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Heavy metal removal from sewage sludge under citric acid and electroosmotic leaching processes

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Abstract: The heavy metals present in sludge are very harmful to the environment and the human body. It is necessary to remove them before sludge disposal. In this study, an ex situ method for removing heavy metals from sludge using electroosmosis was designed, and experiments were conducted to study the effects of electroosmosis voltages (30 V, 40 V and 50 V), citric acid concentrations (0.03 mol/kg, 0.06 mol/kg, 0.09 mol/kg and 0.12 mol/kg) and the power supply (continuous and interrupted) on the removal rate of heavy metals (Cu, Cr, Cd, Zn and Pb). The study found that the combination of the citric acid pretreatment and electroosmosis can effectively improve the removal rate of heavy metals. An appropriate increase in the voltage and citric acid concentration can improve the removal rate of heavy metals. The best combination was determined to be 40 V and 0.09 mol/kg. Under these conditions, the removal rates of Cu, Cr, Cd, Zn and Pb, were 14.39%-41.28% (continuous power supply) and 21.78%-42.36% (interrupted power supply). The interrupted power supply effectively improved the removal rates of Cd and Zn but reduced the removal rates of Cr and Pb. The power supply mode had no significant effect on the removal rate of Cu.

Heavy metal speciation was analyzed by the BCR method, and the relationship between the ratio of easily removed metal speciation and the removal rate was studied. The increase in the ratio of easily removed speciation was accompanied by an increase in the removal rate, indicating that citric acid and electroosmosis increased the removal rate by increasing the ratio of easily removed speciation. However, the high pH value around the cathode caused by the electrochemical reaction was not conducive to the removal of heavy metals.

Keywords: sludge; electroosmosis; heavy metal; acidification; heavy metal speciation

1 Introduction

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Sewage sludge, a byproduct of sewage treatment processes, is rich in nitrogen (N), phosphorus (P), potassium (K) and organic matter. It is a popular practice to dispose of sewage sludge via land use, and many countries currently use this method. However, it can be difficult to convince the government and land users to agree on this method because of the presence of toxic metals and bacteria in the sludge. Therefore, it is necessary to separate the heavy metals from the sludge [1,2].

The methods for the removal of heavy metals from sludge are chemical extraction, electrokinetic remediation, filtration, ion exchange, adsorption on activated carbon, membrane technologies, microbiological leaching, phytoremediation, etc. [3-9]. The electrokinetic process aims to remove the heavy metals using an electric field, which promotes several complex mechanisms such as electrodialysis electric migration, electrophoresis, and electrolysis. This approach is conducive to the transportation of pollutants [10,11]. These effects cause the heavy metals to concentrate around the cathode, which allows for their removal. The advantages of electrokinetic remediation are that it is simple (i.e., simple equipment), flexible (i.e., can be used for in situ or ex situ treatments), relatively inexpensive, effective and environmentally friendly [12,13]. Electric repair can remove multiple heavy metals at the same time and can also be combined with bioremediation, phytoremediation and some traditional remediation technologies [9,14-22]. Since the 1980s, the electrokinetic process has been applied in soil restoration and has been highly successful at the laboratory scale [14,23-25]. However, there are only a few reports on in situ field applications [26,27,28]. Studies on the removal of heavy metals from sewage sludge are still incipient and are limited to the experimental stage.

Xiong [29] found that the migration degree of heavy metals depended on their physical morphological characteristics. Kim [30-33] used two different methods to extract heavy metals and analyzed their effects on electrokinetic restoration. It was found that electrokinetic restoration could change the metal speciation so that the metal was removed more easily. Wang and colleagues [34] also used electrokinetic remediation to remove heavy metals and analyzed metal speciation in the sludge by controlling the pH value of the cathode or by acidizing the sludge to improve the removal rate. It was found that the metal removal rate was improved by decreasing the hardly removed fractions of the heavy metal. The results of the study by Yuan [35] indicated that the removal rate of metals in an easily removed speciation was higher

with the application of an electromotive action in the sludge. Thus, the heavy metal speciation was a major factor that influenced metal removal.

Ma [36] found that some heavy metals can be removed from sludge by electroosmotic dehydration under inert anodes. When the working voltage was 40 V, the removal rates of Cr, Ni, Zn, Cu, and Pb were 7.29％-17.79％. Thus, dehydration can remove some heavy metals, but it is still not efficient enough. Other means, such as preacidification and different power modes, are needed to reinforce the removal of heavy metals.

Among the studies regarding the acidification of sludge, citric acid (a type of low molecular organic acid) is a natural chelating agent that has a strong complexation of certain heavy metals. The citric acid can extract heavy metals by lowering the pH value and by chelation and is easily biodegradable. Many studies have used citric acid to study the heavy metal removal rate of acidified sludge. Karwowska [37] studied the removal rate of heavy metals (Zn, Cu, Cd, Ni, Pb) from industrial wastewater sludge collected from the metallurgy industry using EDTA and citric acid. The results showed that when the concentration of the citric acid was 0.500 M, the removal rates of Zn, Cu, Cd, Ni and Pb ranged from 32%-98%. Wang and colleagues [38] studied the removal rate of heavy metals in mixed sludge from industrial and urban wastewater using citric acid and ultrasonic treatment. The optimum conditions for removing 53.5%, 40.2%, 35.4%, and 13.1% of Zn, Ni, Cr, and Cu, respectively, using this system was a 20 min ultrasonic treatment with 0.2 mol citric acid. Obviously, pretreatment with citric acid is advantageous for the removal of heavy metals.

Some researchers have used citric acid acidification to improve the heavy metal removal rate under electrokinetic remediation. Pei [39] found that after an electrokinetic remediation experiment, the removal rates of Zn and Cu increased. Jakobsen and colleagues [40] suspended a sludge in 0.25 M citric acid and exposed it to an electric DC field to study the removal of Cd. The Cd removal rate reached 70% after two weeks of treatment. However, there are few studies on the use of acidification of sludge and electrodialysis to remove heavy metals from sludge. It is cardinal to study the effect of acidification and electroosmosis on the removal of heavy metals in sludge.

Ma [41] proved that an electroosmotic leaching technology can simultaneously

remove moisture and heavy metals from a sludge. However, the continuous power condition was not conducive to the removal of water in the sludge, and the energy consumption was too high. Therefore, this study chose an interrupted power supply and a continuous power supply to explore the removal of heavy metals.

Different from traditional electrokinetic processes, this research studied the removal of heavy metals in a sludge during electrodialysis dehydration. A relatively high voltage was used to improve the efficiency. This approach is an ex situ method for removing heavy metals from sludge. The purposes of this study were (1) to evaluate the effects of voltage, citric acid acidification and power supply on the removal of Cu, Cr, Cd, Zn and Pb by electroosmotic leaching and analyze the factors affecting the removal rate of heavy metals, essentially, to find the best combination of the voltage, citric acid concentration and preliminary power supply mode; and (2) to analyze the speciation distribution of the heavy metals after electroosmotic leaching under the different conditions and assess the relationship with the heavy metal removal rate. This study provides a basis for future studies on the removal of heavy metals from acidified sludge using electrodialysis.

2 Materials and Methods

2.1 Materials

The sludge used in this study was obtained from the Xianyang Road Sewage Treatment Plant in Tianjin, China. The plant has a built-up scale of 450,000 m^3/d, with a maximum treatment capacity of 585,000 m^3/d. The plant uses the A/O anaerobic phosphorus removal process, supplemented with chemical phosphorus removal. The sludge uses a mid-temperature anaerobic digestion and centrifugal dehydration. The characteristics of the sludge before use in the experiment are shown in Table 1 and Table 2.

