Deep Eutectic Solvent-Assisted Washing of Nickel from Polluted Mine Soil

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Abstract

Recently, nickel pollution in soil has become a hot topic in research. Therefore, the key solution for washing remediation is to find effective, inexpensive and ecology friendly washing agents to remove nickel from polluted soils. In this paper, diethylene glycol-choline chloride ionic liquids (DCILs) combined with composite acid was used as an eluting agent to remove nickel in contaminated mine soils. The nickel removal rates when using the composite acid or the DCILs were 48.77% and 4.5%, respectively. The removal rate increased to 57.60% when using the composite acid combined with 3% (v/v) DCILs as an optimum eluant; this experimental result indicated that the optimum eluant based on the composite acid and DCILs was successfully determined, and it had a significant effect on the extraction process. The BCR speciation analysis showed that the removal rates ranked as follows: oxidisable fraction (92.18%)>acid extractable fraction (85.41%)>reducible fraction (79.07%)>>residual fraction (23.34%) after extraction under optical conditions, which implied that the optimal eluant played a critical role in the mobility of the nickel removal rate and effectively reduced the bioavailability and environmental risk of the nickel. To sum up, DESs-assisted washing is a promising method in the field of removing heavy metals from contaminated soil.

Keywords: diethylene glycol-choline chloride ionic liquids, extraction, heavy metal, mine soil, nickel

INTRODUCTION

Recently, heavy metal pollution in soil has become a hot topic in research (Chen et al. 2016). Nickel contamination is attracting considerable attention due to its highly toxic and carcinogenic properties and its ability to enter the food chain through various pathways (Yadav et al. 2013). Nickel can accumulate and induce toxicity in the biological systems of humans, animals, plants and microorganisms, which poses a significant hazard. Therefore, it is necessary to develop a practical technology to remedy nickel-polluted soil nickel (Abedi et al. 2015).

Remediation methods for polluted soil with heavy metals can be loosely divided into physical, chemical, biological and phytoremediation methods (Fedje et al. 2015). Soil washing with various chemical solutions has been a prevalent and efficient method in remediation (Mahar et al. 2016). Soil washing technologies are acknowledged as one of the most efficient ways to repair contaminated soil due to their low cost, lack of secondary pollution and reliable remediation (Chen et al. 2015). In addition, they can be used to address both high and medium levels of soil pollution. Various eluting agents, such as inorganic drench lotion (Marchand et al. 2016), artificial chelating agents (Freitas and Nascimento 2016) and class drench lotion (Satyro et al. 2014), have been widely applied to remove nickel from contaminated soil. These eluting agents have destructive physical and chemical properties; hence, different leaching solutions are required because the current eluting solutions are not feasible on a large scale (Gitipour et al. 2016). Therefore, the key solution for washing remediation is to find effective, inexpensive and ecology friendly washing agents to remove nickel from polluted soils.

Ionic liquids (ILs), which also go by the name of ambient-temperature molten salts or room-temperature ionic liquids, are liquids at normal atmospheric temperature (Mouradzadegun et al. 2015). ILs are considered to be the best eluants and hold great promise because of the low toxicity and environmental friendliness they have exhibited in the past 20 years (Tian et al. 2010). Deep eutectic solvents (DESs) are a class of ionic liquids because 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

Table 1. The physical and chemical properties of the soil samples

property	pH	organic matter	sand (>0.05mm)	Silt (0.002-0.05mm)	Clay (<0.002mm)
content	6.53	3.75 g kg^{-1}	1.66%	28.59%	69.75%

temperature (Zhang et al. 2013). These intriguing physical and chemical features have attracted abundant interest in the field; hence, DESs have been successfully and widely applied in the preparation and synthesis of fuel cells, catalysts, and materials, and the electrodeposition of metals (Gan and Zhao 2015, Hasan et al. 2015, Mu et al. 2015). Mukhopadhyay has been reported the synergistic behaviour between a polyol-based DESs and saponin on lead (Mukhopadhyay et al. 2016). His results indicated that extraction using the mixture of DESs and saponins performed better rather than individually using the materials. DESs are a new and green heavy metal washing promoter and are popular and widely applied, but they have been scarcely applied for soil washing.

