Ethyl lactate enhances ethylenediaminedisuccinic acid solution removal of copper from contaminated soils

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ABSTRACT

A new approach using aqueous ethyl lactate-modified [S,S]-ethylenediaminedisuccinic acid (EDDS) washing solutions for the removal of Cu from field-contaminated soils was examined in the laboratory. At pH 7 the maximum extraction efficiencies of Cu were about 41% by EDDS solution (EDDS:Cu molar ratio = 8), and <2% by ethyl lactate solution. However, greater extraction efficiencies of up to 50% were achieved by amending the EDDS solution with ethyl lactate (EDDS:Cu molar ratio = 2, ethyl lactate:Cu molar ratio = 25). The pH of the extraction solution did not have a significant effect on the extraction of Cu. The washing agent could also be regenerated quite effectively for economy of use. Sequential extraction results showed that the two most bioavailable Cu fractions, i.e., the acid extractable and reducible fractions, were significantly reduced. The mechanism responsible for the enhanced extraction efficiency in the presence of ethyl lactate is the increased the stability constant of Cu–EDDS complexes in the presence of ethyl lactate, which enhanced desorption of Cu from soil.

1. Introduction

Heavy metal contamination of soils has become a serious problem worldwide, and developing efficient remediation technologies has drawn great attention from science and engineering communities. Soil washing is a commonly used remediation technology, which removes contaminants from soil matrices to liquid phase by desorption and solubilization [1,2]. The advantage of this method is the high potential extraction efficiency and the specificity for heavy metals [3]. Screening of environmentally friendly and efficient extraction solvents is an essential step in ensuring the success of soil washing treatments. Acid washing and chelator washing are currently the two most prevalent methods in soil washing [4,5]. However, acid washing might be lethal to soil micro flora and destroy physical structures and chemical properties of soils [6,7]. Ethylenediaminetetraacetic acid (EDTA) is a strong chelating agent which has been intensively studied. However, the low biodegradability and thus high persistence of EDTA in the environment could cause a rather high risk of metal leaching down to groundwater [8–12].

In the past several years, [S,S]-ethylenediaminedisuccinic acid (EDDS), a structural isomer of EDTA which has a similar chelating ability but is highly biodegradable, has been regarded as a potential replacement for EDTA [13,14]. EDDS has been widely accepted as an effective, safe and environmentally benign chelator for use in soil washing [15–18] and chelant-enhanced phytoextraction [19–21].

Recently, ethyl lactate has been recognized as a "green solvent" due to numerous attractive properties including its high solvency power, complete biodegradability, ease of recycling, non-corrosive, non-destructive to atmospheric ozone, and relatively inexpensive [22,23]. These properties make it to be an attractive co-solvent for potentially use in the removal of contaminants from soils.

The source of the metal and its form can also affect the extraction efficiency. It has been found that significantly larger extraction efficiencies are obtained when chelating agents are applied to artificially contaminated soils than to soils with field contamination [24]. Then, aged, field-contaminated soil, rather than artificially contaminated soil, must be used to evaluate the extraction efficiencies. The objective of this study was to investigate the effects of ethyl lactate on the extraction efficiency of Cu by EDDS solution from field-contaminated soils. A series of batch extraction experiments were performed to determine the efficiencies with which different EDDS/ethyl lactate mixtures removed Cu from soils. To keep treatment costs low, recycled and reused chelating agent for further extraction cycles was also studied.

