

Choline Chloride-Urea Deep Eutectic Solvent Enhanced Removal of Lead from Mining Area Soil in the Presence of Oxalic Acid

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Abstract

Choline chloride-urea deep eutectic solvent (ChCl-urea DES) is a potential soil heavy metal eluent due to its advantages of low cost and simple synthesis, easy to biodegrade, and non-toxic. In this paper, the effect of ChCl-urea DES on the removal of lead from soil in the presence of oxalic acid was investigated. The experimental results indicate that ChCl-urea DES has a significantly enhanced effect on lead removal, the lead removal rate obviously increase from 49.8% to 71.1% as 3% of ChCl-urea DES was added to 0.2 mol/L oxalic acid under the condition of shaking time of 4 h and liquid/solid ratio of 10:1, the results suggest that ChCl-urea DES play a synergistic role with oxalic acid in the removal of lead from soil. Speciation analysis of lead was conducted using BCR sequential extraction method before and after washing. The result of speciation analysis indicates that oxalic acid-ChCl-urea DES was more effective in reducing the content of lead in each fraction than oxalic acid alone, particularly for acid-soluble fraction, followed by oxidation fraction and reducible fraction. The increased removal percentage is ranked in descending order: acid extracted fraction (36.2%) > reducible fraction (28.0%) > oxidizable fraction (22.6%) > residual fraction (18.0%). ChCl-urea DES can effectively remove most of mobile and bioavailable lead in contaminated soils in the presence of oxalic acid. The results are helpful to develop ChCl-urea DES based environment-friendly soil heavy metal washing system.

Keywords: choline chloride-urea deep eutectic solvent, oxalic acid, lead, soil, removal, BCR speciation

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INTRODUCTION

In recent decades, lead contamination in soil has attracted much concern due to its highly toxic and carcinogenic properties (Guo et al. 2016, Xiao et al. 2016), high concentrations of lead in soils can cause long-term risks to humans and ecosystems (Cui et al. 2016, Li and Chi 2017). Therefore, green, efficient and economic soil remediation technologies for lead contaminated soil are urgently needed (Boteva et al. 2016, Sima et al. 2015).

The remediation technologies for metal-contaminated soil include chemical, physical, or biological techniques (Lim et al. 2016). Of these techniques, soil washing is an effective way to remediate lead contaminated soil because it can permanently remove lead from soil (Wang et al. 2017). Moreover, soil

washing is also a relatively simple, simple operation and useful ex situ remediation technology (Mohanty and Mahindrakar 2011). The washing solution is a key factor in the successful application of soil washing technique. Several washing solutions (Wasay et al. 2001), including chelating agents (e.g. ethylenediaminetetraacetic acid (EDTA), inorganic acids, and organic acids) (Jho et al. 2015, Wei et al. 2016). They have been widely used in washing of metal-contaminated soil (Habibi et al. 2013, Zhang et al. 2017). Although there are many reports, these eluting agents have destructive physical and chemical properties. Therefore, the key solution of the lead-contaminated soil washing remediation technology is that effective, inexpensive and ecology friendly washing agents can be found (Naghypour et al. 2016).

Ionic liquids (ILs), which also go by the name of ambient-temperature molten salts or room-temperature ionic liquids (Carlesi et al. 2016). Ionic liquids have appeared as green solvents for various applications and have been used for extraction of trace elements in different matrices due to their low vapour pressure, high boiling points and solvent capacity heavy metal compounds (Matong et al. 2017, Thomas and Marvey 2016, Zu et al. 2012). At present, a new class of ionic liquids (DESs) have attracted more attention (Xiong and Anouti 2015), they possess many similar properties and characteristics with ILs, such as a high electrical conductivity, stable chemical properties, and a low vapor pressure, and they are liquid at room temperature (Durand et al. 2013). DESs have been applied as solvents in different chemistry fields due to the attractive properties of DESs (Thanu et al. 2012). DESs have been successfully and widely applied in the preparation and synthesis of fuel cells, catalysts, and materials, and the electrodeposition of metals (Chowdhury et al. 2007, Khandelwal et al. 2016, Souza et al. 2003, Zainalabidin et al. 2017, Zimmermann et al. 2013).