In this paper, DCILs are combined with a composite acid and used as an eluting agent to remove nickel in contaminated mine soils. In addition, we discuss an optimized BCR sequential extraction procedure for different nickel fractions, investigate the removal performance of removable dynamic nickel and investigate the synergistic extraction effect of DCILs with a composite acid on nickel.

EXPERIMENTAL
Soil Analysis and Characterization

Soil samples were collected from the top 15-25 cm layer of an abandoned plantation near a nickel mine in southern Yunnan Province, China. All the samples were preserved after air drying and passed through a 100 mesh screen. Then, certain soil samples were utilized to quantify their physicochemical properties and the qualities of the different nickel fractions before and after washing with the BCR sequential extraction procedure. The physicochemical characteristic analysis of the soil samples is shown in **Table 1**.

Preparation of diethylene glycol-choline chloride Ionic Liquids

The diethylene glycol-choline chloride ionic liquids were prepared by stirring mixtures of diethylene glycol and choline chloride (mole ratio 2:1) at 80° C until homogeneous colourless liquids were generated, and then, they were preserved in a vacuum dryer (Ciocirlan et al. 2010).

Table 2. The BCR sequential extraction procedure for nickel fractionation

Step	Reagent	Condition	Fraction
1	32 ml CH$_3$COOH	shaken 16 h at room temperature and then centrifuged at 3000 rpm for 20 min	Acid extractable fraction
2	40 ml NH$_2$OH·HCl (pH =1.5)	shaken 16 h at room temperature and then centrifuged at 3000 rpm for 20 min	Reducible fraction
3	10 ml H$_2$O$_2$ 1 M NH$_4$OAc (pH = 2)	digested for one hour then evaporated to dryness, shaken 16 h at room temperature and then centrifuged at 3000 rpm for 20 min	Oxidisable fraction
4	10 ml HF-HNO$_3$-HCl	digested on a hot plate	Residual fraction

Washing Experiments

In the batch experiments, 0.500 g of sieved air-dried soil was added to 10 mL of a composite acid containing various concentrations of phosphoric acid, tartaric acid, citric acid, and the mixture was shaken for 5 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 15 min in order to separate the solid residue from the washing solution. The concentration of nickel in the supernatant liquor from the washing solution was measured using a flame atomic absorption spectroscopy method. All experiments were implemented in triplicate.

Sequential Extraction Procedures

The purpose of this work was to assess the extraction effectiveness of the composite acid solution, nickel fractions were extracted using an optimized BCR sequential extraction procedure to measure the redistribution pattern of the nickel (Tokalıoğlu et al. 2015). The procedure was applied for the separation of nickel from soil into acid extractable, reducible, oxidisable and residual fractions, and the details are shown in **Table 2**.