Table 1 Physical properties of the sludge.

pH	7.2
Color	Gray black
Ash (%)	52
Density (g/cm^3)	1.02
Moisture content (%)	81

Table 2 Content of heavy metals in the sludge.

Cu	183.7 mg/kg
Cr	322.7 mg/kg
Cd	22.0 mg/kg
Zn	584.0 mg/kg
Pb	117.9 mg/kg

2.2 Experimental facility

The experimental facility used for the electroosmotic leaching of heavy metals in the sludge is shown in Fig. 1. The continuous and interrupted power supply was provided by DC power (DH1716A-10, Beijing).
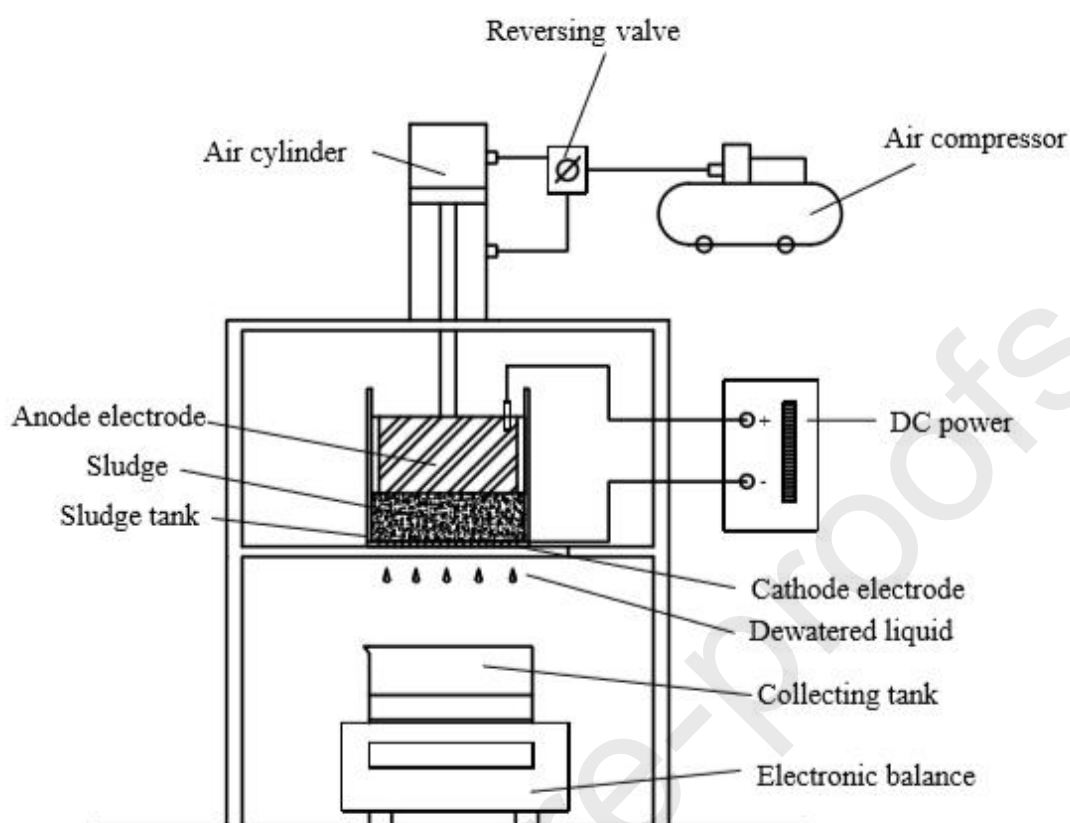
Fig. 1 Experimental set-up.

A carbon rod (90 mm diameter, 50 mm height), with strong conductive ability and resistance to corrosion during the dewatering process, was parceled into 5 mm acrylonitrile–butadiene–styrene (ABS) to be used as the anode. The sludge tank (100 mm inner diameter, 100 mm height) was made of hard rubber, and its bottom consisted of closely interspersed 5 mm holes. A 100-mesh stainless steel mesh was placed at the bottom of the sludge tank to be used as the cathode. The piston (100 mm diameter) of the air cylinder of an air compressor provided the required pressure.

The operation was as follows. Sludge (wet weight 78.5 g) was put into the sludge tank and propelled by the anode at a speed of 10 mm per minute with an air pressure of 0.05 MPa. After the prepress, the anode and cathode were connected to the DC power supply. The water was separated from the sludge and moved toward the cathode under the action of an electric field. Simultaneously, the speciation of the

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heavy metals was changed by acidification and oxidation, and the metals flowed into the collecting tank.

After the test, the power was turned off, the sludge was separated from the carbon rod, the device was cleaned and the next test was conducted. Meanwhile, the sludge and dewatered liquid were collected after the treatment to determine the content of heavy metals and to analyze heavy metal speciation. Each batch of experiments was repeated three times, and the average of the data was used for analysis.

2.3 Experimental procedure

According to the study of Ma [41], an excessive working voltage leads to an excessive current, which then leads to rapid drying of the anode, large amounts of gas generated near the electrode and an increase in resistance; thus, a low working voltage affects the removal of moisture in sludge. Although excessive dehydration has little effect on sludge dewatering, it consumes more energy. Therefore, the working voltages used in this test were 30 V, 40 V, and 50 V, and the duration of the electrical dehydration was set to 6 min. The experimental conditions were divided into the following three groups to study the removal rate of the heavy metals.

Group A: A quantity of 78.5 g of sludge was placed in the sludge tank. Electrolysis was performed with continuous voltages of 30 V, 40 V, and 50 V for 6 min.

Group B: A quantity of 78.5 g of sludge was put in a beaker for acidification, as per Liu [42]. The quantity of citric acid added to the four groups of dry sludge was set at 0.03 mol/kg，0.06 mol/kg，0.09 mol/kg, and 0.12 mol/kg. The detailed process for acidification was as follows: 12 mL of 0.2 mol/L, 0.4 mol/L, 0.6 mol/L, and 0.8 mol/L citric acid were put into each beaker and then stirred (YK120, Shanghai) at 150 r/min for 30 min, and then allowed to stand for 11.5 h. The continuous voltages of 30 V, 40 V, and 50 V were applied to the four acidified mixtures.

Group C: The amount of sludge and the acid treatment used were the same as those for Group B. Power was supplied for 1 min and then interrupted for 30 s, followed by recycling and the process was repeated 6 times. The voltage was maintained at 30 V, 40 V, and 50 V during the power supply .

2.4 Metal analysis

The collected sludge was air-dried, flattened, purified, and ground through a 1 mm sieve. The sample was quartered, and 20 g was ground in an agate mortar to enable it to pass through the 100-mesh nylon sieve completely. It was sealed at room temperature (approximately 25°C) for subsequent detection of heavy metal content and speciation.

The concentrations of the metals (Cu, Cr, Cd, Zn, and Pb) in the sludge sample were analyzed by high-pressure microwave digestion (WX-8000, Shanghai) and atomic absorption spectrophotometry (WFX-130B, Beijing).

For heavy metal speciation, Tessier and colleagues [43] divided the sediment and heavy metal in soils into five fractions: exchangeable, carbonate, manganese oxides, organic matter bound, and residual. The European Community Bureau of Reference (BCR) divides heavy metal speciation into acid soluble/exchangeable, reducible, oxidizable, and residual speciation [44]. In recent years, the BCR criteria have been widely used; thus, BCR was chosen to analyze the metal speciation in this study.

