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Effect of Different Pretreatment Solutions on Electrokinetic Remediation of Heavy Metals from Municipal Solid Waste Incineration Fly Ash

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The presence of carbonate and alkaline oxides leads to the strong acid buffering capacity and high pH of municipal solid waste incineration (MSWI) fly ash, hindering the removal of heavy metals (HMs) during electrokinetic remediation (EKR). Acid pretreatment offers the possibility to solve this problem. In this study, four pretreatment solutions (deionized water, HNO_3, HCl and HAc) were investigated with the aim of lowering the high acid buffering capacity of MSWI fly ash. A series of laboratory scale EKR experiments were conducted with different pretreatment conditions and operating parameters. The experiment with HCl pretreatment showed the best removal of HMs. Then, an orthogonal experiment was designed to explore the optimum EKR conditions based on acid pretreatment. The results showed that the best leaching efficiencies of Pb (94.23%), Zn (89.09%), Cu (88.21%) and Cd (84.97%) were obtained after 15 d, at a voltage gradient of 2 V/cm and with the addition of 0.05 mol/L citric acid to the catholyte every day. The carbonate and alkaline oxides in fly ash were significantly reduced after the EKR treatment, as confirmed by XRD analysis. Sequential extraction of Pb, Zn, Cu and Cd indicated that the oxidizable and reducible states were converted to a more stable compound after treatment.

Keywords: Electrokinetic remediation; Acid pretreatment; MSWI fly ashes; Heavy metals; Removal efficiency; Buffering capacity

1. INTRODUCTION

Municipal solid waste is a mixed waste with a complex composition that contains a considerable amount of heavy metals (HMs). Generally, the contents are as follows: Pb 750~2500 g/t, Cu 450~2500 g/t, Cd10~40 g/t, Zn 900~3500 g/t, Cr 100~450 g/t, and Hg 2~7 g/t [1]. Incineration is an effective method for municipal solid waste treatment. HMs and inorganic salts volatilized at high temperatures chemically react to produce municipal solid waste incineration (MSWI) fly ash during the cooling process [2-5]. With the promotion of waste incineration technology, the production of MSWI fly ash is increasing [6]. The fine particle size and large specific surface area of fly ash lead to easy leaching and release of HMs, including Pb, Cu, Cd and Zn, which are highly environmentally hazardous [7]. The release of harmful substances into the environment threatens the health of the surrounding population and ecological environment if fly ash is not properly disposed [8,9].

Currently, there are two possible ways of handling fly ash: landfilling after certain treatment and processing as secondary material. The latter mainly includes the solidification/stabilization and recovery of HMs [10-12]. Common curing methods mainly include melting, sintering, room temperature curing and chemical curing. [13]. However, these technologies also have certain limitations. For example, although the leaching toxicity is effectively reduced after treatment, the content of HMs remains unchanged, and the volume of final products after treatment significantly increases, generating secondary waste [14,15]. Moreover, the final products after landfill are repeatedly washed by acidic landfill leachate over time, and there still exists a risk of releasing HMs into the environment [16].

In this context, electrokinetic remediation (EKR) technology is proposed to remove HMs from MSWI fly ash. Recently, EKR, believed to be an effective technology for removing contaminants from fine solid grains, has been widely used to remediate polluted soils and sewage sludge, which has the advantages of a significant effect, i.e., a high efficiency, low price, no secondary pollution and universal application [17,18]. Electric technology relies on external electric fields acting directly on contaminated samples. Some physicochemical reactions, including water electrolysis, electromigration, electroosmosis, and electrophoresis, occur when direct current is applied [19]. Due to water hydrolysis, the treated substances close to the anode are gradually acidified, and the cathode gradually alkalizes [20]. The acidification process is usually advantageous because the majority of metals are activated at low pH [21]. In this process, heavy metal ions are dissolved and transferred to specific areas through electromigration, electroosmosis and electrophoresis to achieve the removal of HMs [22-24].

During the waste incineration process, the alkaline medium, such as hydrated lime, is added to neutralize acidic gas, which results in a high content of carbonate and alkaline oxides in MSWI fly ash [25]. The presence of carbonate causes a strong acid buffering capacity (the acid neutralization capacity of MSWI fly ash is approximately 3.0~6.0 meq/g). It is not conducive to the formation of acid peaks during electrokinetic remediation [26]. Ouhadi et al. investigated the EKR of kaolinite contaminated by carbonate. They found that the efficiency of removing pollutants from kaolinite samples contaminated with 30% carbonate was significantly reduced to 5% compared with that without carbonate [27]. Therefore, reducing the acid buffering capacity is meaningful to the enhancement of the removal efficiency of HMs on EKR.

Currently, HNO_3 is often used as a pretreatment solution to reduce the acid buffering capacity of MSWI fly ash, and it has been considered an effective technique to enhance removal of the heavy metal ions from MSWI fly ash. Huilin Li et al. investigated the role of HNO_3 as a pretreatment solution in the EKR process, indicating that moderate acidification before the EKR experiment was conducive to the leaching of HMs in the EKR process, and increased the amount of heavy metal ions migration [28]. However, it is reasonable to consider that pretreatment with other acids also has obvious potential for the treatment of MSWI fly ash. Gordon C. C. Yang et al. obtained excellent results using HAc as the cathode reservoir fluid for the treatment of silt loam soil [29]. Furthermore, Anwar Ahmad investigated washing metal-contaminated soils with 0.1 mol/L HCl, which showed some promise as a remediation technique, rapidly and effectively removing some HMs (e.g. Cd, Pb, Zn and Ni) from contaminated soils [30]. In this study, the effect of pretreatment with different acids on the EKR of MSWI fly ash was investigated.