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Table 1
Physical and chemical properties of soils used in this study.

	pH	Clay (g kg^{-1})	Silt (g kg^{-1})	Sand (g kg^{-1})	C_{org} (g kg^{-1})	Cu (mg kg^{-1})	Cr (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
Soil 1	7.8 ± 0.15	62.7 ± 6.11	654 ± 10.7	283 ± 12.8	23.3 ± 1.56	1094 ± 7.64	68.9 ± 8.49	58.7 ± 4.17	202 ± 13.7
Soil 2	6.9 ± 0.18	80.4 ± 9.48	715 ± 9.63	204 ± 11.6	35.7 ± 2.43	439 ± 9.37	46.3 ± 7.68	61.5 ± 9.31	144 ± 10.7

2. Materials and methods

2.1. Soils

Soils used in the experiments were collected from two locations at a copper-mine site in Tangshan, Nanjing, China. Soil 1 was collected from the center of the site, and soil 2 was 500 m away. Soils were taken from the top 20 cm layer, air-dried and then passed through a <2 mm sieve prior to use. The total Cu and other heavy metal concentrations were determined by inductively coupled plasma torch – atomic emission spectrometry after digesting the soils using 4:1 concentrated HNO$_3$ and HClO$_4$ (v/v) [25]. The pH of the soil was measured in a 0.01 M CaCl$_2$ solution at 1:2.5 ratio of soil: solution (w/v) using a pH meter. The soil texture and organic carbon content were measured by the procedures described by Avery and Bascomb [26]. Selected physicochemical properties of the collected samples are given in Table 1.

2.2. Batch extraction

A series of batch extractions were conducted to compare extraction efficiencies of EDDS for Cu from the soils in the presence and absence of ethyl lactate. For the extractions using EDDS, 0.8 g aliquots of contaminated soil were mixed with 40 mL of different concentrations of EDDS, resulting in EDDS:Cu molar ratios of 0, 1, 2, 4 and 8, respectively. For the extraction using ethyl lactate, 0.8 g soil samples were mixed with 40 mL of different concentrations of ethyl lactate, resulting in ethyl lactate:Cu molar ratios of 1, 2, 4, 8, 10 and 25. For the extractions using EDDS/ethyl lactate combinations, 0.8 g soil samples were extracted with 40 mL of EDDS solution (EDDS:Cu molar ratios = 1 and 2) containing different amounts of ethyl lactate (ethyl lactate:Cu molar ratios = 1, 2, 4, 8, 10 and 25). The pH values of the solutions were adjusted to ∼7 using 0.1 M NaOH or HNO$_3$.

The effect of pH on the extraction efficiency from soil 1 was also examined. The samples were treated as described previously. The molar ratio of ethyl lactate:Cu was set at 10, and the EDDS:Cu ratio was set at 2. The pH values of the solutions were adjusted to 3, 7 and 9 using 0.1 M NaOH and HNO$_3$.

According to the preliminary experiments, the mixtures were equilibrated on a shaker at 150 rpm for 24 h at 25 ± 1 °C, and then centrifuged at 4000 rpm for 30 min. The concentrations of copper in the extracts were measured using a flame atomic absorption spectrophotometer. All experiments were conducted in triplicate.

2.3. Extraction stability of recycled chelating agent

The extraction stability of recycled ethyl lactate and EDDS was evaluated by combining 0.8 g of soil 1 with 40 mL of solution at a 2:1 EDDS/Cu molar ratio containing an ethyl lactate:Cu molar ratio of 10. The pH of the mixture was adjusted to ∼7. The mixture was shaken for 24 h and then centrifuged. The concentrations of copper in the extracts were analyzed for the first time. Then the extraction solution was regenerated by vortex mixing with 0.4 g 001 × 7 resin of which the pH was adjusted to ∼2. Before the extraction solution was reused, the pH was adjusted back to ∼7. The recycled ethyl lactate and EDDS solution was taken and used for Cu removal from a fresh soil sample. The supernatant was then recovered and regenerated in the same way for a third time. All extractions were performed in triplicate.