3 Results and Discussion

3.1 Removal rate of heavy metals

3.1.1 Removal rate of heavy metals without acidification and with the continuous power supply

Under the continuous power supply, the moisture and heavy metals in the sludge were driven by the electric field and migrated from the interior of the sludge to the plate and thus were completely removed from the sludge [45,46]. This experiment was conducted under the Group A experimental conditions. The removal rates of the five metals without acidification are shown in Fig. 2. When the voltage increased, the removal rate increased and reached its highest value at 50 V. The removal of the different metal speciation showed similar behaviors, and their overall concentrations decreased with increasing voltage, which was in agreement with the results reported by Maketon [47]. Overall, the removal rates of Pb and Cr were higher than those of Cd, Zn and Cu.

During the dehydration stage of electroosmosis, the acidic and oxidizing

conditions produced by the electrochemical reaction improved the leaching of the heavy metals. Water electrolysis is the most common redox reaction in the electrokinetic process. The oxidation reaction of water on the anode electrode generates protons (H^+), and the reduction reaction on the cathode electrode generates hydroxyl ions (OH^-) [48,49]. The H^+ accumulated near the anode compete with the heavy metal ions for adsorption sites on the surface of the sludge particles and can also change the speciation of the heavy metals, making it easier for the heavy metals to migrate, thus increasing the removal rate of the heavy metals. However, although the removal rate of the heavy metals increased with increasing voltage, the maximum removal rate was still at a low level (<20%). This may be due to the deposition of the heavy metals because of the OH^- accumulated near the cathode [50]. Therefore, subsequent experiments were conducted to evaluate whether the preacidification with citric acid and the interrupted power supply would further improve the removal of heavy metals.

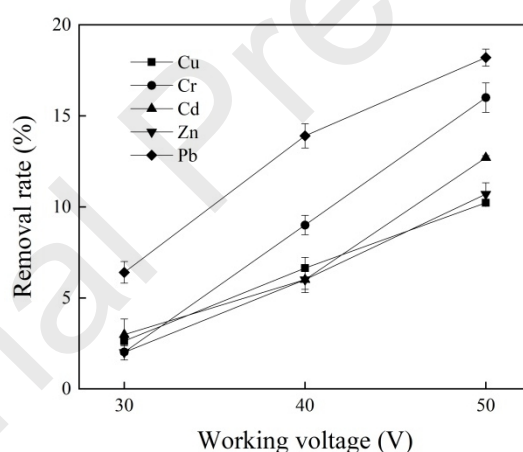**Fig. 2** Removal rate of the heavy metals without acidification and with the continuous power supply.

3.1.2 Removal rate of heavy metals with acidification and the continuous power supply

The addition of citric acid changed the pH value of the sludge, changed the reaction environment, and formed complex structures of heavy metals [51]. This experiment was conducted under the Group B experimental conditions. The removal

rates of the five metals with acidification and the continuous power supply are shown in Fig. 3.

With the continuous power supply, the removal rates of the samples with citric acid were higher than those samples that were not acidified. This was because (1) citric acid can release H^+ after entering the sludge, which can compete for active adsorption sites on the surface of the sludge particles with heavy metal ions, causing it to desorb from the surface of the sludge particles [52]; (2) the addition of citric acid reduced the pH value of sludge, leading to a rapid decrease in net negative surface charge and, thus, the soil's affinity for heavy metal ions decreased [53]; (3) the soluble organic combination with heavy metals formed by the functional groups, such as carboxyl and hydroxyl, can inhibit the readsorption of heavy metals on the surfaces of the sludge particles [52], the hydrolysis of heavy metals around the cathode under an alkaline environment caused by an electrochemical reaction was suppressed at the same time; (4) the OH^- produced by electrolysis of the water near the cathode were neutralized by the citric acid, thereby hindering the electrodeposition of the metal [51,54].

At 30 V, the removal rate increased when the dosage of citric acid increased. At 40 V, the trends in the removal rate were irregular. At 50 V, the removal rate first increased and later decreased. When the concentration of citric acid was unchanged, with the voltage increasing, the removal rate of most heavy metals increased in lower concentrations (0.03 or 0.06 mol/kg), and the tendency was irregular in higher concentrations (0.09 or 0.12 mol/kg). This meant that the citric acid had a limit on the improvement of heavy metal removal in the sludge by electrodialysis. Exceeding this limit will reduce the removal rate of the heavy metals.

The coordination ability of the citric acid with the heavy metal ions was strongly dependent on the pH value. Within a certain range, major forms of citric acid changed from H_3L, H_2L^-, and HL_2^- to L_3^- as the pH value increased. HL_2^- and L_3^- always showed greater chelating ability with the heavy metals than H_3L and H_2L^- [55]. A high citric acid concentration and voltage may cause the low pH value of the system. The chelating ability of the citric acid to the heavy metals was weak, which caused heavy metals to be readsorbed by the sludge or precipitated by hydrolysis after migrating to the vicinity of the cathode, making the removal rate of the heavy metals show little change. The higher the citric acid concentration, or the higher the voltage, the more

pronounced is this phenomenon observed (Fig. 3).

Meanwhile, some studies [55,56,57] have reported that the effect of the pH value on the desorption of heavy metals from sludge is quite different between different heavy metals. This phenomenon may not be controlled by a single mechanism, for example, formation of compounds between metals and hydroxyl groups, aluminum hydrolysis at the exchange sites, competition about adsorption sites and acid-catalyzed dissolution reactions, all of which can occur [58]. Therefore, the optimum conditions are different for different heavy metals.

The peaks of removal rates of most heavy metals under experimental condition Group B were obtained with 50 V and with the low citric acid concentration (Table 3). Therefore, the optimal conditions involved a voltage of 50 V and a citric acid concentration of 0.03-0.09 mol/kg. Compared with the experiments without acidification, under the optimum conditions, the removal rates of five heavy metals increased by 4.99%-30.26% (Table 3). Similar trends are also mentioned in the relevant literature [51].

Table 3 Peaks of heavy metals removal rates under experimental conditions Group A and Group B and their difference.

Heavy metals	Peaks in Group A (%)	Peaks in Group B (%)	Difference of peaks between Group A and Group B (%)
Cu	10.22	35.42 (0.09 mol/kg, 40 V)	25.20
Cr	16.00	39.53 (0.06 mol/kg, 50 V)	23.53
Cd	12.7	27.52 (0.09 mol/kg, 50 V)	14.82
Zn	10.70	15.69 (0.09 mol/kg, 50 V)	4.99
Pb	18.20	48.46 (0.03 mol/kg, 50 V)	30.26

Contents in brackets are the conditions when the peaks are reached.

Compared with other studies [39,40,51], the removal rate of the heavy metals was slightly lower. However, in our experiments, sludge dewatering and heavy metal removal are carried out simultaneously. In addition, compared to 5 d [39,51] and 14 d [40], our experiment was only 6 min. This very short time had a great advantage in improving efficiency. Bioleaching is another promising treatment for removing heavy metals from sewage sludge [59], and acidification with citric acid and electrodialysis

also provide a great time advantage compared to the bioleaching experimental time: 12 d [60], 15 d [61] and 20 d [8].