The study systemically discussed the influence of different pretreatment solutions on HMs removal during EKR process and the optimum operating parameters based on acid pretreatment. In this study, we have discussed (a) the controlled electrokinetic remediation of MSWI fly ash pretreated by different pretreatment solutions (deionized water, HNO_3, HCl, HAc), (b) the effect of pretreatment solution concentration on HMs removal, and (c) the optimal experimental parameters of EKR on the basis of acid pretreatment. The developments of current and pH were recorded during the electrokinetic process. Furthermore, BCR sequential extraction and X-ray diffraction (XRD) were performed to explore the reinforcement mechanism of fly ash in the acid-pretreated EKR system.

2. EXPERIMENTAL

2.1. Materials

The MSWI fly ash samples were collected at the TongXing Waste Incineration Power Generation Plant, Chongqing, China. MSWI fly ash samples were dried at 105 °C for 12 h and sieved through 200 mesh sieves.

2.2. Apparatus

EKR experiments were carried out in a rectangular reactor (Fig.1). The rectangular reactor was separated into three chambers: a cathode chamber, an anode chamber and a sample chamber (10 cm×7 cm×8 cm, L×W×H). The sample chamber was equally divided into three regions (I, II, III) from anode to cathode. The cathode and anode chambers were separated from the fly ash samples by a 0.74 mm nylon mesh. The anode and cathode were titanium plate and stainless steel plate connected to a DC power supply. The electrolyte was deionized water for all experiments. The sample pH and system current were measured every 12 h during EKR. After the EKR treatments, the fly ash in three sample regions was collected for further analysis. All the experiments in this study were carried out in a fume hood.

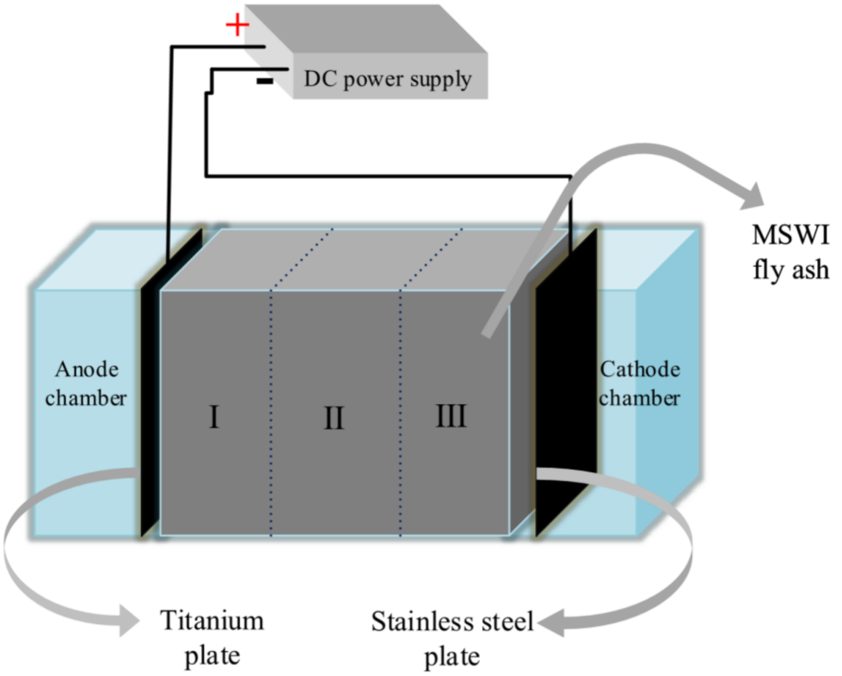

Figure 1. Electrokinetic remediation experimental setup.

2.3. Experimental work

Before EKR, the fly ash samples were pretreated with four different pretreatment solutions (deionized water, HNO_3, HCl and HAc) in a liquid-solid ratio of 4:3 (volume/mass, V/m) for 12 h, and the acid concentration was 2 mol/L. Then, the pretreated fly ash samples were poured into the sample chamber for EKR. In the controlled experiment, EKR was carried out at a voltage gradient of 1.5 V/cm for 15 d with the only variable being the pretreatment solutions to analyze the effect of different pretreatment solutions on the removal efficiency of HMs. The controlled experimental conditions are shown in Table 1.

Table 1. Controlled experimental conditions.

Test NO.	Pretreatment			Electrokinetic remediation	
	Liquid–solid ratio (V/m)	Pretreatment solution	Soaking time (h)	Proposing time (d)	Voltage gradient (V/cm)
A1	4:3	deionized water	24	15	1.5
A2	4:3	HNO_3	24	15	1.5
A3	4:3	HCl	24	15	1.5
A4	4:3	HAc	24	15	1.5

Based on the results of the controlled experiments, the acid concentration was considered a variable factor in the single-factor experiment. The single-factor experiment aimed to evaluate the effect of acid concentration on HMs removal. The experimental layout is given in Table 2.

Table 2. The layout of the experiments with different acid concentrations.

