Effective removal of heavy metals from industrial sludge with the aid of a biodegradable chelating ligand GLDA

Qing Wu, Yanrui Cui, Qilu Li, Jianhui Sun*

School of Environment, Henan Normal University, Key Laboratory for Yellow River and Huai River Water Environmental and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, No. 46, Jianshe Road, Xinxiang 453007, Henan, China

HIGHLIGHTS

- A novel readily biodegradable chelating ligand was employed to remove heavy metals.
- The effects of different conditions on the extraction with GLDA were probed.
- Species distribution of metals before and after extraction with GLDA was analyzed.
- GLDA was effective for Cd extraction from sludge samples under various conditions.
- GLDA offers special insights in the effective removal of heavy metals.

ARTICLE INFO

ABSTRACT

Tetrasodium of *N,N*-bis(carboxymethyl) glutamic acid (GLDA), a novel readily biodegradable chelating ligand, was employed for the first time to remove heavy metals from industrial sludge generated from a local battery company. The extraction of cadmium, nickel, copper, and zinc from battery sludge with the presence of GLDA was studied under different experimental conditions such as contact times, pH values, as well as GLDA concentrations. Species distribution of metals in the sludge sample before and after extraction with GLDA was also analyzed. Current investigation showed that (i) GLDA was effective for Cd extraction from sludge samples under various conditions. (ii) About 89% cadmium, 82% nickel and 84% copper content could be effectively extracted at the molar ratio of GLDA:M(II) = 3:1 and at pH = 4, whereas the removal efficiency of zinc was quite low throughout the experiment. (iii) A variety of parameters, such as contact time, pH values, the concentration of chelating agent, stability constant, as well as species distribution of metals could affect the chelating properties of GLDA.

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1. Introduction

High level of heavy metal residues in sludge is one of the major obstacles for the sludge disposal. The techniques currently employed for wastewater treatment result in the generation of large quantities of sludge that needs to be disposed off [1]. One of the most potential routes for sludge disposal (especially the sewage sludge) is the land application by recycling of the valuable components (nitrogen/phosphorus-contained species, and organic matters) within the sludge [2]. However, industrial sludge generated from the battery factories, metal plating facilities as well as tanneries contains large amounts of heavy metals [3]. It is well known that several types of metals, such as chromium, copper, lead, mercury, and cadmium, are particularly harmful and toxic to human beings and ecological environments [4]. They can accumulate in living organisms, causing various diseases and disorders. They are also non-biodegradable and could remain indefinitely in the soil environment [5,6]. In most of the developing countries, the sludge disposal on nearby uncultivated lands is fairly universal. Such practices certainly lead to heavy metal contamination of the biosphere [7,8]. In this regard, the effective removal and regeneration of heavy metals from sludge is quite imperative.

Pioneer work on the removal of heavy metal ions was initiated by Dudzinska and Juang [9,10] by using complex agents such as nitrilotriacetic acid (NTA), citric acid (CA), and ethylenediaminetetraacetic acid (EDTA). In particular, EDTA has been proven as an effective chelating agent for heavy metal decontamination [11–13]. However, these agents can pose a high risk of metal leaching to the groundwater due to their refractory nature [14]. Hence, replacement of such ligands by more environmental friendly

ones would be highly desirable. To this end, tetrasodium of *N,N*-bis(carboxymethyl) glutamic acid (GLDA) has been introduced as a biodegradable chelant, where its production is based on a green chemistry process involving the fermentation of readily available corn sugars [15]. GLDA exhibits good chelating capacity towards a plethora of metal ions, it also possesses excellent biodegradability, with more than 60% of GLDA degraded within 28 days [16]. Another notable feature is that the ecological footprint of GLDA is far smaller than those from traditional counterparts because of its efficient manufacturing process [17]. Previous studies with regard to the usage of GLDA have centered on its applications in terms of detergents, cosmetics, and boosting agents for disinfecting products [18]. To the best of our knowledge, utilizing GLDA as a chelating reagent to remove heavy metals from industrial sludge has not been reported so far.