The removal of heavy metals using electroosmosis was accompanied by dehydration. Yu [62] showed that with the progress of electroosmotic dehydration, the water content of the sludge near the anode gradually decreased, and the resistance gradually increased. When the water content fell to a certain range, the sludge resistance can increase dramatically, which caused increasingly difficult electroosmotic dehydration. The addition of the citric acid increased the conductivity of the sludge and thus accelerated this phenomenon. The sharp increase in the resistance also caused a rapid decay of the current, which was detrimental to the removal of heavy metals. The higher the voltage, the higher the citric acid concentration, and the more obvious this phenomenon is. This was also the reason for the decrease in the heavy metal removal rate at high voltage or high citric acid concentration. Therefore, the interrupted power supply experiment was conducted to evaluate its effect on the heavy metal removal rate.
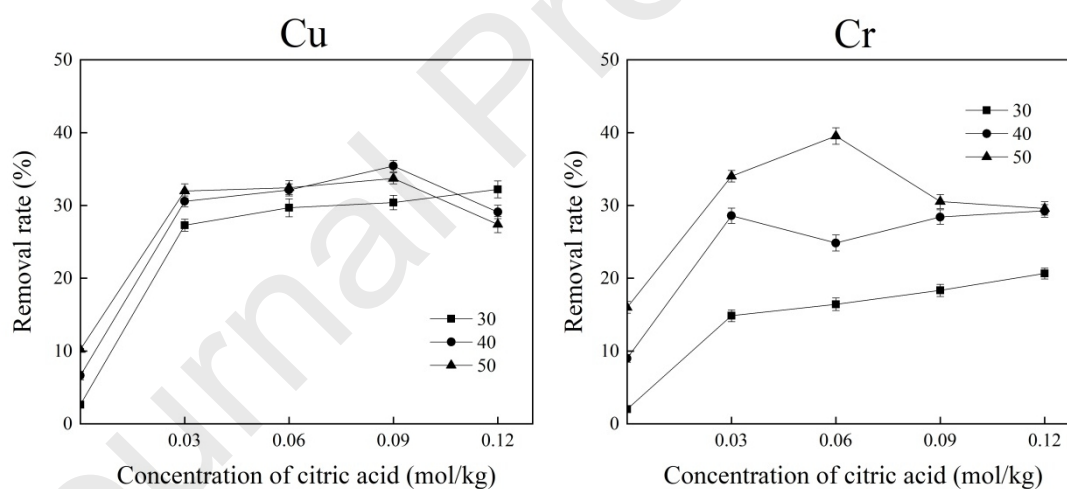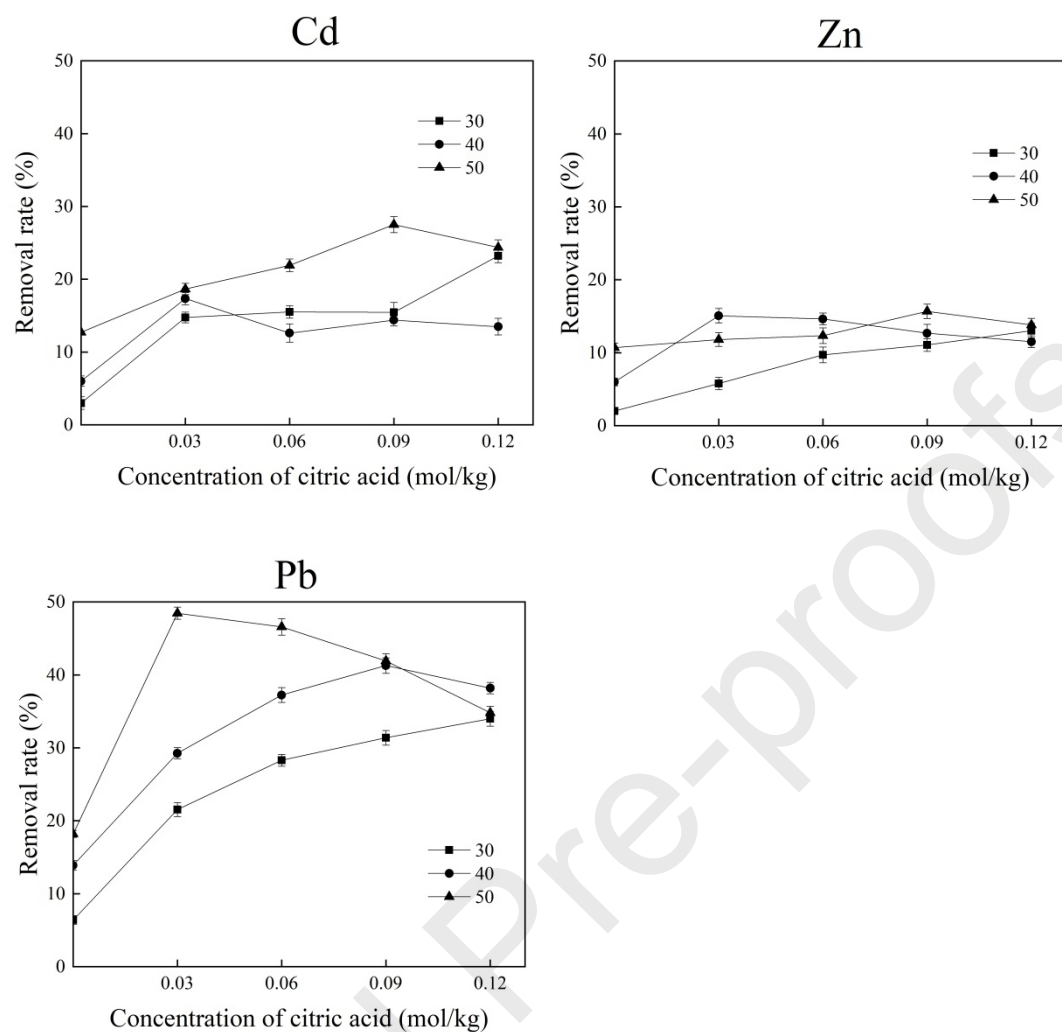
Fig. 3 Removal rate of heavy metals with acidification and the continuous power supply.

3.1.3 Removal rate of heavy metals with acidification and the interrupted power supply

This experiment was conducted under the Group C experimental conditions. The removal rates of heavy metals with acidification and the interrupted power supply are shown in Fig. 4. Comparing Fig. 4 and Fig. 3, it was observed that the interrupted power supply improved the removal rate of heavy metals as a whole. This was because heavy metal removal under electroosmosis was accompanied by dehydration. Under continuous dehydration conditions, the sludge near the anode was rapidly dried

and cracks appeared. The bubble films enwrapped the electrode, resulting in increased sludge resistance, and the current decayed rapidly, which was insufficient to promote the moisture near the cathode to move toward the cathode. These factors all had a negative impact on the removal of heavy metals. However, the interrupted condition mitigated this phenomenon by allowing moisture that has not been completely removed from the sludge to reflow into the sludge, thereby reducing the sludge resistance and dissolving the heavy metals in the water. When power was supplied again after the interruption, the heavy metals were removed from the sludge along with the water driven by the electricity, which further reduced the amount of heavy metals in the sludge.

At 30 V, with the increase of citric acid concentration, the removal rate of heavy metals increased (except Cu); at 40 V, with the increase of citric acid concentration, the removal rate of heavy metals increased first and then decreased (except Cd); at 50 V, with the increase of citric acid concentration, the removal rate of heavy metals had no obvious regulation. When the citric acid concentration was unchanged, in most cases, the increased voltage caused the removal of heavy metals to increase first and then decrease or continue to decrease. The results showed that with the interrupted power supply, the optimal conditions involved a voltage of 40 V and a citric acid concentration of 0.06 to 0.09 mol/kg (Table 4).

Table 4 Peaks of heavy metals removal rates under experimental conditions Group C.

Heavy metals	Peaks in Group C (%)
Cu	39.65(0.06 mol/kg, 40 V)
Cr	23.29(0.06 mol/kg, 40 V)
Cd	42.36(0.09 mol/kg, 40 V)
Zn	22.09(0.09 mol/kg, 40 V)
Pb	40.44(0.09 mol/kg, 40 V)

Contents in brackets are the conditions when the peaks are reached.