Test NO.	Pretreatment			Electrokinetic remediation	
	Liquid–solid ratio (V/m)	Concentration (mol/L)	Soaking time (h)	Proposing time (d)	Voltage gradient (V/cm)
B1	4:3	2	24	15	1.5
B2	4:3	4	24	15	1.5
B3	4:3	6	24	15	1.5
B4	4:3	8	24	15	1.5

The orthogonal experiment was conducted to identify the optimum operating parameters in EKR based on the results of a single-factor experiment regarding concentration. The main factors in orthogonal experiment, were citric acid concentration, voltage gradient and proposing time, and the corresponding levels are listed in Table 3. During orthogonal experiment, 10 ml of different concentrations of citric acid was added on a daily basis.

Table 3. Orthogonal experimental layout (three factors with three levels, L9(3^4)) and the leaching efficiency (%) of HMs in ensuing EKR experiments.

Test NO.	Factors			Leaching efficiency			
	A[a]	B[b]	C[c]	Pb	Zn	Cu	Cd
T1	1 (0 mol/L)	1 (1 V/cm)	1 (5 d)	46.05	-12.28	-62.57	-11.32
T2	1	3 (2 V/cm)	2 (10 d)	77.76	53.29	50.13	82.69
T3	1	2 (1.5 V/cm)	3 (15 d)	82.20	61.21	58.03	72.27
T4	2 (0.05 mol/L)	1	2	86.06	55.70	49.69	82.01
T5	2	2	1	67.14	48.58	-18.52	30.99
T6	2	3	3	94.23	89.09	88.21	84.97
T7	3 (0.1 mol/L)	1	3	88.84	56.39	55.67	68.31
T8	3	2	2	85.48	63.83	45.91	85.02
T9	3	3	1	57.71	41.48	-25.57	28.71

[a] Citric acid concentration (mol/L).

[b] Voltage gradient (V/cm).

[c] Proposing time (d).

2.4. Analysis and calculation

The elemental composition of MSWI fly ash samples was confirmed by X-ray fluorescence (XRF, 1800CCDE). Based on the standardized diffraction patterns, the phases of the MSWI fly ash samples were measured by X-ray diffraction (XRD-6000, Shimadzu, Japan) and analyzed by means of professional software (MDI Jade 6.5). The speciation of the HMs was analyzed by the BCR sequential extraction procedure. The total content of HMs was determined using a combination of microwave digestion (MD) and ICP-MS (4500, Agilent, USA). The leaching toxicities of HMs in both pre- and post-experiment samples were analyzed by the leaching toxicity acetic acid buffer solution method (HJ/T300-2007). Triplicate samples were made for the above analysis. The removal efficiency and leaching efficiency of HMs in MSWI fly ash were calculated using the following formula:

$$\mathrm{y} = \frac{c_0 - c_i}{c_0} \times 100\%$$

y: Removal efficiency or leaching efficiency; c_0: Total content or leaching toxicity of HMs in the original fly ash samples; c_i: Total content or leaching toxicity of HMs in the treated fly ash samples.

3. RESULTS AND DISCUSSION

3.1. MSWI fly ash characterization

The elemental composition of the MSWI fly ash samples is shown in Table 4. The major elements in MSWI fly ash are Ca, Cl, O, Na and K. Pb, Zn, Cu and Cd are the primary HMs present in fly ash with a cumulative percentage of 1.1007% (i.e. Pb 0.2647%, Zn 0.7279%, Cu 0.0860%, Cd 0.0221%). The total contents of Pb, Zn, Cu and Cd in the original MSWI fly ash samples were 2110.13 mg/kg, 6071.54 mg/kg, 657.56 mg/kg, and 196.95 mg/kg, respectively. The leaching toxicities were 12.37 mg/L Pb, 24.03 mg/L Zn, 2.98 mg/L Cu, and 4.29 mg/L Cd.

Table 4. Semi-quantitative elemental analysis (%) of the MSWI fly ash.

Ca	Cl	O	Na	K	S	Si	Mg	Zn	Fe
36.77	23.51	20.37	7.13	5.51	2.21	1.22	0.74	0.73	0.55
Al	Pb	Ti	P	Br	Sr	Cu	Sn	Mn	Cd
0.29	0.26	0.20	0.12	0.11	0.09	0.09	0.06	0.02	0.02

3.2. Effect of pretreatment solutions on HMs removal

During pretreatment, heat release and bubbling phenomenon were observed with the addition of acid due to the presence of carbonates and alkaline oxide in the MSWI fly ash [31]. In addition, the higher the acid concentration, the more bubbles and heat were produced.

pH is one of the crucial factors affecting HMs migration during EKR. The pH development during EKR treatment is shown in Fig. 2. The high initial pH of MSWI fly ash was due to a high content of alkaline oxides, e.g., Na_2O, CaO and K_2O, consistent with the elemental composition of Ca, Na and K in the XRF result [32]. Basically, the pH trend under different pretreatment conditions is similar. A gradual increase in pH was observed in sample regions I-III. The lower pH in region I and higher pH in region III were due to the production of H^+ and OH^- at the anode and cathode, respectively. In addition, a lower pH value was observed in regions I and II in test A3 than in tests A1 and A2, which was the consequence of the weakened acid buffering capacity of MSWI fly ash caused by HCl pretreatment, and thus, the acidification of fly ash was accelerated. It was deemed to create favor conditions for metal ion desorption and migration, inducing higher HMs removal in the EKR process. However, a sudden pH change in regions II and III was seen, causing precipitation of metal hydroxides and blocking of the pores [33]. In test A4, the pH was relatively steady and fluctuated around 7 in region I. This phenomenon was mainly due to the reaction of HAc and metal ions that resulted in the generation of acetate buffer solution. This hindered the acidification of sample regions near the anode.

