactions of different chemical species in the cadmium-CAIW system without soil at different pHs were simulated by the software MINTEQA2 to better understand the desorption mechanisms of cadmium using CAIW. The total concentration of cadmium in the system for the simulation is 0.5 mM. The concentrations of different cadmium species in the solution system versus system pH are shown in Figure 5. At pHs 2 to 4.5, Cd²⁺, CdCl⁺, and CdSO₄ (aq) are the dominant species in the system. However, the zeta potential of the soil particle surface is less negative in this range of soil mixture pHs, resulting in the desorption of a high proportion of cadmium. When soil mixture pH is in the range of 4.5 to 8.5, most of the cadmium in the system complexes with citric acid to form Cd[Citrate]²⁺, or with acetic acid to form Cd[Acetate]⁺. Although cadmium is sorbed onto soil particle surfaces by stronger electrostatic forces in this range of soil mixture pHs, the formation of soluble cadmium chelates significantly enhances the desorption of cadmium from soil particle surfaces by CAIW at neutral soil mixture pHs. Cadmium precipitates become the dominant species when the pH is higher than approximately 9. It is very difficult to solubilize precipitated cadmium again.

4. CONCLUSIONS

Several conclusions can be drawn from this experimental study on desorption of cadmium from a natural Shanghai clay using synthesized CAIW:

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- a. CAIW is very effective in desorbing cadmium from soil particle surfaces at soil mixture pHs of lower than 5. However, the proportion of cadmium desorbed decreases significantly with increase in soil mixture pH. When the soil mixture pH is higher than a threshold value, the proportion of cadmium that can be desorbed becomes negligible. The threshold soil mixture pH increases with initial sorbed concentration of cadmium on the soil particle surface.
- b. The cadmium desorption efficiency of CAIW also depends on the initial sorbed concentration of cadmium on the soil particle surface. The proportion of cadmium desorbed increases with increase in initial sorbed concentration.
- c. Complexion of cadmium with citric acid and acetic acid are the dominant mechanisms for cadmium desorption in the <u>soil mixture</u> pH range of 4 to 8. At higher <u>soil mixture</u> pHs, precipitated cadmium is difficult to be desorbed.
- d. CAIW may be a promising enhancement agent for the remediation of heavy metal-contaminated soils. The use of CAIW as an enhancement agent can put the waste product to a productive use.

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Table 1. Properties of materials

Property	Value			
Soil				
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			
Synthesized CAIW				
рН	3.87			
Concentration of citric acid (mg/L)	3000			
Concentration of Acetic acid (mg/L)	5500			
Concentration of SO ₄ ²⁻ (mg/L)	2001.1			
Concentration of Ca ²⁺ (mg/L)	504.5			
Concentration of Cl ⁻ (mg/L)	984.4			
Concentration of NH ₄ ⁺ (mg/L)	45.1			
Concentration of Na ⁺ (mg/L)	958.9			

Table 2. Accumulative formation constants of cadmium complexes with citrate and acetate [42]

Cd Complexes	Accumulative Formation Constants	
CdH ₂ (Citrate) ⁺	7.9	
CdH(Citrate)	3.05	
Cd(Citrate) ⁻	3.10	
Cd(Acetate) ⁺	1.5	
Cd(Acetate) ₂	2.3	
Cd(Acetate) ₃	2.4	
where $(Citrate) = C_3H_5O(CO)$	O) ₃ ^{3–}	
$(Acetate) = CH_3COO^-$		