As described in section 3.1.2, a low pH value near the anode was detrimental to the removal of heavy metals by electroosmosis in the addition of citric acid. The interrupted power supply slowed down the attenuation of the current, making the

current of the entire system larger compared with the continuous power supply. A larger current resulted in a more severe electrochemical reaction, causing a lower pH value near the anode and a higher pH value near the cathode compared with those for the continuous power supply. Therefore, the optimum condition for the interrupted power supply was 40 V instead of 50 V.

Compared with the continuous power supply, the interrupted condition was conducive for the removal of Cu, Cd, and Zn. The removal rate of Cu increased most at 40 V and 0.06 mol/kg, from $32.13 \pm 0.83\%$ to $39.65 \pm 0.82\%$. The removal rate of Cd increased most at 40 V and 0.09 mol/kg, from $14.39 \pm 0.77\%$ to $42.36 \pm 1.01\%$, and in other conditions, the removal rates increased to greater than 10%. The removal rate of Zn increased most at 40 V and 0.12 mol/kg, from $11.51 \pm 0.80\%$ to $20.94 \pm 0.09\%$, but decreased slightly under certain conditions. However, the removal rates of Cr and Pb were lower in the interrupted power condition than in the continuous power condition. The reduction was not significant at the low voltage and low acid concentration but was significant at high voltage. The removal rates of Cr and Pb decreased most at 50 V and 0.06 mol/kg, from $39.53 \pm 1.14\%$ to $20.72 \pm 1.08\%$ and $46.59 \pm 1.13\%$ to $27.12 \pm 0.13\%$, respectively.

These data showed that Cu, Cd and Zn were satisfactorily removed by the interrupted power supply from the whole, and the removal rate of Cd was the highest. The type of power mode had no significant effect on Cu, indicating that the acid concentration may be a major factor in improving its removal rate. For Cr and Pb, the interrupted power supply was adverse to their removal, especially at high voltage and high acid concentrations. The reason for this phenomenon may be related to the transformation of metal speciation and the stability of heavy metals in conditions without an electric current.

Many electrochemical reactions occur simultaneously during the electrodialysis of the sludge. Moreover, the large specific surface area of the sludge provides a number of sites for the interactions of sludge particles with the heavy metals. These interactions are sludge specific, heavy metal specific, dynamic, reversible and pH dependent. The coupling of electrochemical reactions with sludge-metal interactions makes the electrodialysis process extremely complex [49]. The pH change and the complexation reactions associated with the addition of citric acid also add to the complexity. Simultaneously, the migration of heavy metals during electroosmosis was

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also a result of the transfer competitions between different free metal ions, metal complexes and metal chelates [63]. Other metal cations and salts present in the sludge can also affect the speciation of heavy metal ions. Therefore, heavy metal removal rates using electroosmotic leaching after the addition of citric acid were affected by various mechanisms. The differences between heavy metals were obvious, so the regulations remained to be further studied.
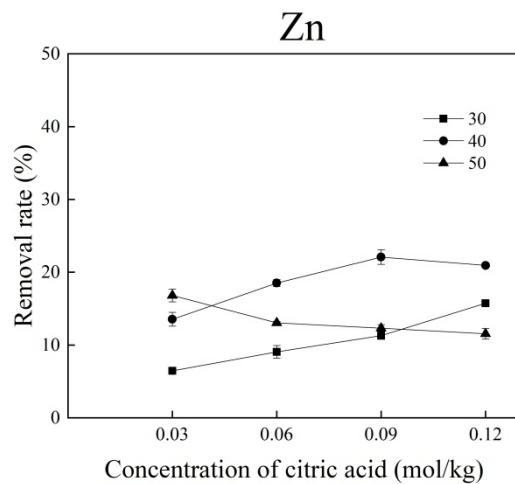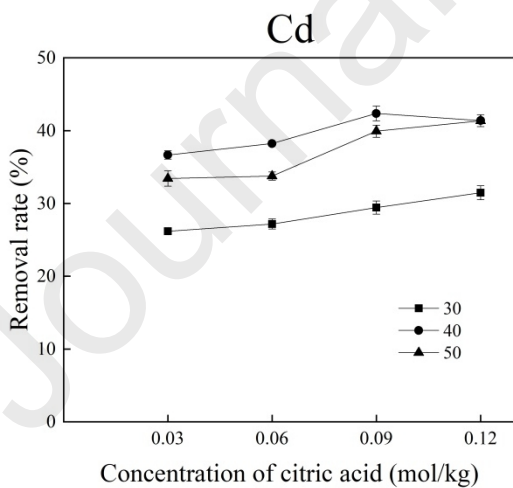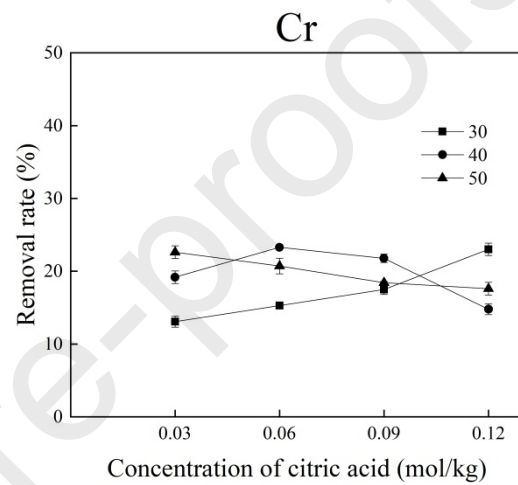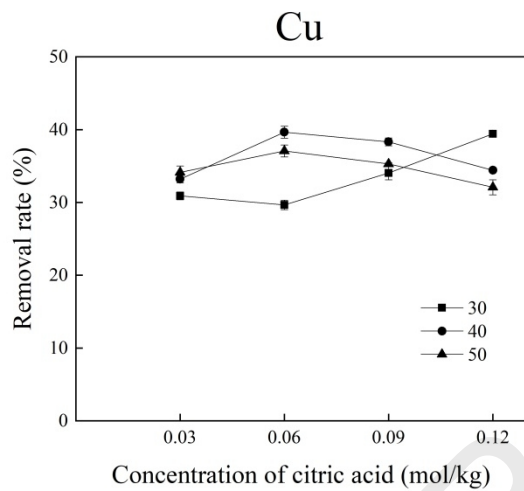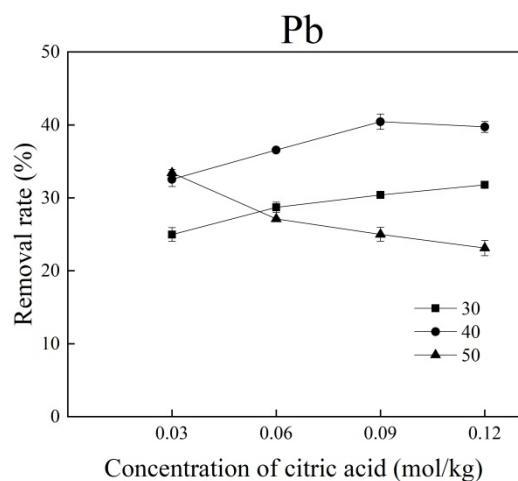
Fig. 4 Removal rate of heavy metals with acidification and the interrupted power supply.

3.2 Analysis of heavy metal speciation under different conditions

According to the results above, the metal removal rate was the highest with voltages of 40-50 V and with citric acid concentrations of 0.06-0.09 mol/kg. Meanwhile, the low voltage and high concentration of acid will be more conducive to the removal of most metals and to energy savings [64]. Therefore, a voltage of 40 V and an acid concentration of 0.09 mol/kg were chosen to analyze the heavy metal speciation in this chapter. The operating conditions are shown in Table 5. The processes were the same as those in Chapter 2.4.