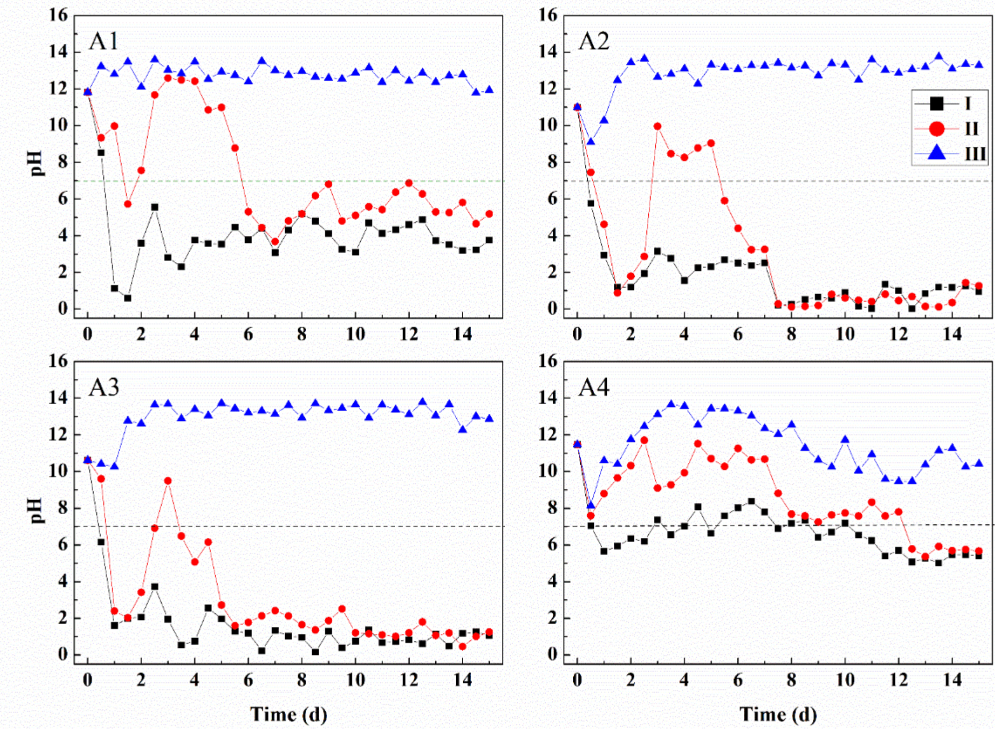

Figure 2. Change in pH versus time.

Generally, current is an index of the concentration and migration rate of removable ions in a sample chamber during EKR treatment. The development of current in the experiment with different pretreatment solutions is illustrated in Fig. 3. The high initial current was seen in the four tests due to the large amount of Ca^{2+}, Na^+ and K^+ desorption in the MSWI fly ash pore fluid during soaking pretreatment. A noticeable decrease in current occurred in the early phase. It was the result of free ion migration towards electrode chambers, causing a decrease in free ions in the sample chamber. After approximately 3 d, an increase in current was observed, which indicated the release of metal ions into the electrolyte. The release was probably the result of the dissolution of carbonates and hydroxides in MSWI fly ash caused by acidification. In the middle and later phases of the EKR, the current gradually decreased regardless of minor fluctuations because OH^- migration from the cathode caused metal ion regeneration, precipitation or adsorption on the surface of the MSWI fly ash particles, which resulted in the reduced porosity of MSWI fly ash particles near the cathode area, increasing the migration resistance of ions [34]. As shown in Fig. 3, a lower current was observed in test A4 than under the other experimental conditions. This phenomenon was in accordance with the inference that the generation of acetate buffer solution by acetic acid with metal ions hindered the acidification of the fly ash sample.

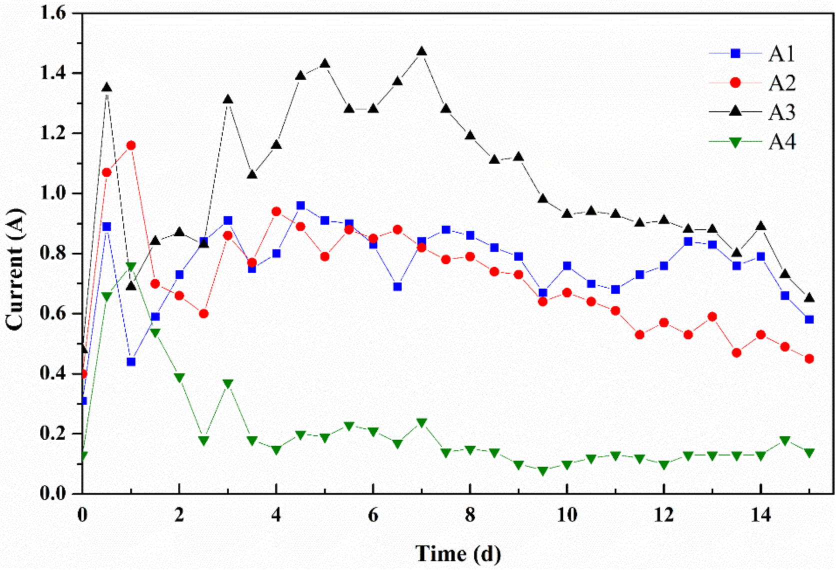

Figure 3. Change in current versus time.