There are large amounts of cadmium and nickel present in the industrial sludge, which has recently become a focus of our research. As priority environmental pollutants, cadmium and nickel have received more attention with respect to their transportation, decontamination, and biological enrichment [19–21]. To realize effective decontamination and removal of primary pollutants, getting a full grasp on their distribution/fraction is of great significance. It has been well received that the determination of the total amounts of elements does not give an accurate estimation of the potential environmental impact, since it is becoming apparent that both bioavailability and toxicity strongly depend on the chemical forms of heavy metals [22]. To date, Tessier [23] and BCR [24,25] (the Community Bureau of Reference, now the European Union "Measurement and Testing Programme") sequential extraction methods have been widely applied to the field of metal fractionation to deal with different environmental samples [26]. Compared with others, BCR procedures possess better reproducibility, precision and achieve comparable performances [24]. In the typical BCR sequential extraction, the metal elements are divided into acid-soluble, reducible, and oxidizable fractions. As for the modified BCR sequential extraction method, two additional fractions, water-soluble and residual ones, are also considered.

In this work, GLDA has been utilized as an environmentally friendly chelating reagent to remove heavy metals from industrial sludge. The extraction performances were evaluated by the removal of cadmium, nickel, copper, and zinc from battery sludge, where the effects of pH value, contact time, molar ratio of GLDA/metal on the removal efficiency in the presence of GLDA were probed. The extraction experiments were carried out under controllable conditions requiring additional treatments subject to environmental regulations of China. Moreover, the distribution of heavy metals in the sludge sample prior to and after the extraction with the aid of GLDA was investigated using the modified BCR sequential extraction procedure.

2. Materials and methods

2.1. Industrial sludge and chelating agents

The sludge sample was collected from the battery Co., Ltd. wastewater treatment plant in Xinxiang city (Henan Province, China; Geographical coordinates 35.20°N, 113.51°E). The sludge was air-dried, ground, and subsequently sieved to the size less than 150 μm. The final material was collected and stored in desiccators.

Tetrasodium of *N,N*-bis(carboxymethyl) glutamic acid (GLDA) was purchased from Akzo Nobel Chemicals Co., Ltd. It has a relative molecular mass of 351.1, solid content > 47%, density ≈ 1.400 g cm^{-3}. This material shows good solubility in aqueous solutions over a wide range of pH values. The structure of GLDA can be described as follows [27]:

Table 1
Chemical reagents and analytical conditions for the modified BCR sequential extraction.

	Fraction	Agents and procedures	Extraction time (h)
Step 1	Water-soluble	20 mL deionized water	16
Step 2	Acid-soluble	20 mL HOAc (0.11 M, pH 2.8)	16
Step 3	Reducible	20 mL NH$_2$OH·HCl (0.5 M, pH 2)	16
Step 4	Oxidizable	10 mL H$_2$O$_2$ and 25 mL NH$_4$OAc 5 mL H$_2$O$_2$ (30%, pH 2) heat to 85 °C for 1 h and add 5 mL H$_2$O$_2$ (30%, pH 2) heat to 85 °C for 1 h and then add 25 mL NH$_4$OAc (1 M, pH 2)	1 1 16
Step 5	Residual	HCl–HNO$_3$–HF–HClO$_4$	7
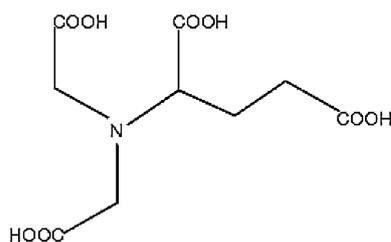
All other chemicals used in the study were in analytical grades.

2.2. Sequential extraction experiments

To probe the speciation/fraction of the heavy metal components within the sludge, the samples were analyzed using the modified BCR sequential extraction procedure. The steps and defined metal fractions are shown in Table 1.

Operationally, sequential extractions were conducted using 0.5 g sludge sample. Following each extraction step, the resultant suspensions were centrifuged and the supernatants were filtered through a 0.45 μm membrane filter, after which the obtained residue was washed by deionized water and the filtrate was transferred into the volumetric flask. The start of the next-round extraction process was marked by adding the extraction agent into the residue. The filtrate was acidified to pH < 2 before further analysis.