Table 5 Operating conditions for heavy metal speciation.

Experimental conditions	Voltage (V)	Concentration of citric acid (mol/kg)	Power supply mode
Group 1	40	/	Continuous power supply
Group 2	40	0.09	Continuous power supply
Group 3	40	0.09	Interrupted power supply

The contents of Cu, Cr, Cd, Zn, and Pb in the sludge were determined by using high-pressure microwave digestion coupled with atomic absorption spectrophotometry. The tested samples were obtained from four parts of the sludge：sludge after dewatering, sludge liquor, suspended solid in sludge liquor, and sludge on the cathode mesh. The contents of each sample are shown in Table 6. The heavy metal speciation could only be deduced by the speciation of metals in the samples because heavy metal speciation was changed by citric acid and electricity during the whole process.

Table 6 Heavy metal contents of each part of the sludge.

Experimental conditions	The source of test samples	Cu (mg)	Cr (mg)	Cd (mg)	Zn (mg)	Pb (mg)
Group 1	sludge after dewatering	6.89	11.67	0.83	21.87	4.08
	sludge liquor	5.96	11.21	0.70	19.91	4.49
	suspended solid in sludge liquor	0.14	0.23	0.02	0.44	0.08
	sludge on cathode mesh	0.21	0.38	0.03	0.69	0.13
Group 2	sludge after dewatering	3.83	7.83	0.71	17.28	2.35
	sludge liquor	9.36	15.56	0.90	25.39	6.22
	suspended solid in sludge liquor	0.09	0.18	0.02	0.41	0.06
	sludge on cathode mesh	0.18	0.39	0.03	0.74	0.12
Group 3	sludge after dewatering	3.12	6.94	0.35	9.46	2.58
	sludge liquor	9.85	16.14	1.18	32.27	5.85
	suspended solid in sludge liquor	0.09	0.20	0.01	0.28	0.08
	sludge on cathode mesh	0.24	0.49	0.04	0.78	0.17

The heavy metal speciation in the sludge after dewatering was analyzed using the BCR method. Heavy metals in acid soluble/exchangeable speciation easily dissolve in water. Metals in the reducible speciation are mainly bound to carbonates and bound to

Fe-Mn oxides. The carbonate bound metals are easily dissolved and released under acidic conditions, and the metals bound to Fe-Mn oxides are released when the redox potential is changed. Heavy metals in acid soluble/exchangeable and reducible speciation are unstable. They have a certain impact on the environment and are easily removed by electroosmosis. Because the citric acid and electric current constantly affected the sludge, some of the metals in the sludge liquor were in the acid soluble/exchangeable speciation, and some were in the reducible speciation. It was difficult to distinguish the ratio of metals in the acid soluble/exchangeable speciation and reducible speciation. Therefore, the follow-up analysis combined metals in the acid soluble/exchangeable and the reducible speciation and named this the easily removed speciation. The suspended solids were the products of the matter in the sludge liquor, and the heavy metal speciation was the same as that in the sludge liquor. The sludge in the cathode mesh, which was left in the cathode because of pre-compaction, only accounted for 2% of the total sludge. Furthermore, the heavy metal speciation of the sludge in the cathode mesh was the same as that in the sludge after dewatering because it was present throughout the experiment.

Through the above analysis, the content of the heavy metal speciation in the sludge was obtained under different conditions. To determine the effect of acid concentration and voltage on the change in heavy metal speciation, a bar chart of the heavy metal speciation was created and is shown in Fig. 5. The result for each speciation was the sum of the corresponding speciation of the four parts sludge.

Fig. 5 shows that with a voltage of 40 V and without citric acid, the ratio of the easily removed speciation of each metal increased. The increase in the easily removed speciation of Zn and Cu was over 40%. There are similar trends in the corresponding literature [51,65,66]. Simultaneously, the ratio of metals in the residual speciation decreased significantly. The change in the ratio of heavy metals in the oxidizable speciation was small and irregular, and the largest change occurred in Cd, which was only 5.33%. This indicated that most of the easily removed speciation after the application of voltage were converted from the residual speciation. The cause of this phenomenon may be that (1) the pH value of the system was lowered due to the electrochemical reaction after energization; (2) under the continuous voltage, the steady state of the residual speciation was destroyed and transformed into acid soluble/exchangeable speciation. Due to the different properties of heavy metals, the

changes after electrolysis were not the same.

As an organic acid, citric acid can input H^+ into the system to change the speciation of the heavy metals. With a continuous voltage of 40 V, the ratio of metals in easily removed speciation increased with a citric acid concentration of 0.09 mol/kg. The easily removed speciation of Cu and Cr increased the most, with increases of 23.55% and 17.93%, respectively. The residual speciation decreased steadily. The change in oxidizable speciation was larger than that without the acid addition, and the ratio of the oxidizable speciation of most heavy metals (except Zn) was lowered. It can be inferred that the addition of citric acid can further reduce the pH value of the system and transform the heavy metals from the residual speciation to the easily removed speciation. Moreover, the heavy metal ions can also compete with organic matter in the sludge through chelation, making partially oxidizable speciation convert to easily removed speciation.

Under the same acid treatment, different modes of power supply had different effects on the metals. When exposed to the interrupted power supply, compared with the continuous power supply, the ratio of the metals in an easily removed speciation for Zn, Cu, and Cd increased, while that of Cr and Pb decreased. For the ratio of metals in the residual speciation, Cu, Cr, and Cd changed slightly and that of Zn decreased, while that of Pb increased. For the interrupted power supply, different metals had different changes (Fig. 5). For Cu and Cr, the ratio of each speciation changed little, although the ratio of easily removed speciation increased; for Cd, the residual speciation and the oxidizable speciation continued to transform into easily removed speciation; for Zn, the ratio of oxidizable speciation increased slightly; for Pb, the ratio of easily removed speciation decreased, and the ratio of residual speciation increased, indicating that the interrupted power supply caused partial easy removal of Pb into residual speciation. The different changes in the different heavy metals may be related to the change in the pH value, as well as the stability of different speciations of different heavy metals in the absence of a current.