2.4. Sequential extraction

Copper fractionation in soil was determined by a sequential extraction using the Commission of the European Communities Bureau of Reference method. This scheme consists of extractions using 0.1 M acetic acid (CH$_3$COOH, pH 2.85), 0.1 M hydroxyl ammonium chloride (NH$_2$OH·HCl, pH 2), hydrogen peroxide (H$_2$O$_2$) + 1 M ammonium acetate (NH$_4$Ac, pH 2), and aqua regia (3HCl/7HNO$_3$, v/v), which corresponding to the acid extractable, reducible, oxidizable, and residual fractions, respectively. The detailed method was reported by Quevauviller et al. [27]. Soil samples analyzed included the soils before and after EDDS treatment in the presence/absence of ethyl lactate (molar ratio of EDDS:Cu = 2, and ethyl lactate:Cu = 10, pH 7).

2.5. Mechanism of enhanced extraction of Cu by EDDS/ethyl lactate solution

To evaluate the possible formation of Cu–EDDS–ethyl lactate ternary complexes, the absorptions of Cu/EDDS and Cu/ethyl lactate aqueous mixtures over wavelengths ranging from 400 to 900 nm were measured by an ultraviolet-visible spectrophotometry. A series of Cu/EDDS/ethyl lactate mixed solutions with different molar ratios were also measured. The concentration of Cu (Cu(NO$_3$)$_2$) was kept at 1 mM, EDDS and ethyl lactate applied were in excess with eight and 50 times the Cu concentration [28,29].

Potentiometric titration was used to measure the conditional stability constant of Cu–EDDS. The temperature was controlled by a thermostatic bath at 25 ± 0.1 °C. Ethyl lactate was added at various concentrations to a cell containing 50 mL of 1.00 mM EDDS and 1.00 mM Cu. After thermal equilibrium was reached, the solution in the cell was titrated under magnetic stirring with 0.1 M KOH standard solution. During titration, disturbance by carbon dioxide was avoided by purging N$_2$ into the system until the end point was reached. The experiment was conducted using 3–5 replicates. The reproducibility of the titration was within 0.02 pH units. The BEST program was used to calculate and optimize the stability constant [30].

3. Results and discussion

3.1. Extraction with EDDS

The efficiency of Cu extraction from soils by EDDS is presented in Fig. 1. In the absence of EDDS, less than 4% of Cu was released into solution for both soils. The addition of EDDS resulted in a significant increase in the extraction of Cu, and approximately 37.9% and 35.0% of Cu was removed from soils 1 and 2 (EDDS:Cu molar ratio = 1), respectively. Considering that other competing cations (such as Zn, Pb, Cr etc) are also present, higher EDDS concentrations (EDDS:Cu molar ratio >1) were also tested. Above a molar EDDS:Cu ratio of 1 the extraction efficiency for Cu increased slightly with further increases in the EDDS:Cu molar ratio. The extraction of Cu by EDDS can be explained by the formation of Cu–EDDS complexes. It is expected that the extractability increases with the stability constant of metal–ligand complexes. EDDS and EDTA form Cu complexes of nearly equal strengths, with logarithms of the stability constants being >18 [31]. However, EDDS is preferred in soil washing applications because it is readily biodegradable in the
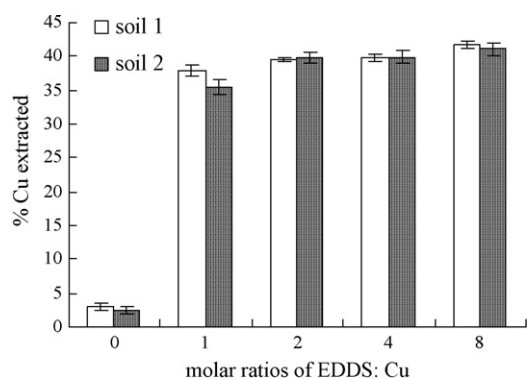
Fig. 1. Extraction efficiency of copper from soil 1 and soil 2 at different molar ratios of EDDS to Cu at pH 7.

Fig. 3. Effect of pH on extraction efficiencies of copper from soil 1 (molar ratio of EDDS:Cu = 2, of ethyl lactate:Cu = 10).

environment, while EDTA is not [3,14,21]. Tandy et al. [3] reported that up to 67% of the Cu in a contaminated soil was extracted by a washing solution with EDDS. The relatively low extraction efficiency in this study is probably due to the elevated content of Cu-bearing ore minerals in the mine soil. The sequential extraction results given below support this view.