2.3. Extraction experiments

Heavy metal extraction experiments were carried out in conical flasks in aqueous suspensions. The tests were performed under different pH parameters (pH value ranged from 1 to 12), different molar ratio of GLDA:M(II) in the sludge samples (ranged from 1:1 to 10:1), and different contact time (2, 4, 6, 8, 10, 12, 24, 48, and 72 h) in order to determine the optimum conditions in terms of metal removal efficiency.

Batch extraction experiments were conducted at a solid (mass) to solution (volume) ratio of 1:50. For each run, a sludge sample (0.5 g) was suspended in a 25 mL solution and the reaction time was fixed at 24 h except for the effect of contact time experiments. It is noted that the contact time experiment was carried out at GLDA:M(II) = 1:1 and at a natural pH condition (pH = 12). The pH value of the suspension system was adjusted by dosing HNO$_3$ or NaOH, and the acidified solutions were stored in plastic centrifuge tubes. The suspensions were processed at 200 rpm at room temperature, subsequently centrifuged at 3500 rpm for 20 min, and filtered

Table 2
Characterized heavy metal contents in the sludge compared to the legal standard.

Parameters (unit)	Value	Acid soil (pH < 6.5)[a]	Alkaline soil (pH ≥ 6.5)[a]	Environmental soils[b]
Water content (%)	98.5			
pH	11.5			
Cd (mg kg⁻¹)	172,300	5	20	1
Ni (mg kg⁻¹)	22,225	100	200	200
Zn (mg kg⁻¹)	1700	2000	3000	500
Cu (mg kg⁻¹)	237	800	1500	400
Ca (mg kg⁻¹)	130,500			
Mg (mg kg⁻¹)	9300			
Fe (mg kg⁻¹)	56,750			

[a] National Standard of the People's Republic of China GB 18918-2002: Discharge standard of pollutants for municipal wastewater treatment plant (mg kg⁻¹).
[b] National Standard of the People's Republic of China GB 15618-1995: Environmental quality standard for soils (mg kg⁻¹).

through a 0.45 μm membrane filter. The solutions were properly stored at 4 °C prior to analysis.

2.4. Analytical methods

The pH value of the sludge sample was determined by employing a PHS-3 C Professional pH meter (Shanghai, China). The sludge sample was pretreated by an SISP DS-360 graphite digestion apparatus (Guangzhou, China) with the aid of the concentrated $HCl–HNO_3–HF–HClO_4$ solution at 150–190 °C. The concentrations of the dissolved heavy metals in the digestion solutions and extraction solutions were measured by using an inductively-coupled plasma mass spectrometry (PerkinElmer, USA). Species distribution of heavy metals in the sludge sample before and after extraction with GLDA was analyzed by the modified BCR sequential extraction method.

The extraction efficiency (%E) was calculated according to the following equation:

$$\%E = \frac{(V \times C)}{(M \times m)} \times 100\% \tag{1}$$

where V is the volume of the extraction solution (mL), C is the concentration of the metal dissolved in the extraction solution ($\mu g\,L^{-1}$), M is the mass of the sludge sample (g), and m is the concentration of the metal in the sludge sample (mg kg⁻¹).

The extraction and sequential extraction experiments were conducted from September 2013 to May 2014. A minimum of triplicate extraction runs and related analysis was made for all samples.

3. Results and discussion

3.1. Characterization of sludge

Table 2 displays the general information (water content, pH value, main metal species *etc.*) of the sludge sample obtained after detailed characterization. The molar sum of the heavy metals (Cd, Ni, Zn and Cu) in sludge is 1945 mmol kg⁻¹. The content of Cd and Ni is 172,300 and 22,225 mg kg⁻¹, respectively, both of which are beyond the environment quality standard for soils (1 and 200 mg kg⁻¹ for Cd and Ni, respectively) and the discharge standard of pollutants for municipal wastewater treatment plant in China (5 and 100 mg kg⁻¹ for acid soil where pH < 6.5, 20 and 200 mg kg⁻¹ for alkaline soil where pH > 6.5 for Cd and Ni, respectively). Disposal of such sludge on nearby unused lands would lead to serious heavy metal contaminations with a string of negative consequences for the biosphere.
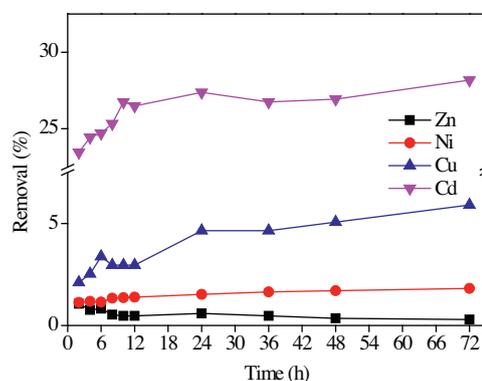