It was recently reported by Mukhopadhyay et al. (2016) that the synergistic behaviour between a polyol-based DESs and saponin on lead could be used to remove lead from a contaminated soil. His results indicated that extraction using the mixture of DESs and saponins performed better rather than individually using the materials. The removal efficiency of lead can reach 72 %. This result shows fairly good application prospects of DESs in heavy metal contaminated soils remediation. But, saponin used in Mukhopadhyay's system is much expensive as soil heavy metal eluent when compared with organic acid. Moreover, the environmental problems of quaternary ammonium compounds (QACs) have attracted a great attention due to that QACs can cause toxic effects on fish, algae, bacteria, daphnids, etc. at relatively low concentrations and persistent residue in environment (Nica et al. 2017, Zhang et al. 2015), some studies have provided worthy information on the toxicological peculiarity of some widely used quaternary ammonium compounds (QACs) on soil microbial and important activity parameters (Sarkar et al. 2010).

One of the most widespread DESs used in different fields is choline chloride-urea eutectic mixture (Abbott et al. 2002, Thanu et al. 2012). It is very low cost of raw materials and simple synthesis, easy to biodegrade, and non-toxic as a potential soil heavy metal eluent when compared with quaternary ammonium salt-choline

chloride based DES. The aim of this paper is to develop ChCl-urea DES based environment-friendly and low cost soil heavy metal washing system. Low concentration ChCl-urea DES combined with oxalic acid was used as a composite eluting agent to remove lead from contaminated mining area soil. The speciation of lead before and after washing was analyzed by BCR sequential extraction. The synergistic extraction effect of ChCl-urea DES on oxalic acid eluent was discussed.

EXPERIMENTAL

Materials

Soil samples were collected from the top 1-20 cm surface layer of soil around the mining area disposal site located in Yunnan Province, China. All the samples were preserved after air drying and passed through a 100 mesh screen and the visible plant materials and coarse debris were removed before further processing.

The total amount of lead in soil was using the AAS (Shimadzu AA-6300 atomic absorption spectrophotometer). The amount of lead in soil is 1.891×10^3 mg/kg. The amount of lead in soil is 1.891×10^3 mg/kg. The physicochemical characteristic analysis of the soil samples were as follows: pH 3.7; organic matter, 2.35 g/kg; and cation exchange capacity (CEC), 10.11 cmol/kg. The results showed that the content of sand in the soil samples was 21.48%, the content of grain was 77.52%, and the content of clay was only 1.00%.

Preparation of ChCl-urea DES

The ChCl-urea DES was prepared by stirring mixtures of urea:ChCl = 2:1 at 80°C until homogeneous colourless liquids were generated, and then, the liquid was stored in a vacuum dryer (Gao 2016).

Soil Washing

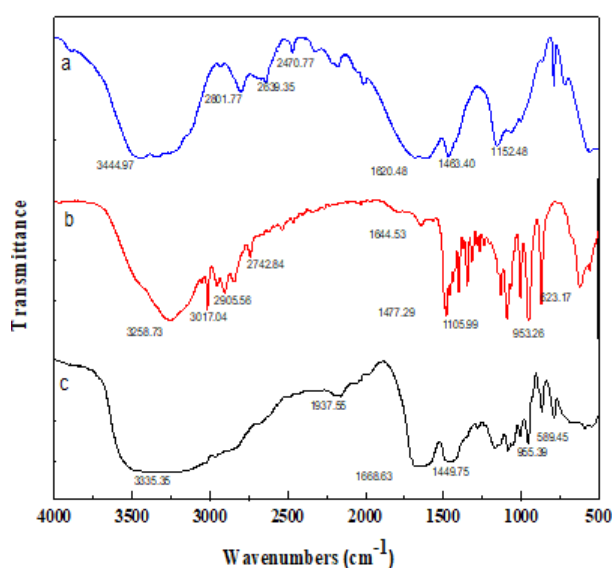
In the batch experiments, 0.500 g of sieved air-dried soil was added to 10 mL 0.2 mol/L of oxalic acid, and the mixture was shaken for 4 h on a horizontal shaker at a speed of 300 rpm at 25°C. Then, the suspension was centrifuged at a speed of 4,000 rpm for 20 min in order to separate the solid residue from the washing solution. The concentration of lead in the eluent was measured by flame atomic absorption spectroscopy method. All experiments were carried out in triplicate.