3.2. Effect of ethyl lactate on extraction

Ethyl lactate on its own without EDDS did not increase Cu removal. Less than 2% of the Cu was extracted from the soil at an ethyl lactate:Cu molar ratio of 25 (data not shown). However, the addition of ethyl lactate into EDDS solution significantly increased the extraction efficiency of Cu from soils (Fig. 2). At an ethyl lactate:Cu molar ratio of 25, the extraction efficiencies increased to 48% and 50% for soil 1, with the EDDS:Cu molar ratios of 1 and 2, resp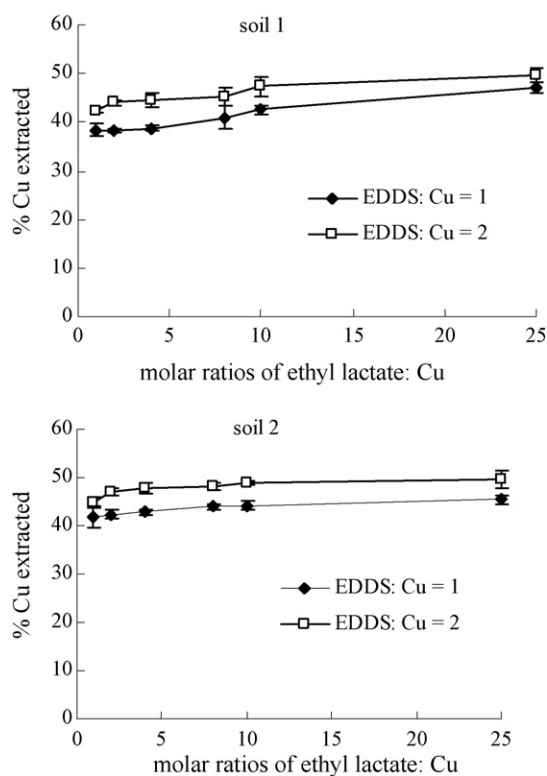ectively. A similar result was observed for soil 2. This suggests that it is feasible to enhance the extraction efficiency of Cu from contaminated soils by amending the EDDS solution with ethyl lactate. The mechanism for this will be discussed later.

3.3. Effect of pH on extraction

At pH 3, EDDS (molar ratios of EDDS:Cu = 2, ethyl lactate:Cu = 10) could extract about 50% of Cu from soil. Increased the pH to 7 and 9, did not significantly affect the extraction efficiency (Fig. 3). The pH of the extraction solution is a crucial factor to consider when comparing studies on chelate extraction. In general, the lower the pH is, the greater the extraction efficiency for toxic metals is. However, in this study the extraction efficiencies remained nearly the same for the soil at pH values of 3, 7 and 9, which is consistent with the statement by Tandy et al. [3]. The competition between Ca and the target pollutant metals in soils for the available chelating agents is of particular importance at a low chelant:metal ratio, and therefore influences the extraction efficiency of metals. Tandy et al. [3] found that the competition between heavy metals and Ca appeared to be an important factor in extraction with EDTA but not with EDDS when pH < 8. In addition, Tandy et al. [3] estimated that the stability constants for formation of Cu–EDDS complexes were relatively constant at pH values from 3 to 8. Therefore, it can be concluded that pH does not have a significant effect on the extraction of Cu by EDDS solution with ethyl lactate, based on the above reasons and the results in this study.