Fig. 1. Effect of contact time on the extraction of Cd, Ni, Cu and Zn. Conditions: GLDA:M(II) = 1:1, without pH adjustment (at a natural pH = 12).

3.2. Effect of contact time on the extraction

In order to attain optimum extraction performance of heavy metals, the effect of contact time on the removal efficiency was studied. Fig. 1 shows the kinetics of Cd, Ni, Cu, and Zn extraction from the sludge sample using GLDA (GLDA:M(II) = 1:1; pH = 12) with a reaction time of 72 h. It is obvious that the extraction of Cd and Cu exhibits a relatively fast initial step (within 24 h), followed by a smoother release of metals. Extraction of Ni and Zn are much slower than that of Cd or Cu. In general, our investigations showed that the extraction efficiency increased with the increasing of contact time, however, only slow increase was observed after 24 h (up to 72 h). Therefore, 24 h was chosen as the optimum reaction time for the subsequent experiments, the finding of which is also consistent with other reports regarding the extraction time [13]. This observation could be explained by the fact that the removal efficiency is not changed with the increase of contact time once the chelating process reaches equilibrium.

3.3. Effect of pH conditions on the extraction

The comparison study on the removal efficiency of Cd, Ni, Cu, and Zn at different pH values with/without the presence of GLDA was conducted. It is found that the removal efficiency of heavy metals decreases rapidly as pH value increases in the absence of GLDA (Fig. 2). Although a general trend goes that the values of the efficiencies are entirely augmented by the GLDA dosage over a wide pH range from 3 to 12, at GLDA:M(II) = 1:1, the removal efficiency of heavy metals still declines as pH value increases. The extraction efficiency at pH = 3 in the absence of GLDA is 24%, 17%, 57% and 24% for Cd, Ni, Cu and Zn, respectively, whilst under identical pH conditions, the efficiency with the presence of GLDA (GLDA:M(II) = 1:1) reaches 76%, 47%, 49% and 32% for Cd, Ni, Cu and Zn, respectively. It is interesting to note that the extraction efficiency of Cd is dramatically affected by the addition of GLDA under alkaline conditions. These results indicate that the pH conditions could exert a significant effect on the extraction efficiency, where strongly acidic conditions with the presence of GLDA are favorable for heavy metal removal.

At low concentrations of the chelating agent, metal extraction shows a strong dependence on pH values of the environment. At a large GLDA:M(II), the pH dependence of the extraction is much less prominent, this is reflected by the trend shown in Fig. 2, where the removal efficiency of heavy metals declines slowly as the pH value increases at a higher GLDA:M(II) = 5:1. Notably, amongst these metals, GLDA functions best with Cd over the whole pH range (the efficiencies are all above 72%), with the peak values occurred
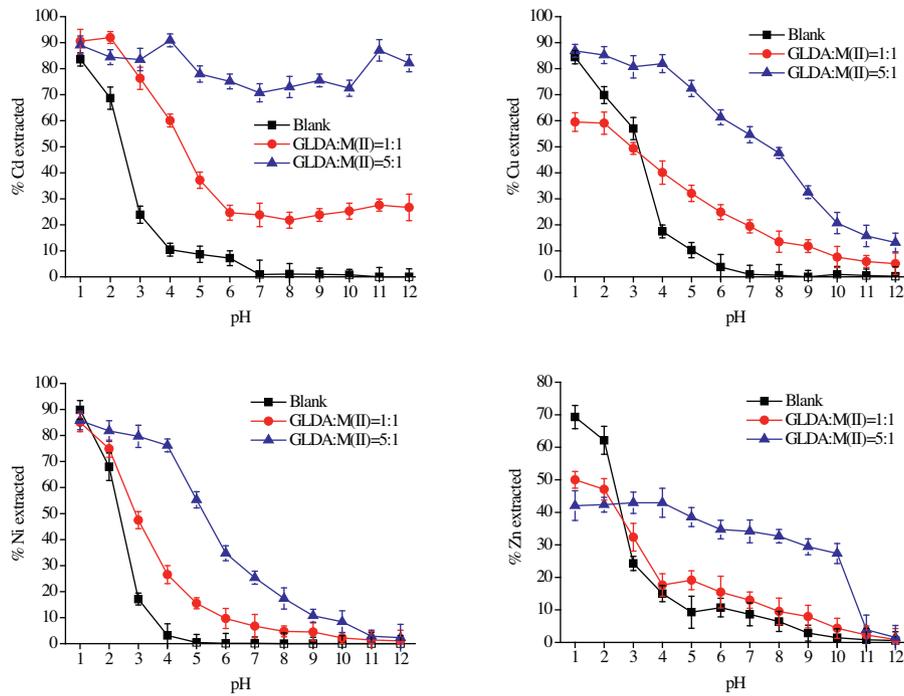
Fig. 2. Effect of the pH values on the extraction of Cd, Ni, Cu and Zn with three different conditions: in the absence of GLDA, in the presence of GLDA with GLDA:M(II) at 1:1 and 5:1.