Speciation Analysis

In order to assess the efficacy of the compound elution system extractions, the redistribution patterns of

Table 1. The BCR sequential extraction procedure for lead fractionation

Step	Fraction	Condition	Reagent
1	Acid extractable fraction	shaken 16 h at room temperature and then centrifuged at 4000 rpm for 20 min	32 ml 0.11 mol/L CH_3COOH
2	Reducible fraction	shaken 16 h at room temperature and then centrifuged at 3000 rpm for 20 min	32 ml $\text{NH}_4\text{OH-HCl}$ (pH = 1.5)
3	Oxidisable fraction	digested for one hour then evaporated to dryness, shaken 16 h at room temperature and then centrifuged at 3000 rpm for 20 min	8 ml 8 mol/L H_2O_2 1 M NH_4OAc (pH = 2)
4	Residual fraction	digested on a hot plate	10 ml $\text{HF-HNO}_3\text{-HCl}$

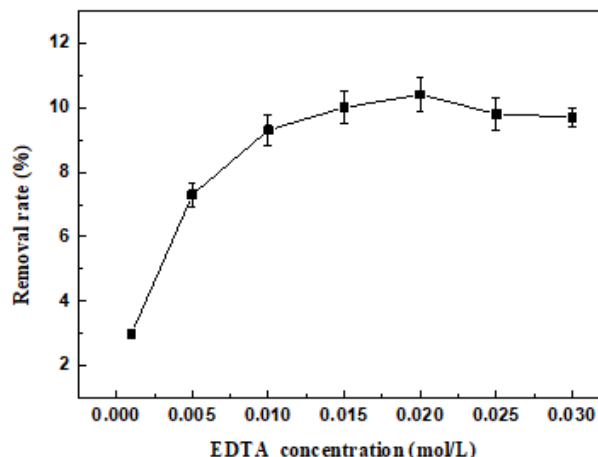
**Fig. 1.** The FTIR of urea (a), choline chloride (b) and synthesis of ChCl-urea DES (c)

lead was determined using the BCR sequential extraction procedure to achieve lead fractionation in soil. The BCR sequential extraction of lead in three soil samples, including original soil, the soil washed by oxalic acid and oxalic acid-ChCl-urea DES was carried out with BCR sequential extraction method in accordance with the following steps, and the details are shown in **Table 1**.

RESULTS AND DISCUSSION

Synthesis and Characterization of ChCl-urea DES

Fig. 1 shows the infrared spectroscopy of urea, choline chloride and ChCl-urea DES respectively. It can be observed that the absorption band of ChCl-urea DES at 3335.35 cm^{-1} (Curve c) was wider than that of choline chloride at 3258.73 cm^{-1} (Curve b) and urea at

**Fig. 2.** Effect of EDTA concentration on the removal rate of lead

3444.97 cm^{-1} (Curve a). This might have resulted from the formation more hydrogen bonds between urea and choline chloride, which existed in the form of N-H...N-H, N-H...O-H, H-O...O-H and O-H...N-H [34]. The $\delta_{\text{as}}(\text{NH}_2)$ at 1620.48 cm^{-1} and 1463.40 cm^{-1} shift to 1668.63 cm^{-1} and 1449.75 cm^{-1} after the formation of strong hydrogen bonds (Curve (a) and Curve (b)). While, the interaction of $\rho(\text{CH}_3)$ and ChCl lead to the band was observed at 1449.75 cm^{-1} (Curve c). Meanwhile, in Curve c, the $\delta(\text{CH})$ at 589.45 cm^{-1} and $\nu(\text{CCO})$ at 955.39 cm^{-1} shows that the structure of Ch^+ is not destroyed in the ChCl-urea DES system. The above absorption characteristic peaks of the ChCl-urea DES are consistent with reported in the literature.

Screening of Eluents

The removal rate of lead from mining soils with EDTA at different concentration is shown in **Fig. 2**. The removal rate of lead increases from 3.0% to 10.4% with increasing concentration of EDTA from 0.001 to 0.02 mol/L, then reach its maximum at 0.02 mol/L of EDTA. While, the removal rate decreases as concentration above 0.02 mol/L.

The tested soil was leached by two kind of organic acids in different concentrations. And the results are shown in **Fig. 3**. The removal rate of lead increase obviously vary from 1.1%-55.8% with increasing oxalic acid concentration from 0.001 to 0.2 mol/L. While, it tends to a stable value as the increase of oxalic acid concentration above 0.2 mol/L. As can be seen, 0.2 mol/L oxalic acid concentration was selected for further studies. Moreover, it can be seen from **Fig. 3** that the removal capacity of citric acid is much lower than that of oxalic acid, the maximum removal rate only reaches 3.5% as the concentration of citric acid vary from 0.001 to 0.4 mol/L.