3.4. Sequential extraction

In order to understand the influence of Cu fractionation on the extraction efficiency, sequential extractions were conducted on the soil samples to determine the Cu associations with soil components both before and after the extraction (Fig. 4). The results showed that Cu is primarily associated with the reducible fraction ($\sim$50%) and the oxidizable fraction ($\sim$25%) for both untreated soils, and followed the order of reducible fraction > oxidizable fraction > acid extractable fraction > residual fraction. It is known that EDDS readily extracts metal from the acid extractable, and part of the reducible and the oxidizable fractions, and has little effect on the residual fraction [32]. This led to the relatively low extraction efficiency ($\sim$40%, molar ratio of EDDS:Cu = 2) in this study. Batch extraction using EDDS solution mainly removed Cu from the acid extractable and reducible fractions, these fractions corresponded to a removal of 10% and 30%, respectively, of the total Cu in soil 1. For soil 2, EDDS removed 11% and 24% of the total Cu in the soil from these two respective fractions. Ethyl lactate-modified EDDS solution (molar ratios of EDDS:Cu = 2, and ethyl lactate; Cu = 10) enhanced extraction efficiency by $\sim$10% for both soils compared with that extracted without ethyl lactate. Overall, ethyl lactate in EDDS solution helped extract more Cu mainly from the acid

Fig. 2. Extraction efficiencies of copper from soil 1 and soil 2 by EDDS solution (molar ratios of EDDS:Cu = 1 and 2) amended by different concentrations of ethyl lactate (molar ratios of ethyl lactate/Cu = 1, 2, 4, 8, 10 and 25) at pH 7.
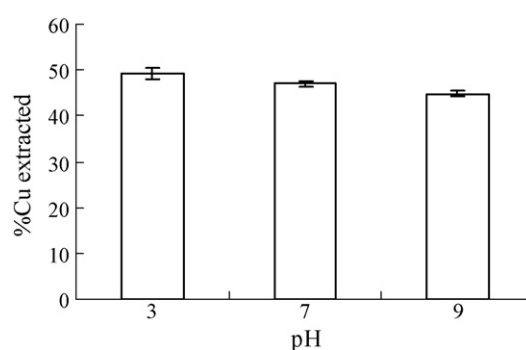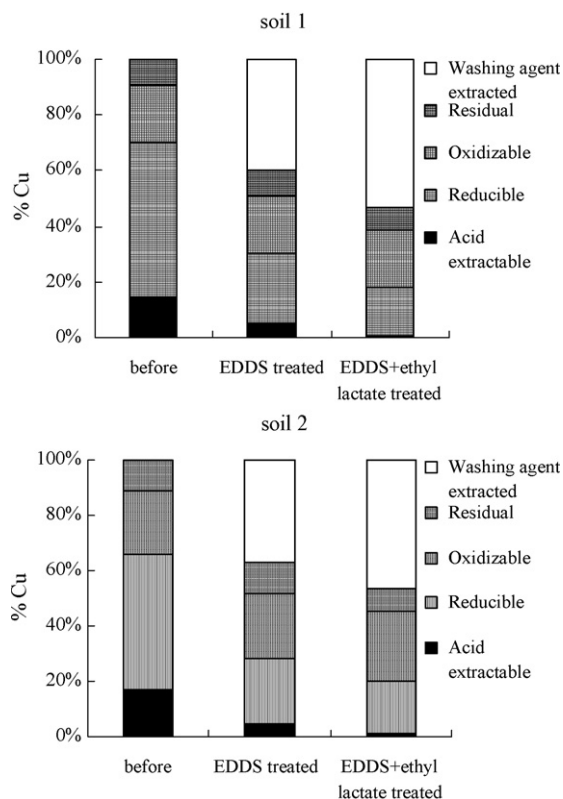
Fig. 4. Copper fractions in soils before and after washing with EDDS and ethyl lactate (molar ratio of EDDS:Cu = 2, of ethyl lactate:Cu = 10, pH 7).

extractable fraction (4.3% for soil 1, and 3.7% for soil 2), and the reducible fraction (5.8% for soil 1, and 4.7% for soil 2). Mulligan et al. [5] reported that the mobility and bioavailability of heavy metals in the acid extractable form and the reducible fraction are greater than those in the oxidizable and residue fractions. This indicates that although the extraction efficiency with ethyl lactate-modified EDDS solution was relatively low (∼50%), it can substantially reduce the bioavailability of soil-contaminating Cu to plants and humans, and thus also the toxicity risks to the environment and human health.