at pH = 4 and 11, whereas Cu and Ni maintains a good removal efficiency at pH ≤ 4, with the peak value occurred at pH = 4.

To understand the metal ion removal with the aid of GLDA, it is necessary to take the metal ion–ligand interaction into consideration. The complexation is characterized by the formation of stable 1:1 metal to ligand complexes as the major species [17]. The reaction between the metal ion and the anion of GLDA under different pH conditions can be interpreted as follows:

$$H_3glda^- + M^{2+} \rightleftarrows [MH_3(glda)]^+ \tag{2}$$

$$H_2glda^{2-} + M^{2+} \rightleftarrows [MH_2(glda)] \tag{3}$$

$$Hglda^{3-} + M^{2+} \rightleftarrows [MH(glda)]^- \tag{4}$$

$$glda^{4-} + M^{2+} \rightleftarrows [M(glda)]^{2-} \tag{5}$$
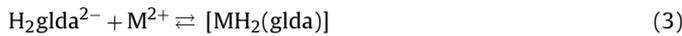
In paper [16], the stability constant ($\log K$) of metal chelate with GLDA (L) were introduced and the sequence of chelating abilities were: $\log K_{CuL}$ (13.1) > $\log K_{Fe(III)L}$ (11.7) > $\log K_{NiL}$ (10.9) > $\log K_{ZnL}$ (10.0) > $\log K_{CdL}$ (9.1) > $\log K_{Fe(II)L}$ (8.7) > $\log K_{MgL}$ (6.1) > $\log K_{CaL}$ (5.2). Apparently, GLDA possesses a strong capability to chelate Cu, Ni, Zn, and Cd. Therefore, it is easy to understand why GLDA can extract heavy metals from sludge quite effectively. However, actual extraction efficiency sequence in this work stays Cd > Cu > Zn > Ni (GLDA:M(II) = 1), which is not consistent with the trend displayed above. This is due to the fact that the stability constant indicating the capability of forming complexes is determined under ideal conditions. However, in the case of real effluents, the impact of competitive parameters, especially the pH values of the environment, should be taken into account [28]. It would result in distinct efficiency sequence in reality compared to the theoretical one. The pH conditions can affect the stability and the effectiveness of the chelating system. The conditional stability constant ($\log K'$) is an indication of the stability of the complex as a function of the pH conditions, as shown in Fig. 3.

With respect to a higher GLDA:M(II) = 5:1, such pH dependence on the extraction efficiency seems weakened (Fig. 2). This suggests that the GLDA concentration is another important factor that affects the extraction of heavy metals. It has been shown in this study

that GLDA is a good metal extractant especially for Cd, however, an appropriate pH and GLDA concentration should be further verified to achieve optimal removal of heavy metals. Therefore, in the next stage of investigations, the solutions of the studied Cu, Zn, Cd and Ni complexes with GLDA possess the following pHs: 12–13 (without any additional adjustments), 11, 7, and 4, respectively.