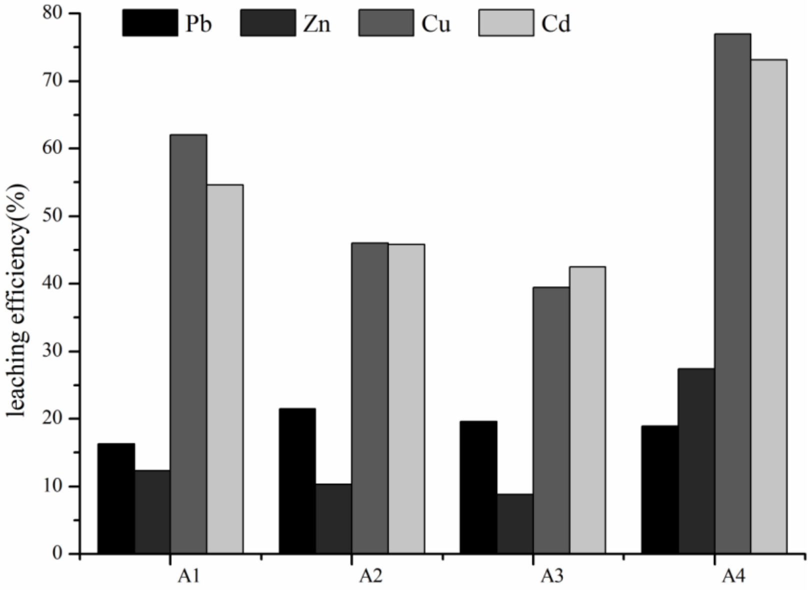

Figure 4. Effect of different pretreatment solutions on leaching efficiency.

The leaching efficiencies of Pb, Zn, Cu and Cd are shown in Fig. 4. The lowest leaching efficiencies of Zn, Cu and Cd were obtained in test A3. The primary causes are as follows. Pretreatment with HCl effectively reduced the acid buffering capacity of fly ash samples and accelerated the formation of acid peaks, which resulted in the dissolution of more metal ions into the pore fluid [28]. Moreover, desorption of metal ions is an essential part of the EKR process, and taking into account the results of removal efficiency, HCl was selected as the pretreatment solution in the following research.

3.3. Effect of acid concentrations on HMs removal

The pH development of fly ash in regions I and II, as well as the leaching efficiency under different pretreatment conditions, are shown in Fig. 5. The fly ash pH in regions I and II presented a similar trend, i.e., a gradual decrease and then maintained at a low pH after 7 d of remediation. The rate of decrease in region II was lower than that in region I because acidification started from the anode. As shown in Fig 5, the pH in B4 was significantly lower than that in B1-B3, which indicated that the higher concentration of HCl was beneficial for the sample acidification, creating a favor environment for HMs release. The leaching efficiencies of Pb, Zn, Cu and Cd in tests B1, B2 and B3 were B3 > B2 > B1. Therefore, it can be deduced that the leaching efficiency was positively correlated with the HCl concentration [28]. However, such a correlation was not observed in B4. The main reasons are as follows: a high HCl concentration significantly reduced the acid buffering capacity of fly ash during pretreatment, and the generation of H^+ near the anode caused the pH in regions I and II to decrease rapidly [35].

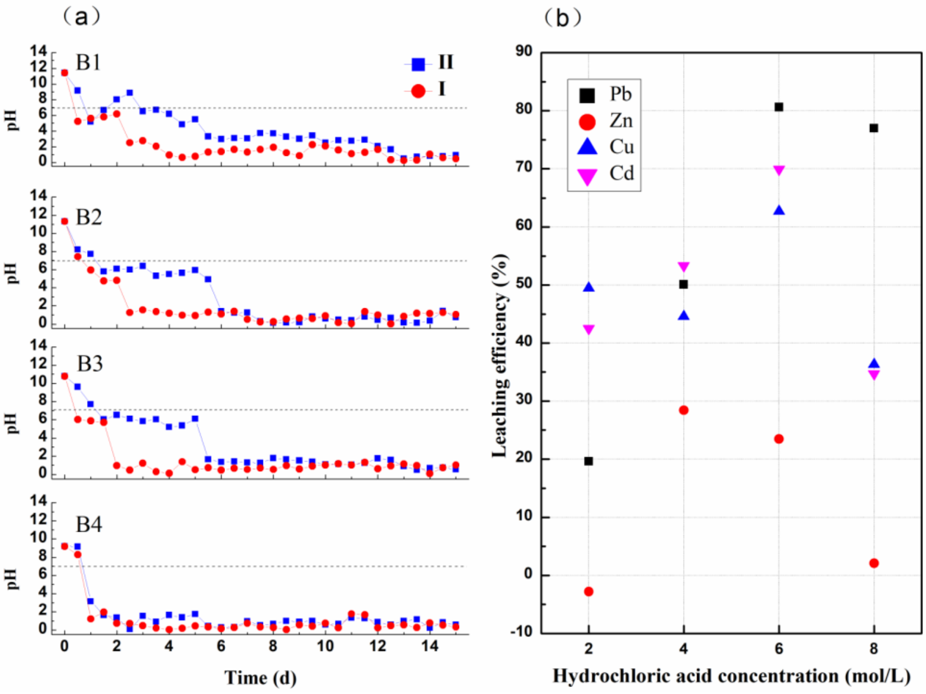

Figure 5. The pH development (a) and leaching efficiency (b) under different pretreatment conditions.