RESULTS AND DISCUSSION
The IR Characterization of the DCILs

The FTIR spectra of the pure choline chloride (ChCl), ethylene glycol and DCILs are represented presented in **Fig. 1** (**A**, **B** and **C**). It can be noted that the absorption bands of choline chloride at 3258.73 cm^{-1} (**Fig. 1(A)**) became broader bands in DCIL (**Fig. 1(C)**). This might have resulted from the formation of more hydrogen bonds between diethylene glycol and choline chloride, which existed in the form of H-O...O-H, O-H...N-H, N-H...N-H and N-H...O-H. The δ s(CH$_2$) at 2944.54 cm^{-1} shifted to 2941.46 cm^{-1} after the formation of strong hydrogen bonds **Fig. 1(B)** and **Fig.**
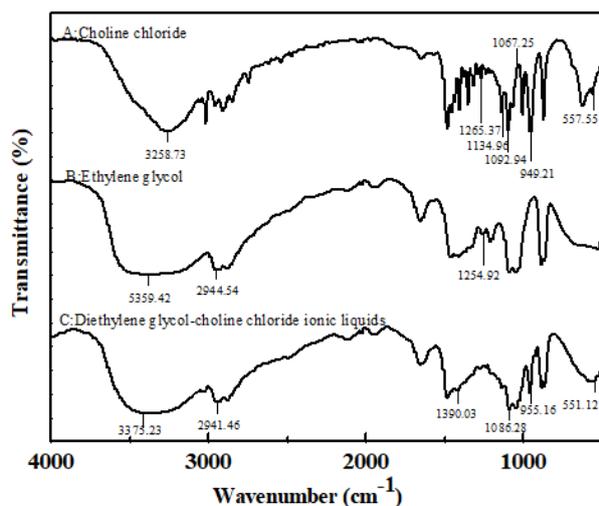
Fig. 1. The IR characterization of ChCl, ethylene glycol and DCILs

Fig. 3. The concentration curve of DCILs on nickel removal rate
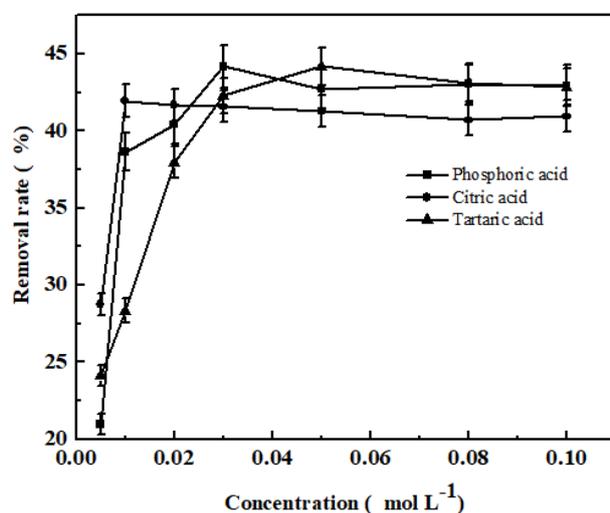

Fig. 2. Optimal concentration of composite acid eluant

1(C)). Absorption bands of δ as(C-N) shifted from approximately 1134.96 cm^{-1} and 1092.94 cm^{-1} to 1390.03 cm^{-1}, which was attributed to the weak effect of alcohol. The bands for ν(C-O) at 1086.28 cm^{-1} and δ (C-H) at 551.12 cm^{-1} were also observed in DCIL (**Fig. 1(C)**), and band for the ν(CCO) at 955.16 cm^{-1} showed that the structure of Ch^{+} was not destroyed in the DCIL system. The above absorption characteristic peaks of the DCILs are consistent with those reported in the literature (Zhang et al. 2013), indicating that the DCIL was successfully synthesized.

Optimal Composite Acid Eluant

Batch experiments were conducted using different concentrations of phosphoric acid, citric acid and tartaric acid in the soil samples, and the results are shown in **Fig. 2**. The extraction of nickel increased rapidly as the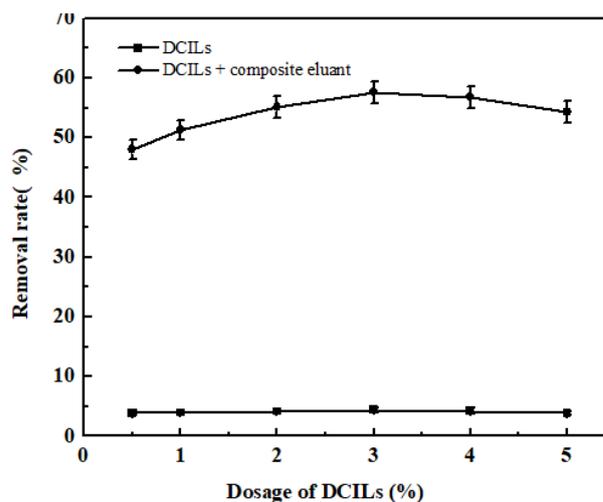 concentration of phosphoric acid and citric acid increased from 0.005 - 0.01 M. For phosphoric acid, the removal efficiency varied from 20.95% - 44.17% as the concentration shifted from 0.005 to 0.03 M. For tartaric acid, the removal efficiency varied from 24.13% - 44.17% as the concentration varied from 0.005 to 0.05 M. The removal efficiency of citric acid reached its maximum value of 41.94% at a concentration of 0.01 M. In addition, as the concentration of citric acid became higher, the removal efficiency did not increase. Hence, the mixture including 0.03 M phosphoric acid, 0.05 M tartaric acid and 0.01 M citric acid was chosen as the optimal composite acid eluant, and a removal efficiency 48.77% was reached under this condition.