3.4. Effect of GLDA concentration on the extraction

In order to examine the effect of GLDA concentrations (*i.e.* the molar ratio of GLDA to heavy metal) on the extraction of heavy metals, different molar ratios of GLDA:M(II) in the sludge ranging from 1:1 to 10:1 under different pH conditions were tested. Batch extraction experiments were carried out at the natural pH (pH = 12∼13), as well as at pH = 11, 7, and 4, respectively. It can be observed in Fig. 4 that the extraction efficiencies of Cd increase prominently under all the employed pH conditions with the increase of the GLDA concentrations. At the natural pH, the optimum extraction efficiencies of all metals reach at GLDA:M(II) = 9:1, where approx. 69%, 5%, 8%, and 1% of Cd, Ni, Cu, and Zn is extracted, respectively. The discrepancy between the theoretical ratio (1:1) and the obtained real ratio (9:1) regarding the optimum extraction
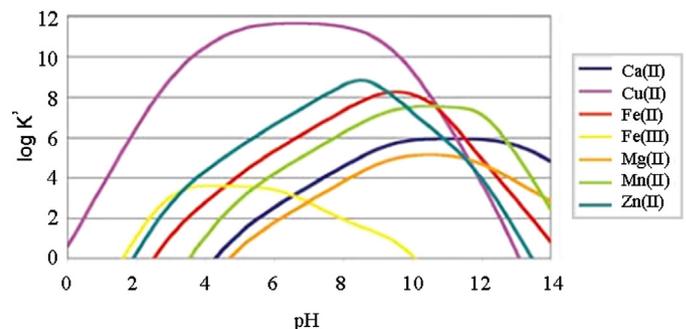

Fig. 3. Theoretical curves of the conditional stability constant ($\log K'$) of GLDA for various metal ions as a function of pH (1:1 metal:chelate complex). [18].
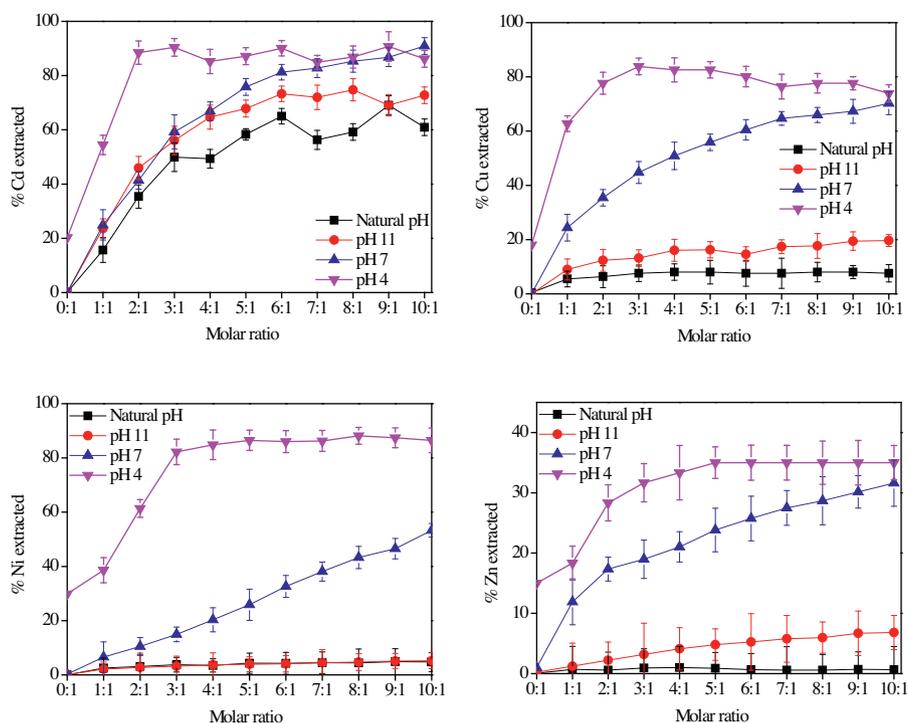
Fig. 4. Effect of the GLDA concentration on the extraction of Cd, Ni, Cu and Zn at natural pH (12–13), pH = 11, pH = 7, and pH = 4.

efficiency occurs due to the reason that there were many substances presented in the sludge apart from the studied metal species, for instance, other non-target metals, such as Ca, Fe, and Mg (as shown in Table 2), could competitively contribute to the consumption of chelating agent with target metals, leading to the great increase of the GLDA:metal ratio. According to the study conducted by Nowack et al. [29], a large excess of chelant is required to solubilize the target metal due to the co-solubilization of Ca and Fe.