When the zeta potential was below zero, the electrolyte in the electrolytic cell migrated from the cathode to the anode under the action of reverse electroosmotic flow, which reduced the migration efficiency of HMs [36,37]. The best leaching efficiencies of Pb, Cu and Cd were obtained in test B3 (80.63%, 62.67% and 69.93%, respectively), while the best leaching efficiency of Zn was obtained in test B2 (28.44%). The leaching toxicity of Zn did not exceed the Standard for Pollution Control on the Landfill Site of Municipal Solid Waste (GB16889-2018). Hence, 6 mol/L was considered the optimal concentration of HCl pretreatment.

3.4. Orthogonal experiment

3.4.1. Change in current

The change in current as a function of time during EKR is shown in Fig. 6. In the first 1.5 d, a remarkable increase in current was observed in all tests for the following reason. Acid pretreatment reduced the acid buffering capacity of fly ash samples, resulting in a rapid pH decline in regions I and II, which made metal ions easier to release into the pore fluid. After 1.5 d, the current steadily declined, which was caused by the free ions moving towards the electrode chamber, resulting in a decrease in free ions in the sample chamber. After 9 d, the current tended to be steady. In the six tests lasting 5 d and 15 d, the current had a significant positive correlation with the voltage gradient, i.e. T9 (2 V/cm) > T5 (1.5 V/cm) > T1 (1 V/cm), and T6 (2 V/cm) > T3 (1.5 V/cm) > T7 (1 V/cm). However, in the three tests lasting 10 d, the current of T8 (1.5 V/cm) was greater than that of T2 (2 V/cm) after approximately 1 d.

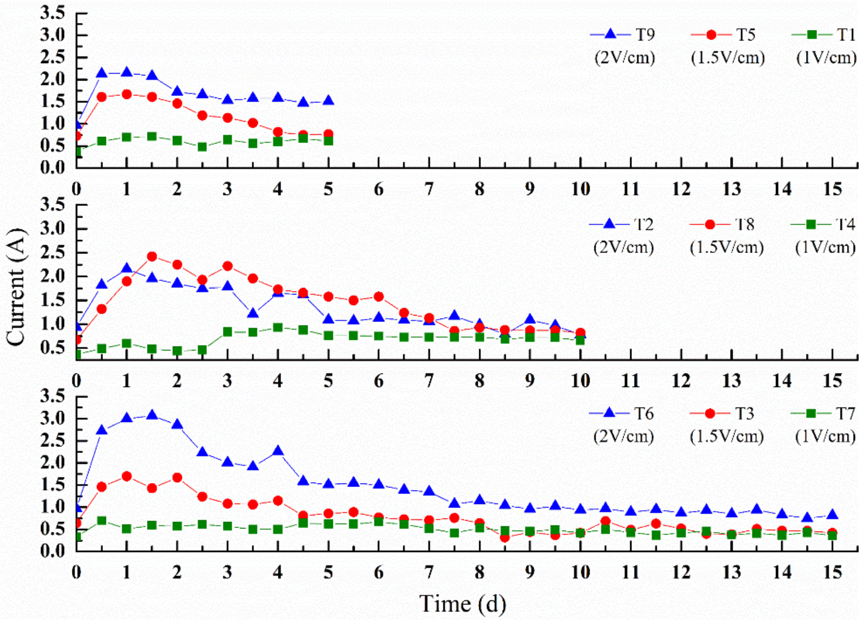

Figure 6. Change in current versus time.

This phenomenon was attributed to two factors: a greater voltage gradient and the cathode chamber without citric acid addition in test T2. In this case, a large amount of OH^- produced by electrolysis of water migrated towards the sample chamber from the cathode. It resulted in HMs readsorption on the surface of fly ash particles or precipitation, increasing the current resistance. The significance of the cathode acidification in orthogonal experiments was confirmed.

3.4.2. Leaching efficiency

The average leaching efficiency of Pb, Zn, Cu and Cd in the orthogonal experiment is listed in Table 3. In 5-d tests T1, T5 and T9, the leaching efficiency of Cu was below 0, which indicated that the Cu leaching toxicity was higher after treatment, similar to Zn and Cd in Test T1. This phenomenon was attributed to the shorter proposing time. After 5 d, the migration rate was lower than the desorption rate of heavy metal ions, which led to an increase in free heavy metal ions, resulting in higher leaching toxicity. The maximum leaching efficiencies of Pb, Zn and Cu were 94.23%, 89.09% and 88.21%, respectively, which were noted under the combination of A2B3C3 factors in test T6. The maximum leaching efficiency of Cd (85.02%) was achieved under the combination of the A3B2C2 factor level in test T8.