Synergetic Effect between the DCILs and Composite Acid Eluant

To assess the synergy between the DCILs and the composite acid eluant, DCILs with dosages varying from 0.5% - 5% (v/v) were added into the composite acid, and then, the batch experiments for the removal efficiency were performed. The nickel removal rate using the DCILs alone was less than 4.5% as the DCILs with dosages in the range from 0.5% to 5% (**Fig. 3**), which implied that using DCILs alone minimally affected the nickel extraction process. In contrast, the synergy between the DCILs and the composite acid eluant could be observed; the removal efficiency of the nickel increased as the percentage of the DCILs increased from 0.5% to 3%, and the maximum value of 57.60% was reached using 3% (v/v) DCILs. The increment in the removal rate of nickel was calculated to be 8.83% under these conditions.
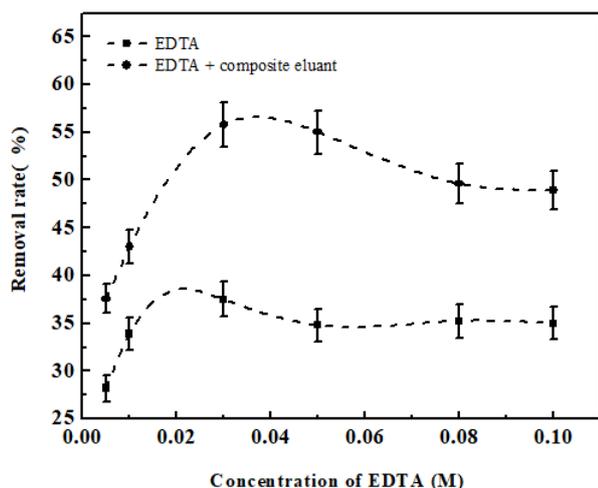
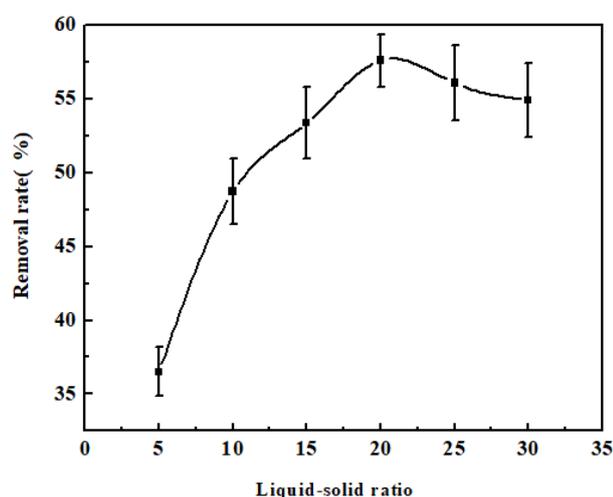**Fig. 4.** The concentration curve of EDTA on nickel removal rate