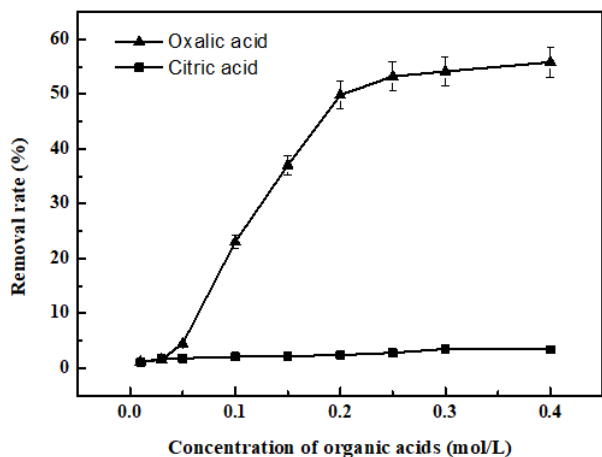


Fig. 3. Effect of oxalic acid and citric acid at different concentration on the removal rates

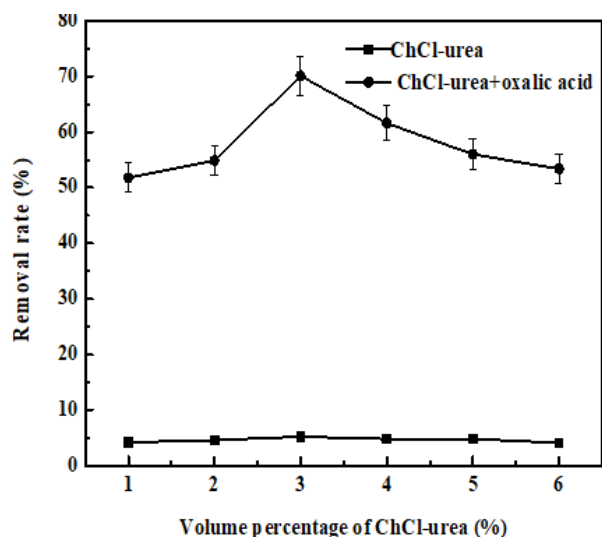


Fig. 4. The removal rates of lead with ChCl-urea DES at different volume percentage from 1 to 6 (%)

Based on the above analysis results, it can be found that the ability to remove lead from the tested soil could be ranked in descending order: oxalic acid (55.8%) > EDTA (10.4%) > citric acid (3.5%), oxalic acid has the highest removal capacity on lead removal. Therefore, 0.2 mol/L of oxalic acid was used as eluent in subsequent experiments.

Effect of ChCl-urea DES on the Removal of Lead

In order to evaluate the effect of ChCl-urea mixture-based DES on the removal of lead, the effect of choline chloride-urea deep eutectic solvent (ChCl-urea DES) on the removal of lead from soil in the presence of oxalic acid was investigated. The result is **Fig. 4**, the removal capacity of oxalic acid for lead is obviously enhanced by ChCl-urea DES. The removal rate reached its maximum of 70.1% and increased by 12.5% than that of oxalic acid alone as 3% (v/v). While, ChCl-

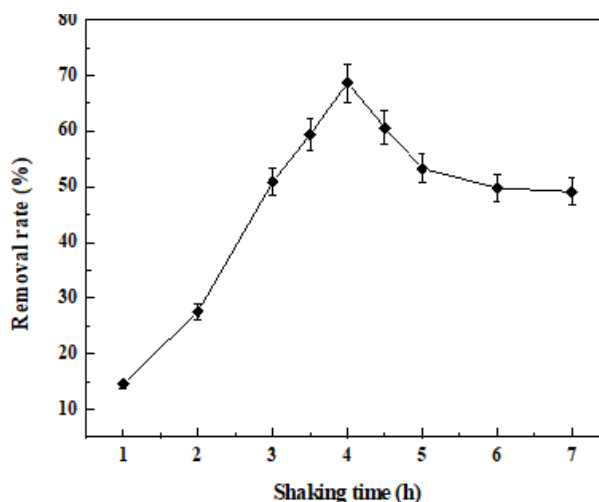


Fig. 5. Effects of shaking time on the removal rates of lead

urea DES itself appear to have little effect on lead removal in the absence of oxalic acid with a maximum removal rate of 5.2%, which implies that ChCl-urea DES play a synergistic role with oxalic acid in the extraction of lead from the tested soil.