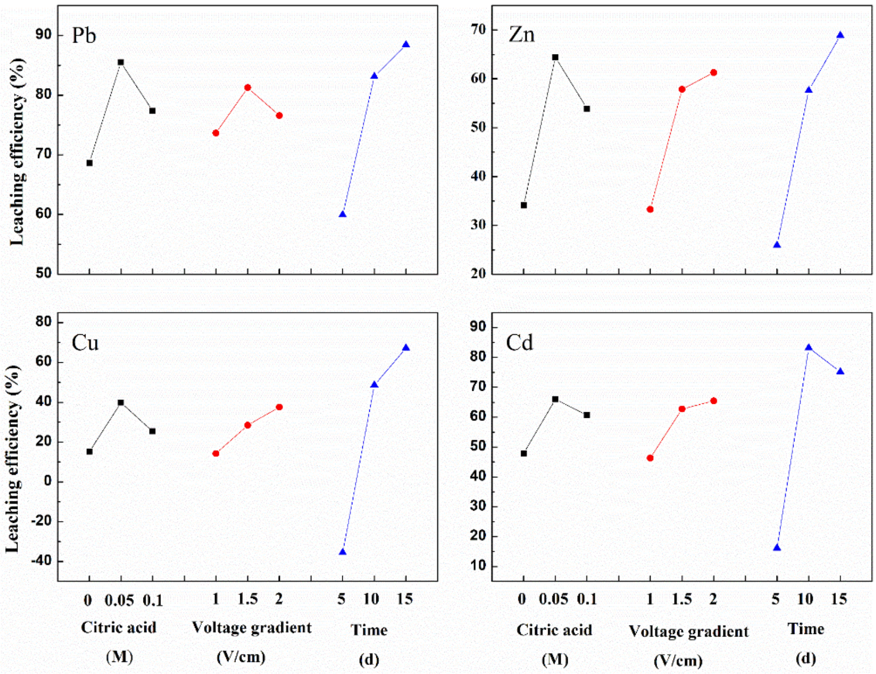

Figure 7. The mean of each factor at different levels on the leaching efficiency of Pb, Zn, Cu and Cd.

The mean of each factor was calculated based on the results of the table as shown in Fig. 7. It can be seen that the mean value of factor A was in the following order A2 > A3 > A1. This finding proved that cathode acidification with citric acid had a positive influence on the removal of Pb, Zn, Cu and Cd. The addition of citric acid effectively controlled the formation of cathode precipitation, and the organic ligand chelated heavy metal ions, reducing the adsorption of heavy metal ions in the MSWI fly ash [38]. The optimal level for citric acid concentration is A2. Furthermore, the best leaching efficiencies of Zn, Cu and Cd were achieved at the B3 level, and B2 was considered the best voltage gradient for Pb. Considering that the factor B had little effect on the leaching efficiency of Pb, the difference between B2 and B3 was insignificant. Thus level 3 (voltage gradient 2 V/cm) was chosen as the best level for factor A. The optimal proposing time regarding the leaching efficiency of Pb, Zn and Cu was achieved with the C3 level, and C2 was considered the best proposing time for leaching of Cd. However, the difference in the Cd leaching efficiency between C2 and C3 was insignificant; thus, C3 was selected as the best level for the voltage gradient. According to the above analysis, the optimum levels were obtained with a citric acid concentration of 0.05 mol/L, a voltage gradient of 2 V/cm, and a proposing time of 15 d in the acid-pretreated EKR system.

3.5. Removal mechanisms of HMs

3.5.1. Removal efficiency

Together with the removal efficiency, the distributions of HMs in the sample chamber of tests A1, A2, A3, A4 and T6 were analyzed (Fig. 8). The removal efficiency of HMs in the experiment with different pretreatment solutions was in the order HCl > HNO_3 > deionized water > HAc, which indicated that pretreatment with HCl facilitated the formation of the acid peak of MSWI fly ash during the EKR process.

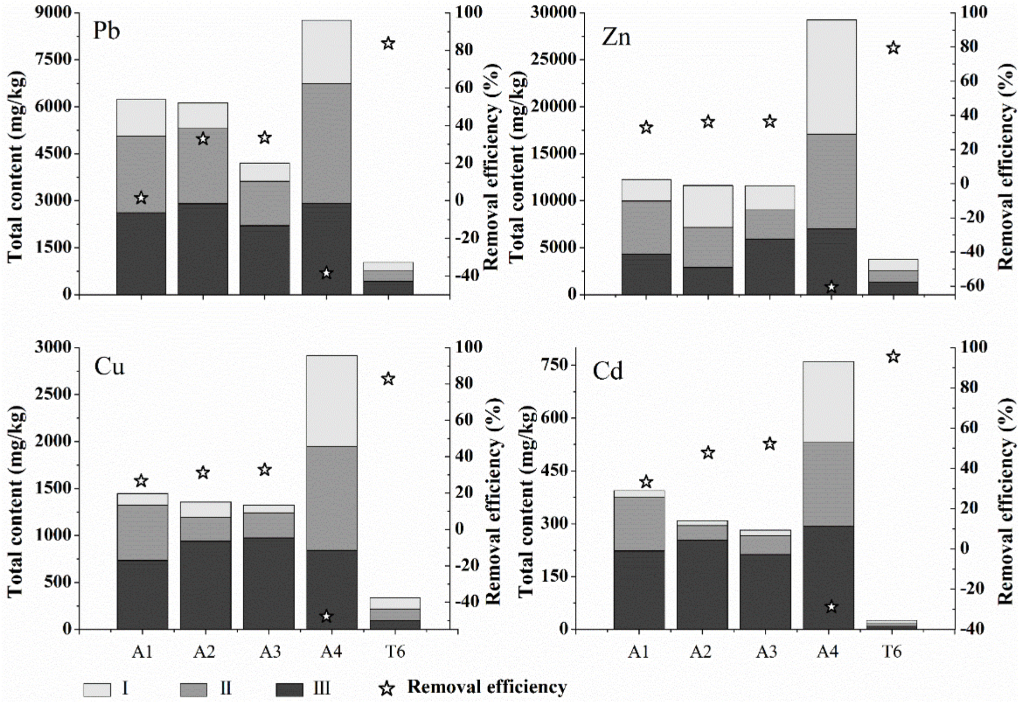

Figure 8. Removal efficiency and the distribution of HMs in different sample regions.