Fig. 5. Effects of liquid-solid ratio on the washing efficiency of polluted soil

To compare the promoting effect of the DCILs and EDTA on the composite acid eluant, batch experiments using the EDTA promoting effect were performed. The results showed the nickel removal rate for EDTA alone varied from 28.20% - 37.49% using EDTA with a concentration range from 0.005 to 0.03 M (**Fig. 4**), which implied that using EDTA alone had a significant extraction effect on the nickel removal. While minimal synergy between EDTA and the composite acid eluant was observed when the addition of EDTA ranged from 0.005 to 0.03 M and reached its maximum value of 55.79% at 0.03 M EDTA. The increment in the removal rate of nickel was calculated to be 7.02% under these conditions. This result illustrates that DCILs had a better synergistic role on the extraction of nickel compared to using EDTA. In addition, the results showed that EDTA was displaced by the DCILs, and adding 3% DCILs to the composite acid eluant was
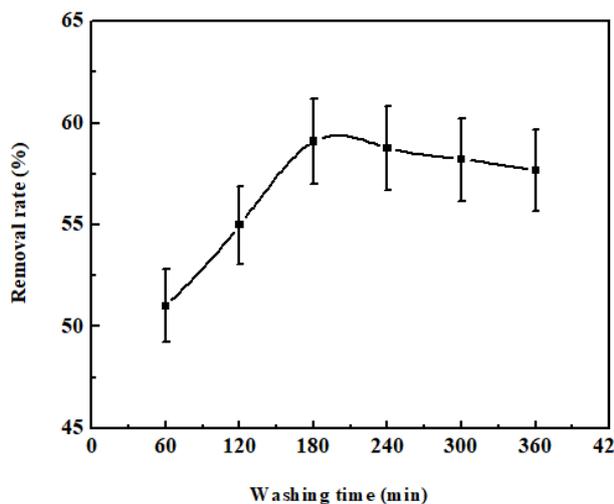

Fig. 6. Effects of shaking time on the washing efficiency of polluted soil

selected as the optimal eluant for the subsequent studies.

Influence of the Liquid-solid Ratio

In theory, a greater solvent volume can dissolve target compounds more effectively and lead to a better removal rate. The effect of the liquid-solid ratio on the nickel removal rate is shown (**Fig. 5**). With the increase in the liquid-solid ratio, the removal rate of the nickel increased sharply at an L/S ratio of 20 and then tended to stabilize. It seemed that by adding the optimal eluant dose, only a small proportion was validly transformed into metal-chelate complexes, while excess doses could lead to the formation of an unwanted residue or form complexes with other cations. Therefore, the optimum liquid-solid ratio of 20 was chosen for the subsequent experiments.