The result above suggests that low concentration of ChCl-urea DES can obviously enhance the removal of soil lead in the presence of oxalic acid via a synergistic effect, so, the oxalic acid-ChCl-urea DES system has been developed for the removal of lead from soil based on this result. As comparison with quaternary ammonium salt choline chloride based system [28], ChCl-urea-based system is non-toxic and easily biodegradable. Moreover, ChCl-urea-based system can be effective at much lower concentration (3%) than that of quaternary ammonium salt choline chloride based system (40% for 1% saponin or 10% for 2% saponin), ChCl-urea-based system is also inexpensive, and easy to prepare and use.

Effect of Shaking Time

Fig. 5 displays the influence of shaking time (from 1 to 7 h) on the removal rate of lead under the condition of 0.2 mol/L oxalic acid, 3% ChCl-urea DES and liquid/solid ratio of 10:1. As the shaking time increases vary from 1 to 4 h, the removal rate of lead from the tested soil also increases from 14.6% to 68.7%, and reaches its maximum, Then the removal rate decrease when the shaking time up to 4 h. Thus, 4h of shaking time was determined as the optimum shaking time.

Effect of Liquid/Solid Ratio

Liquid/solid ratio between eluent and soil is another important factor to affect efficiency of soil washing (Zu et al. 2012). So, the effect of the liquid/solid ratio on the

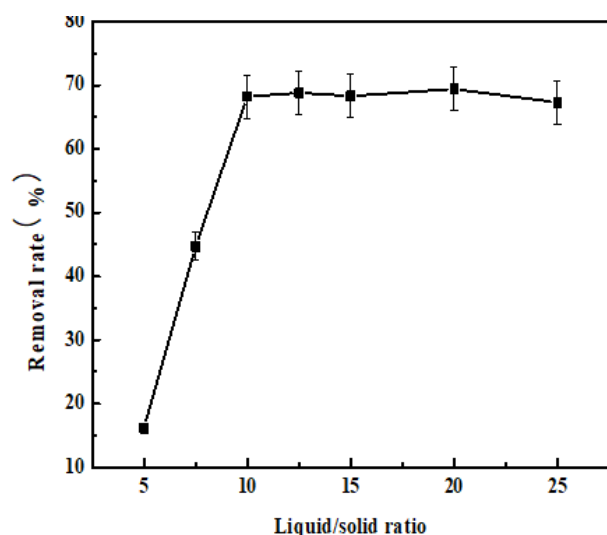


Fig. 6. The removal rate of lead in soil with different liquid/solid ratios

removal rate of lead was investigated, as shown in **Fig. 6**. Increasing liquid/solid ratio has a positive effect on the removal of lead. The removal rate quickly increase from 16.1% to 68.2% with liquid/solid ratio vary from 5:1 to 10:1, and then the removal rate scarcely increase when the liquid/solid ratio above 10:1. So, 10:1 of liquid/solid ratio is chosen as the optimum conditions.

Speciation Analysis before and after Washing

In order to better understand the enhanced effect of ChCl-urea DES on the removal of lead from soil in the presence of oxalic acid, speciation analysis of lead was conducted before and after washing using BCR sequential extraction method.

Fig. 7 displays the variation of lead fractions in the tested soil before and after washing with oxalic acid and oxalic acid-ChCl-urea DES. The content of acid-soluble fraction, reducible fraction, oxidation fraction and residual fraction in the tested soil before washing is 616.5, 223.1, 520.2 and 535.3 mg/kg, respectively, ranked in descending order: acid-soluble fraction > residual fraction > oxidation fraction > reducible fraction. As shown in **Fig. 7**, lead content in acid-soluble fraction, reducible fraction and oxidation fraction was reduced significantly after washing with oxalic acid and oxalic acid-ChCl-urea DES, while the reduction of residual fraction was not remarkably. The result of speciation analysis also indicated that oxalic acid-ChCl-urea DES was more effective in reducing the content of lead in each fraction than oxalic acid alone, particularly for acid-soluble fraction, followed by oxidation fraction and reducible fraction. Moreover, on the basis of data from **Fig. 7**, the removal capacity of