In summary, under the conditions of energization and citric acid, the ratio of the easily removed speciation gradually increased, while the residual speciation and the oxidizable speciation gradually decreased. This indicated that easily remov speciation were formed by the conversion of the residual speciation and the oxidizable speciation under the conditions of energization and citric acid. This may be beneficial for the
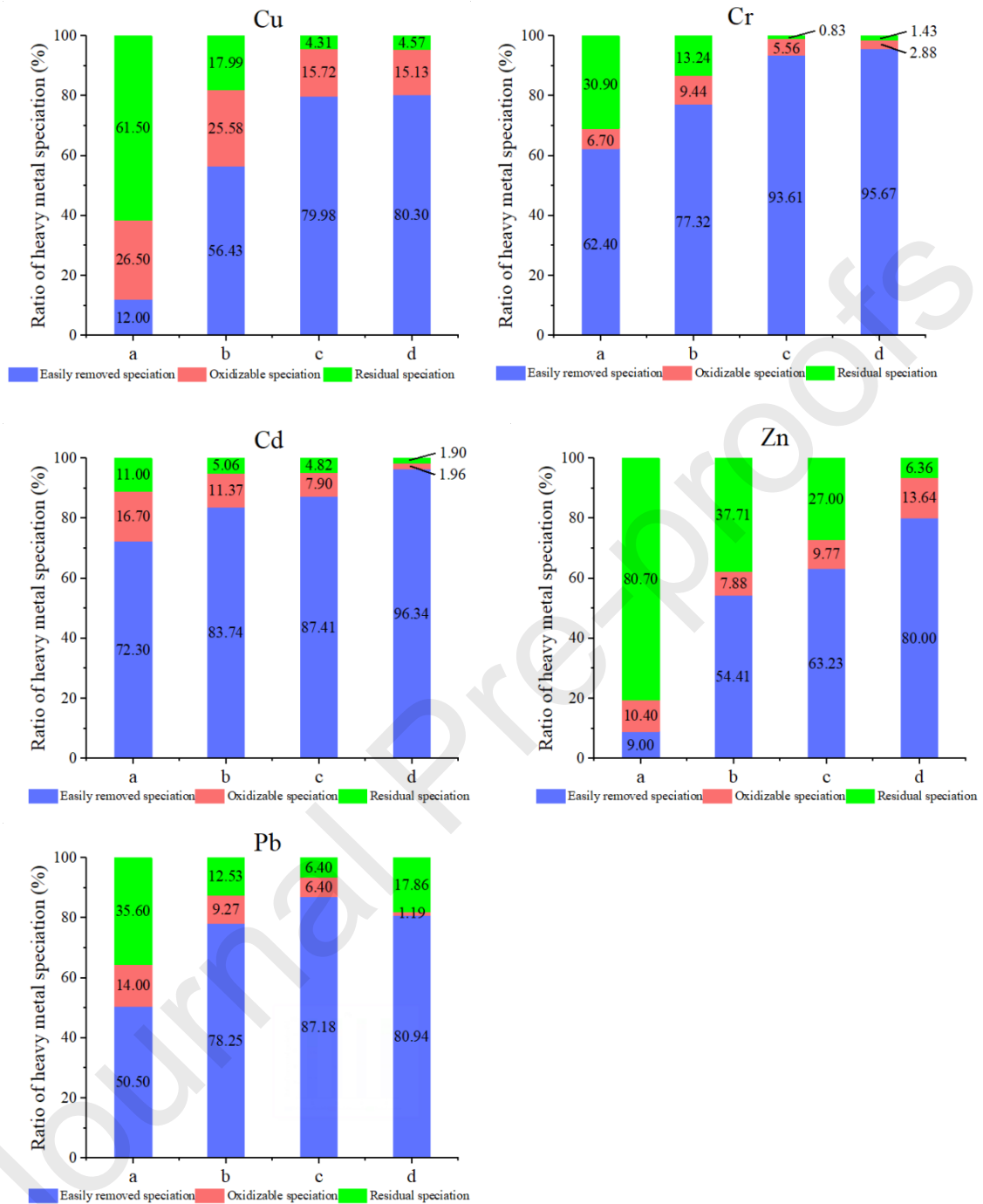
removal of heavy metals.

Fig. 5 Ratios of heavy metal speciation.

a. Initial sludge **b.** 40 V continuous power supply, without citric acid **c.** 40 V continuous power supply, citric acid of 0.09 mol/kg **d.** 40 V interrupted power supply, citric acid of 0.09 mol/kg

3.3 Relationship between heavy metal speciation and the removal rate

The effects of the citric acid treatment, voltage strength, and mode of the power

supply on heavy metal removal and heavy metal speciation under optimal conditions were analyzed. It can be speculated that the removal rate of heavy metals under electroosmosis and acid addition was closely related to the easily removed speciation. Therefore, this chapter expounds the relationship between heavy metal speciation and removal rate. Using the operating conditions of chapter 3.2 as an example, the rate of removal and ratio of metals in the easily removed speciation are shown in Fig. 6.
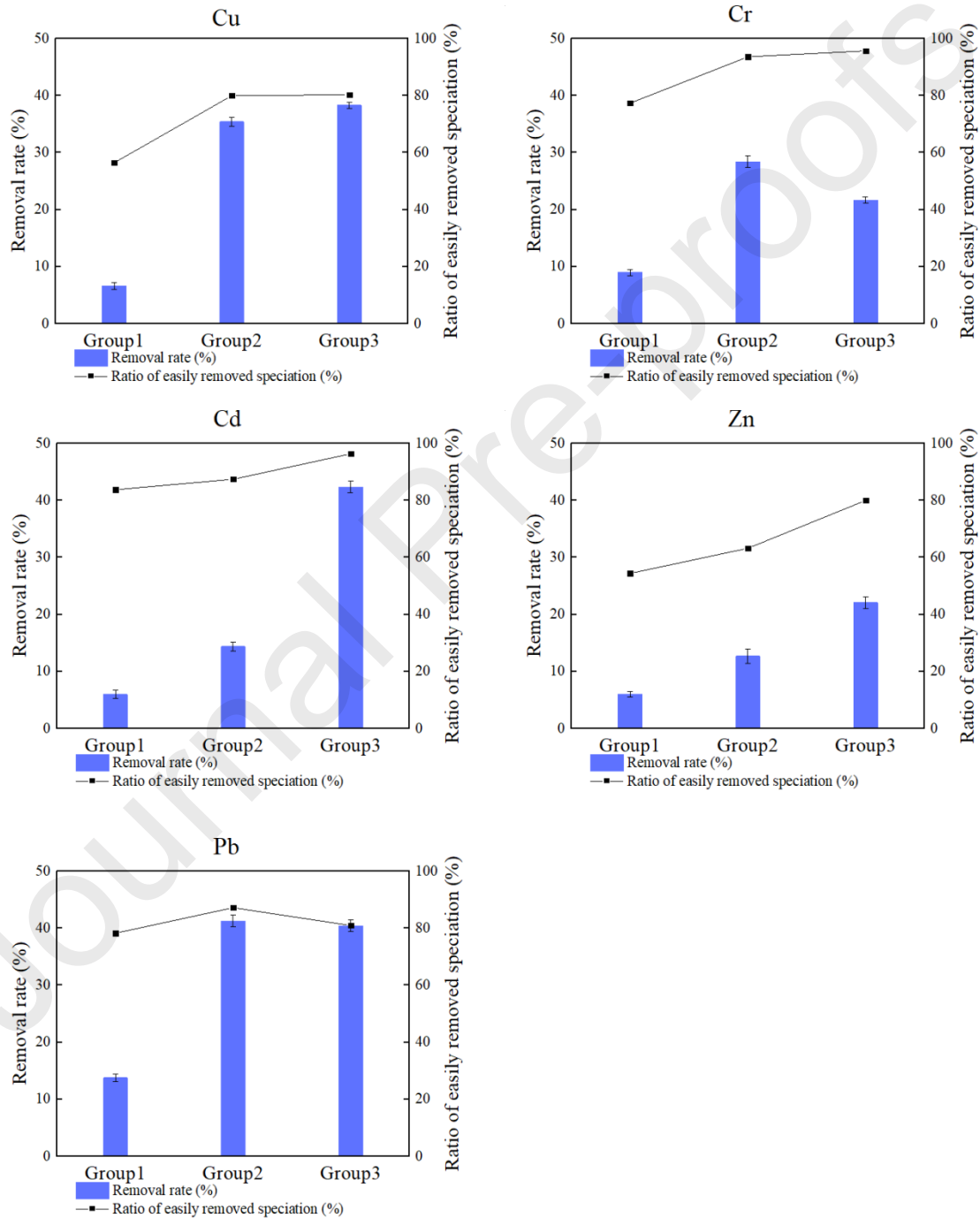

Fig. 6 Removal rates and the easily removed speciation under different conditions.