3.5. Recycling of washing agent

The chelating agent regeneration data confirmed the stability of the ethyl lactate-modified EDDS solution performance even after three regeneration stages (Fig. 5). During the first stage, the
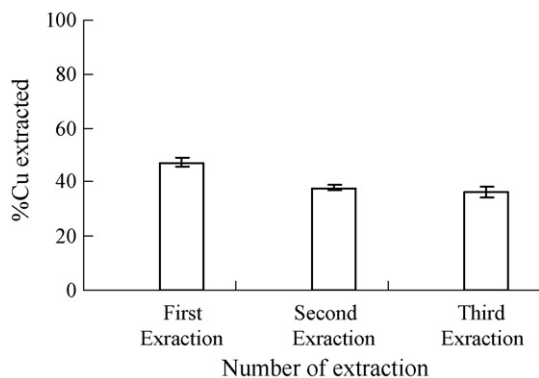

Fig. 5. Extraction efficiencies of copper with recycled washing agent (molar ratio of EDDS:Cu = 2, of ethyl lactate:Cu = 10, pH 7) from soil 1.
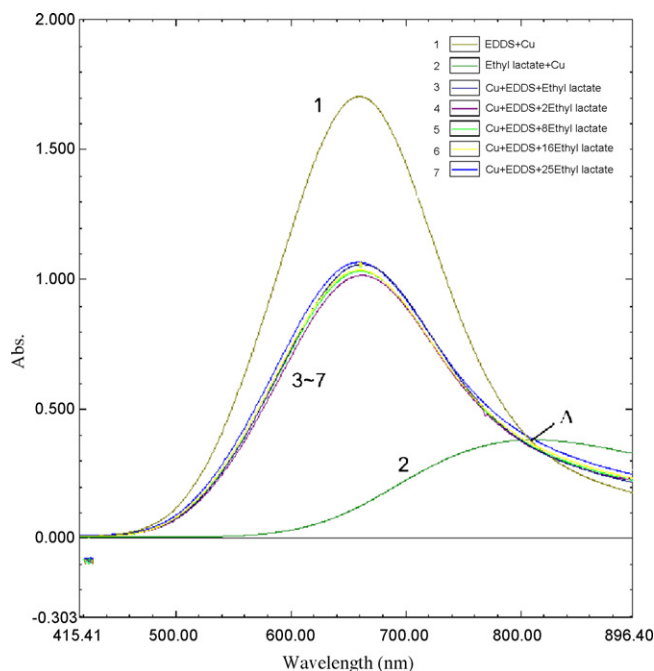

Fig. 6. Ultraviolet-visible absorbance spectra of Cu/EDDS/ethyl lactate mixtures (Curve 1, molar ratio of EDDS:Cu = 8. Curve 2, molar ratio of ethyl lactate:Cu = 50. Curves 3–7, molar ratio of EDDS:Cu = 2 with ethyl lactate:Cu = 1, 2, 8, 16 and 25. pH 7).

percentage removal of Cu from soil 1 was about 48%. When the regenerated solution was utilized during the second stage with a fresh soil sample, Cu removal decreased slightly to 38%. During the third stage, Cu removal was 37%. Clearly, Cu removal by regenerated ethyl lactate and EDDS solution remained stable after an initial decrease after the first extraction stage. As a result, ethyl lactate and EDDS solution may be regenerated quite effectively for economy of use.

3.6. Mechanism of enhanced extraction of Cu by EDDS/ethyl lactate solution

In this study, it is of interest to note that EDDS solution amended with ethyl lactate can apparently enhance the removal rate of Cu from contaminated soils. Several hypotheses were proposed: (1) formation of Cu–EDDS–ethyl lactate ternary complexes enhances the extraction of Cu from soils, (2) the presence of ethyl lactate increases the stability constant of Cu–EDDS complexes in solution, hence affecting degree of desorption of Cu from soil.