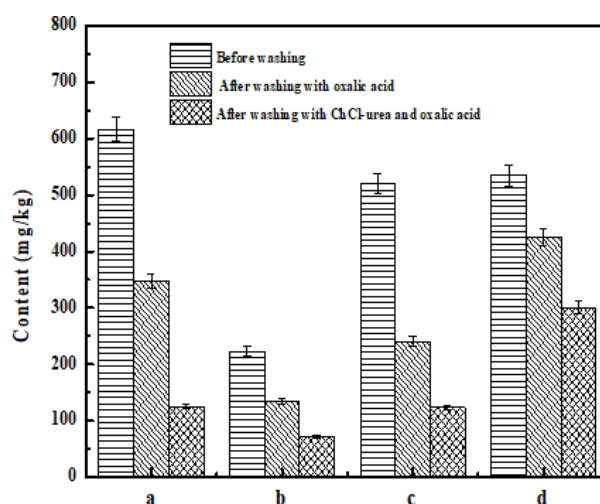


Fig. 7. Speciation distribution of lead in soils before and after washing. **a** Acid-soluble fraction. **b** Reducible fraction. **c** Oxidizable fraction. **d** Residual fraction

lead in each fraction can be expressed as a removal percentage. As shown in **Fig. 8**, the washing treatment with oxalic acid-ChCl-urea DES can significantly increase the removal of lead in each fraction as compared with that with oxalic acid alone, the percentage of lead removal was increased from 43.6% to 79.8% for acid extracted fraction, 39.8% to 67.8% for reducible fraction, 53.8% to 76.4% for oxidizable fraction and 25.8% to 43.8% for residual fraction, respectively, and the increased percentage is ranked in descending order acid extracted fraction (36.2%) > reducible fraction (28.0%) > oxidizable fraction (22.6%) > residual fraction (18.0%).

BCR sequential extractions provide information on potential mobility and bioavailability of trace element in contaminated soils (Pueyo et al. 2003), the non-residual fraction, including acid extracted fraction, reducible fraction and oxidizable fraction, can be considered to be potential mobility and bioavailability (Sungur et al. 2014). It can be seen from **Fig. 7** that the total non-residual fraction of lead was reduced from 1359.8 to 728.7 mg/kg for a total removal rate of 46.4% after washing with oxalic acid alone, while, the total non-residual fraction of lead reduced from 1359.8 to 303.5 mg/kg with a total removal rate of 77.5% as washing by oxalic acid-ChCl-urea DES. These results indicate that low concentration of ChCl-urea DES can effectively remove most of mobile and bioavailable lead in contaminated soils in the presence of oxalic acid, which is helpful to develop ChCl-urea DES based environment-friendly soil heavy metal washing system.

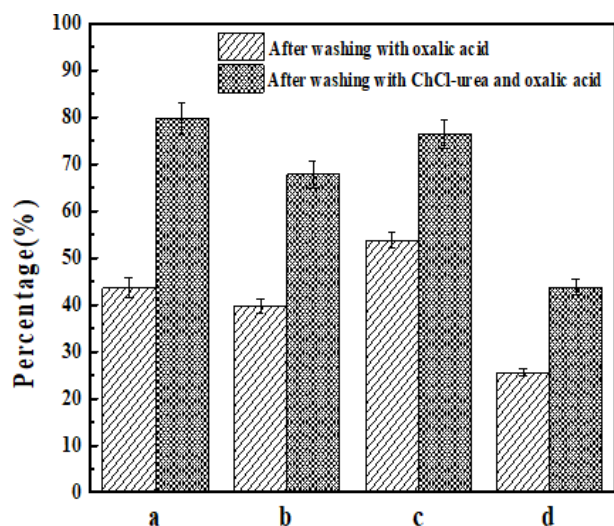


Fig. 8. The percentage of lead removal in soils before and after washing. **a** Acid-soluble fraction. **b** Reducible fraction. **c** Oxidizable fraction. **d** Residual fraction

CONCLUSION

The experimental results indicate that low concentration of ChCl-urea DES can obviously enhance the removal of soil lead in the presence of oxalic acid via a synergistic effect. The BCR sequential extraction indicates that oxalic acid-ChCl-urea EDS is more effective in reducing the content of lead in each fraction than oxalic acid alone, and can remarkably remove most of mobile and bioavailable lead in contaminated soils.

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