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Fig. 6 shows that the ratio of the easily removed speciation and the removal rates were the same; that is, when the ratio of the easily removed speciation increased, the removal rates also increased (except Cr under the interrupted power supply). The results showed that the increase in the ratio of easily removed speciation helped to improve the removal rate. Combined with 3.1 and 3.2, it can be determined that electroosmosis and citric acid increased the removal rate of heavy metals by increasing the amount of easily removed speciation, which made heavy metals dissolve in the water and be removed from the sludge with water. However, there was a difference between the ratio of easily removed speciation and the removal rate, which occurred between 40.5% (Cd, Group 1) and 77.74% (Pb, Group 3) for different metals and different conditions. This indicated a general phenomenon in which a significant portion of the easily removed metals were eventually left in the sludge instead of removed. This may be due to the following reasons. (1) In the vicinity of the cathode, the electrochemical reaction produced an alkaline environment, and heavy metals formed insoluble precipitates due to hydrolysis. Therefore, they cannot be driven by the current and remain in the sludge. Different heavy metals had different degrees of hydrolysis at a particular pH value, resulting in different differences; (2) A large number of studies have shown that the adsorption of heavy metals by sludge is attributed to extracellular polymeric substances (EPS) [67]. The main mechanism by which EPS adsorbs heavy metals is electrostatic interactions and complexation [68]. Generally, the ability of EPS to adsorb metals was stronger at a higher pH value [51]. The high pH environment near the cathode enhanced the adsorption of heavy metals by EPS, making it difficult to desorption. (3) Under the conditions of citric acid addition, citric acid had different chelation abilities to different metals in the different environments, which was also the reason for the difference.

For each heavy metal, there was also a difference in the removal rate and the ratio of easily removed speciation between the continuous power supply with the acid and the continuous power supply without the acid and between the interrupted power supply with the acid and the continuous power supply with the acid. This difference reflected the effects of the citric acid and the interrupted power supply. The difference is shown in Table 7.

Table 7 Difference of in the removal rates of Group 2 & Group 1 and Group 3 & Group 2 and the ratio of easily removed speciation.

Heavy metals		Difference of Group 2 and Group 1	Difference of Group 3 and Group 2
Cu	The removal rate (%)	28.78	2.90
	The ratio of easily removed speciation(%)	23.55	0.32
Cr	The removal rate (%)	19.41	-6.63
	The ratio of easily removed speciation(%)	16.29	2.06
Cd	The removal rate (%)	8.39	27.97
	The ratio of easily removed speciation(%)	3.67	8.93
Zn	The removal rate (%)	6.68	9.41
	The ratio of easily removed speciation(%)	8.82	16.77
Pb	The removal rate	27.48	-0.84
	The ratio of easily removed speciation(%)	8.93	-6.24

Table 7 indicates that, for Cu, Cr and Pb, the addition of acid significantly increased the removal rate and the ratio of easily removed speciation compared to Zn and Cd. The addition of acid was the main factor to improve the removal rate of these three metals. For Cd and Zn, the interrupted power supply can increase the removal rate and the ratio of easily removed speciation more effectively than citric acid. For Cr and Pb, the interrupted power supply reduced the removal rate, indicating that the

interrupted power supply was not conducive to the removal of these two metals under the experimental conditions of this study, which was consistent with the conclusions in 3.1.3.

4 Conclusions

Citric acid acidification and electroosmosis can effectively improve the removal rate of heavy metals. However, when the voltage was too high or the concentration of the citric acid was too large, the pH value of the sludge can be too low, which may affect the sludge dewatering efficiency and adversely affect the removal of heavy metals. Under the experimental conditions in this study, the effect of the interrupted power supply on heavy metals was diverse due to the different properties of the different heavy metals. Therefore, it was necessary to select a suitable power supply mode according to the actual situation.

Electroosmosis and citric acid can effectively improve the easily removed speciation and reduce the residual speciation and oxidizable speciation of heavy metals. Electroosmosis and citric acid increased the removal rate of heavy metals by converting the residual speciation and the oxidizable speciation into easily removed speciation. However, a portion of the easily removed metal remained in the sludge due to hydrolysis precipitation rather than being removed; thus, the high pH value caused by the electrochemical reaction near the cathode severely hindered the removal of heavy metals. A relevant study was still needed to solve this problem before it was applied to practice.

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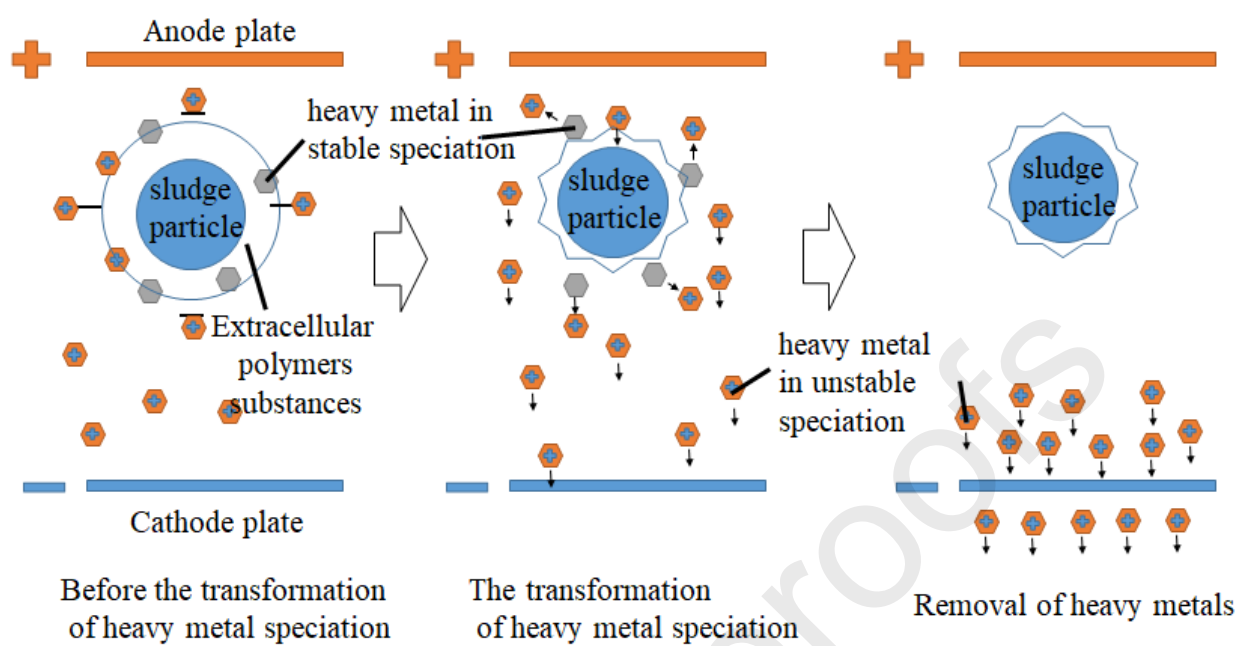
Author Contribution Statement

Ma Degang: Conceptualization, Methodology, Project administration, Funding acquisition, Supervision. Su Meizhong: Writing - Original Draft, Formal analysis, Writing - Review & Editing. Qian Jingjing: Investigation, Methodology. Wang Qian: Formal analysis. Meng Fanyi: Validation. Ge Xiaomei: Data Curation. Ye Yu: Data Curation. Song Chunfeng: Resources.

Declaration of interests

√　The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Anode plate

heavy metal in
stable speciation

sludge
particle

Extracellular
polymers
substances

Cathode plate

Before the transformation
of heavy metal speciation

sludge
particle

The transformation
of heavy metal speciation

heavy metal
in unstable
speciation

sludge
particle

Removal of heavy metals

Highlights

1. Electrodialysis can remove water and heavy metals in sludge

simultaneously.

2. Citric acid can improve the removal rates of heavy metals.

3. Interrupted power supply has different effects on different heavy metals.

4. Acidic condition is more conducive to the transformation of heavy metals to

dissolved speciation.