In the case of pH adjustments, apparent increase of the efficiencies occurs for Cd prior to the molar ratio reaching 8:1 at pH = 11, with the peak value of approximately 75% achieved at GLDA:M(II) = 8:1, whereas the efficiencies of Cu, Zn and Ni show slight increases under such pH conditions. In the neutral medium (pH = 7), great improvements occurs before the molar ratio reaching 7:1 for Cd and Cu, where about 83% Cd and 65% Cu content is extracted at GLDA:M(II) = 7:1, respectively. In the acidic medium (pH = 4), the extraction of Cd, Ni, and Cu exhibits a fast increase as GLDA:M(II) increases from 1:1 to 3:1, whereas only Zn maintains a lower extraction rates throughout the whole process. The optimum removal efficiency is 89%, 82%, 84% and 32% for Cd, Ni, Cu and Zn at GLDA:M(II) = 3:1, respectively (Fig. 4).

The results suggest that a higher GLDA:M(II) lead to more effective extraction of heavy metals, where the extraction efficiencies obtained with GLDA for Cd are amongst the best observed at various conditions. This can be explained by the fact that heavy dosage of chelating agents could facilitate metal ion–ligand complexing reaction to move toward the direction leading to the formation of chelate; an increase of the acid concentration and contact time would in turn result in a corresponding increase of the energy required for the breakage of the chemical bonds of the metals in the sludge [1]. Based on the obtained results, the extraction with GLDA at GLDA:M(II) = 3:1 and pH = 4 could offer a best compromise on extraction efficiency for Cu, Ni, and Cd, moreover, the conditional stability constants of Ca, Mg and Fe are also quite low (log K′ < 4) at pH = 4 (Fig. 3), suggesting that these metal ions would not severely compete with target metals under such circumstance.

3.5. Species distribution of heavy metals in sludge

Species distribution of heavy metals in the sludge sample before and after the extraction with GLDA, as determined by the sequential chemical extraction, was examined. The experiment was performed at pH = 4 and GLDA:M(II) = 3:1. As shown in Fig. 5, Cu and Zn in the sludge sample are mainly in the forms of oxidizable and residual fractions before extraction. Cu has the highest proportion in the oxidizable fraction (60%) with 20% in the residual fraction and Zn mainly in the residual fraction (55%) with 35% in the oxidizable fraction. Cd mainly exists in oxidizable, acid soluble and residual fractions. As for Ni, reducible fraction takes the largest proportion. Previous study has indicated that the water-soluble, acid-soluble and reducible fractions are unstable and sensitive to the environmental conditions [30], which in turn are easily extracted. On the contrary, the residual fraction is stable, and is much harder to remove. The oxidizable fraction can be partly extracted.