Influence of the Optimal Shaking Time

The shaking time is an important factor in soil washing. To understand the washing process and ensure the most appropriate shaking time, an experiment was carried out using soil washing with the optimal eluant, and the results are shown in **Fig. 6**. Increasing the shaking time significantly influenced the extraction of the nickel when shaking time increased from 60 to 180 min. In addition, the nickel removal varied from 51.01% - 59.10% with time. The results showed that the DCILs exhibit a two-step response process, in which a rapid response within 180 min was followed by a subsequent gradual release that appeared over the following hours. Because the nickel removal remained nearly constant during shaking for approximately 180 min, this time was chosen for further experiments.
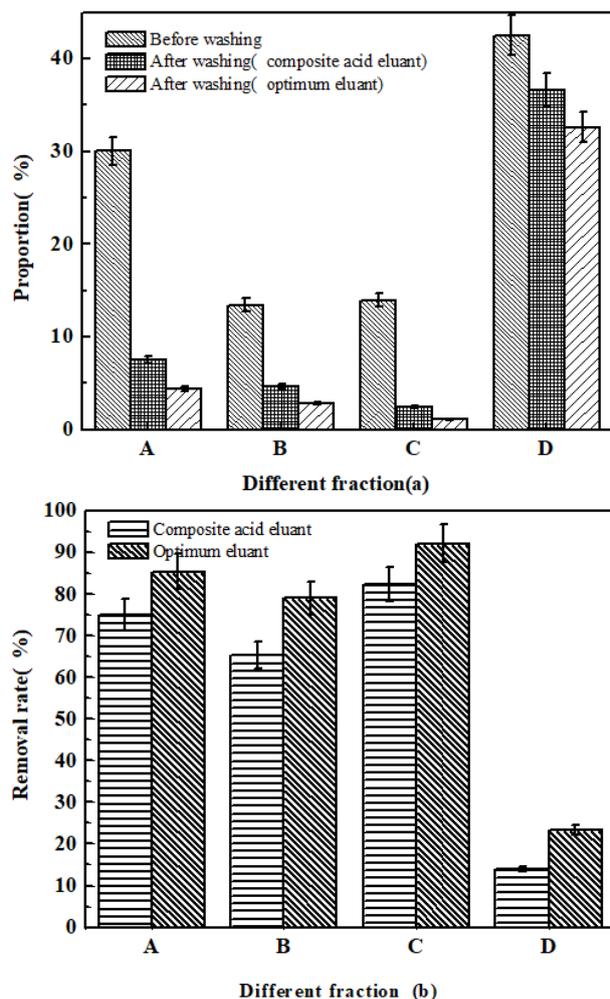
Fig. 7. Residual proportion and removed rate of nickel of different fractions in soil samples before and after washing (A:acid extractable fraction B:reducible fraction C:oxidisable fraction D:residual fraction)

Sequential Extraction of Nickel

To understand the mechanism of the synergetic extraction effect between the DCILs and the composite acid eluant, a BCR sequential extraction procedure was conducted with three samples, including the raw soil samples and worked soils using the composite acid eluant and optimum eluant; the results are shown in **Fig. 7(a)**. The forms of the nickel in the raw soil samples included an acid extractable fraction (30.08%), a reducible fraction (13.43%), an oxidisable fraction (13.94%) and a residual fraction (42.55%). The removable nickel accounted for 57.45% of the soil, which implied that it was a more active soil. After washing with the composite acid and optimal eluant, the residual proportions of each amount were as follows: acid extractable fraction, 7.52% and 4.39%; reducible fraction, 4.64% and 2.81%; oxidisable fraction, 2.45% and 1.09%; and residual fraction, 36.62% and 32.62%, respectively. The proportions of the four fractions were significantly reduced, which implied that the two eluants also played an important role on the removal efficiency of the nickel.

To gain more insight into the nickel removal, the nickel removal rate is shown in **Fig. 7(b)**. By comparing the composite acid eluant and optimum eluant, the removal rates decreased in the following order: oxidisable fraction (82.42% and 92.18%)>acid extractable fraction (75.00% and 85.41%)>reducible fraction (65.45% and 79.07%)>>residual fraction (13.94% and 23.34%), respectively, which implied that the optimal eluant we used played a more critical role during the nickel removal than the traditional acid eluant. The nickel was predominant in the residual fraction, and its average content was 40%, which remained nearly constant. Therefore, it was especially difficult to extract nickel from the remaining soil with the increasing binding strength.

CONCLUSION

In this study, a washing method to restore nickel contaminated soil was initiated by washing with DCILs combined with composite acid as the optimum eluant. The compound eluant had a prominent impact on the extraction, and the removal rate increased by 8.83% using 3% (v/v) DCILs with a composite acid containing 0.03 M phosphoric acid, 0.05 M tartaric acid and 0.01 M citric acid. In addition, the enhanced extraction effect of the DCILs on the composite acid was significantly higher than that using EDTA. The BCR speciation analysis implied that the DCILs in combination with the composite acid could remove 85.57% of the removable nickel from the contaminated mine soil under the optimal conditions. The proposed washing system has broad prospects and applications in the field of remediating contaminated soils containing heavy metals.

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