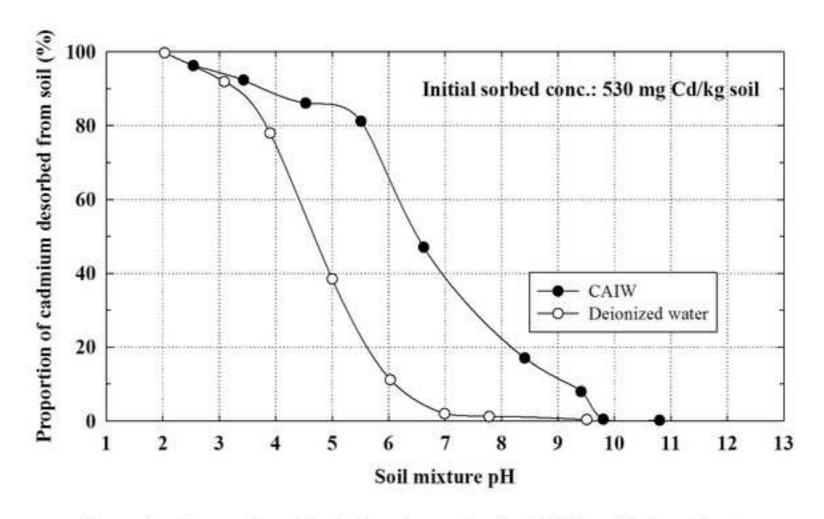


Figure 1. Comparison of cadmium desorption by CAIW and deionzed water

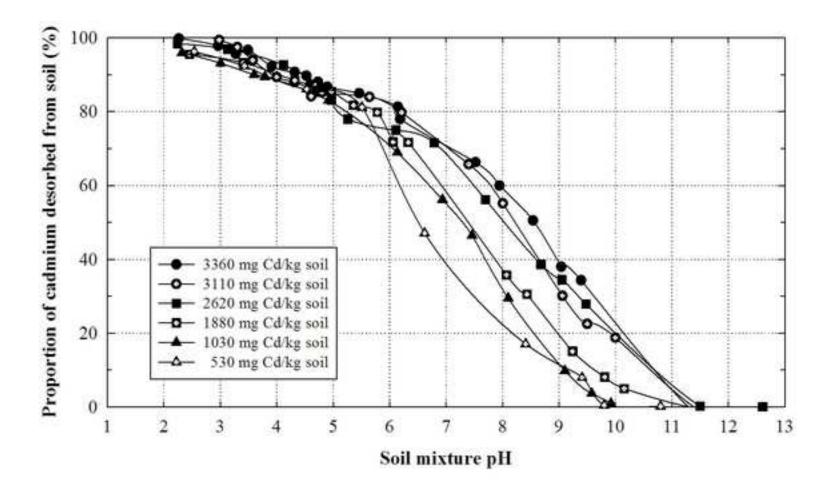


Figure 2. Desorption of cadmium of different initial sorbed concentrations by CAIW

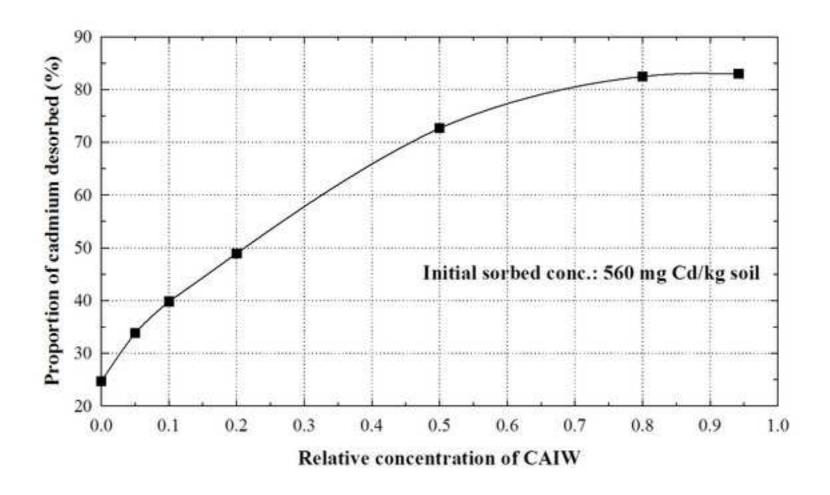


Figure 3. Effect of CAIW concentration on cadmium desorption

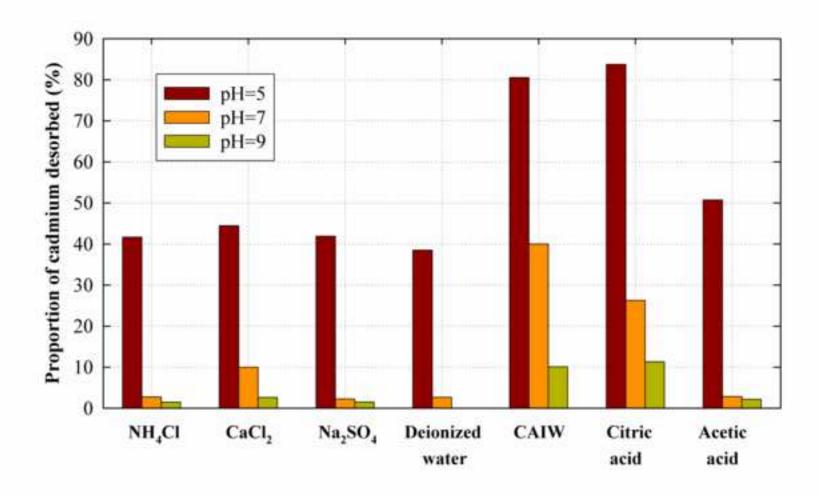


Figure 4. Effect of different constituents on cadmium desorption

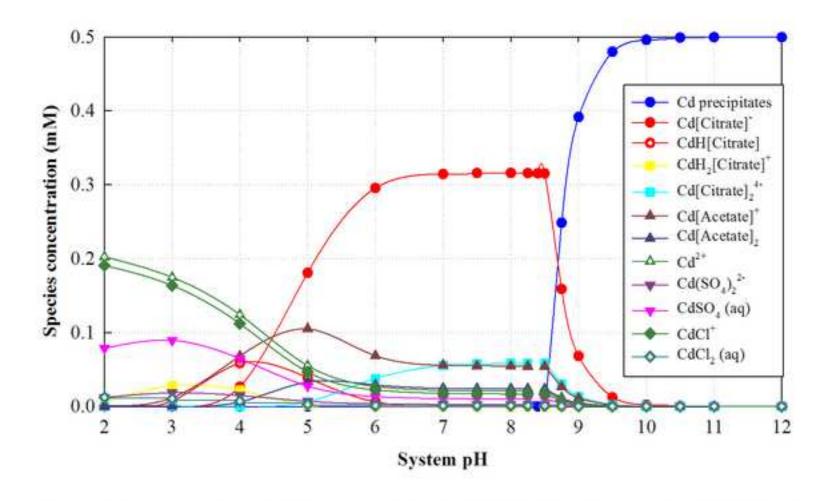


Figure 5. Concentrations of different species in CAIW-Cd (0.5 mM) system by MINTEQA2