To evaluate the possible formation of Cu–EDDS–ethyl lactate ternary complexes, the absorption of Cu/EDDS and Cu/ethyl lactate aqueous mixtures over wavelengths from 400 to 900 nm were measured. The results are shown in Fig. 6. Curve 1 represents the absorbance spectrum of a Cu–EDDS binary system with a molar ratio of EDDS:Cu = 8. Curve 2 represents the absorbance spectrum with a molar ratio of ethyl lactate:Cu = 50. Curves 3 to 7 are the absorbance spectra of a series of Cu/EDDS/ethyl lactate mixtures. If a new chemical species/complex (i.e., Cu–EDDS–ethyl lactate ternary complexes) is produced in the solution, it is expected that there will be a new isoabsorptive point [28,29]. It is obvious that all curves intersect at point A, and no other obvious isoabsorptive points were produced, which suggests that no Cu/EDDS/ethyl lactate ternary complex was created.

Achievement of a large conditional stability constant with heavy metals is critical for screening ligands to clean up contaminated soils. In this study the logarithmic EDDS/Cu stability constant (log Ks) was found to be approximately 19 using potentiometric
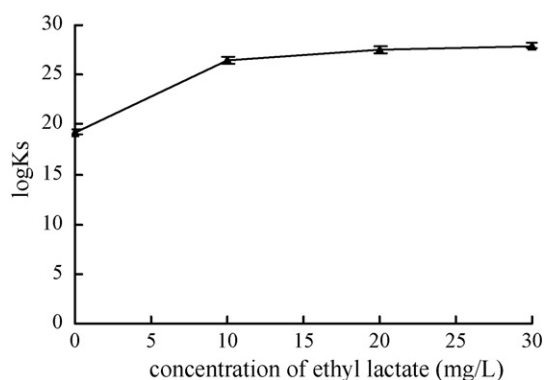
Fig. 7. Effect of ethyl lactate on the stability constant of Cu–EDDS.

titration. The presence of a low concentration of ethyl lactate (i.e., 10 mg/L) increased the logarithmic stability constant to 26, and that was kept constant with increasing ethyl lactate concentrations up to 30 mg/L (Fig. 7). Such a vast increase in stability constant provides an explanation for the increased Cu removal in the presence of ethyl lactate. Fan et al. [33] found that the presence of the co-solvent such as methanol (MeOH), ethanol (EtOH), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) or 1,4-dioxane (DOX) increased the stability constant of Cu-glycine in aqueous solution. As solvent molecules compete with ligands for binding with cations, solvents can influence the binding strength of a ligand. Water, a solvent of high polarity, can strongly compete with ligands for Cu. Therefore, it is reasonable to expect an increase in the stability constant upon addition of a co-solvent such as ethyl lactate, whose polarity is lower than that of water, to an aqueous Cu/ligand solution [33]. It can be assumed that ethyl lactate reduced the overall polarity of the aqueous solutions in our experiments, weakening the affinity of the water molecules to Cu and thus facilitating binding between EDDS and Cu.

4. Conclusions

To summarize, the potential for utilizing ethyl lactate-amended EDDS solution for washing of Cu-contaminated soil has been established. The amendment with ethyl lactate was found to enhance the removal efficiency of Cu from contaminated soils, and this washing solution may also be regenerated quite effectively for economy of use. Sequential extraction indicated that the EDDS/ethyl lactate solution extracted Cu primarily from the acid extractable and reducible fractions. The mechanism responsible for the enhanced extraction efficiency in the presence of ethyl lactate is the increased the stability constant of Cu–EDDS complexes in the presence of ethyl lactate, which enhanced desorption of Cu from soil.

Acknowledgments

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