After the extraction with GLDA, the major content is intensively found in residual fractions, where the metal contents in the other fractions are remarkably reduced. This result indicates that the extracted metals from the sludge with GLDA originate mainly from four fractions, i.e. reducible, acid-soluble, water-soluble, and oxidizable fractions. Before extraction, the total proportion of these four fractions accounts for approximately 93% and 89% for Cd and Ni, respectively. Under the given experimental conditions, the highest extraction efficiency of Cd and Ni reached 89% and 82%, respectively, suggesting a good correlation between the extraction efficiency and the change of species distribution of heavy metals before and after the extraction with GLDA. As the residual fraction is the largest proportion for Zn, it is reasonable that the extraction efficiency of Zn is low in all the experiments. Additionally, the extraction of acid-soluble metals would become less effective when increasing the pH values of the system, maintaining the pH = 4 instead of higher values would be beneficial to the extraction.
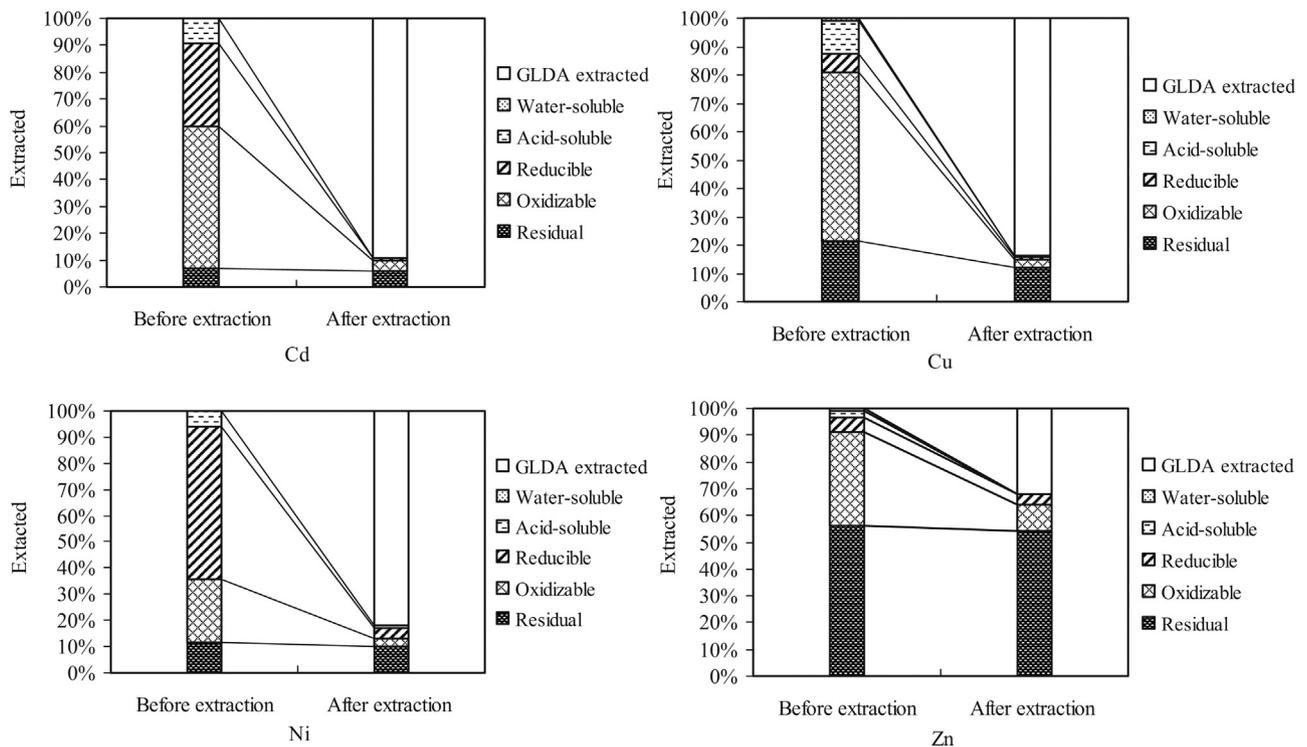
Fig. 5. Species distribution of Cd, Ni, Cu and Zn in the sludge sample before and after extraction with GLDA (extraction conditions: pH = 4, GLDA:M(II) = 3:1).

4. Conclusions

In summary, an environmentally friendly chelating reagent GLDA was employed to remove heavy metals from industrial sludge. The extraction performances were evaluated by the removal of cadmium, nickel, copper, and zinc from the sludge sample, where the effects of contact time, pH value, and molar ratio of GLDA/metal on the removal efficiency were probed. The chelating property was related not only to the stability constant, but also to species distribution of metals, pH conditions, contact time of reaction, as well as the concentrations of chelating agent *etc.* The extracted metals came mainly from reducible, acid-soluble, water-soluble, and oxidizable fractions, where about 89%, 82% and 84% of Cd, Ni and Cu content in the sample was extracted under optimum conditions (pH = 4, GLDA:M(II) = 3:1), respectively. The low extraction efficiency of Zn was attributed to the fact that nearly 60% of Zn existed in the residual fraction of the sludge, making it hard to extract. This work suggests that the biodegradable chelant GLDA, as potential substitute of the conventionally-used EDTA, offers special insights in the effective removal of heavy metals from industrial sludge.

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