The distributions of Pb, Zn, Cu and Cd in tests A1, A2, A3 and A4 showed similar trends, i.e., total content decreased gradually from region III to region I, which is the result of electrolysis of water and electromigration. However, the difference in total content among the three regions in test T6 was not significant. Moreover, the total content of HMs near the cathode in test T6 was significantly lower than that in the other tests. This was due to the addition of citric acid to the cathode, which weakened the focusing effect and compactness of the sample region near the cathode during treatment. The removal efficiency of Pb (83.76%), Zn (79.43%), Cu (82.86%) and Cd (95.58%) in test T6 increased by 50.20%, 43.10%, 50.01% and 43.35% compared with that in test A3, which suggested that the decrease in MSWI fly ash acid buffering capacity by acid pretreatment and the addition of citric acid to the cathode were both beneficial to the removal of HMs in EKR.

3.5.2. Speciation and phase changes

The HMs speciation in the MSWI fly ash objectively reflects its environmental activity. In this paper, the sequential extraction of Pb, Zn, Cu and Cd in original and treated fly ash (T6) was conducted according to the BCR sequential extraction procedure. As illustrated in Fig. 9, Pb, Cu and Cd in MSWI fly ash existed mainly in the residual state.

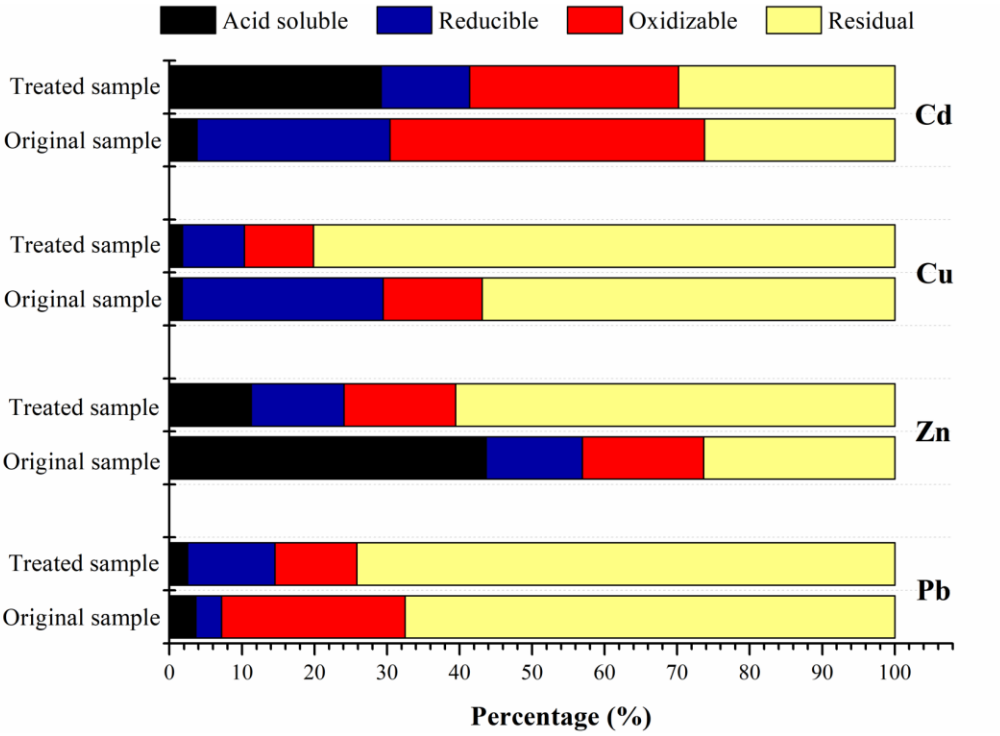

Figure 9. Sequential extraction results for speciation of Pb, Zn, Cu and Cd in original and treated fly ash.

After the EKR treatment, the residual fractions of Pb (67.51%), Zn (26.32%), Cu (56.86%) and Cd (26.24%) in the original fly ash increased to 74.15%, 60.55%, 80.16% and 29.83%, respectively, due to conversion of HMs from an extractable state into a more stable compound after treatment [28]. In addition, the decrease in reducible and oxidizable fractions further verified that acid pretreatment is an effective technique to address the HMs in these states. This inference was verified by XRD analysis (Fig. 10). Original MSWI fly ashes have $CaCO_3$ and $Ca(OH)_2$ phases. This phenomenon leads to a strong acid buffering capacity. However, these phases are not detected in the treated sample as a result of acid pretreatment. The dissolution of these species made the migration of metal ions more efficient in the sample region [39].

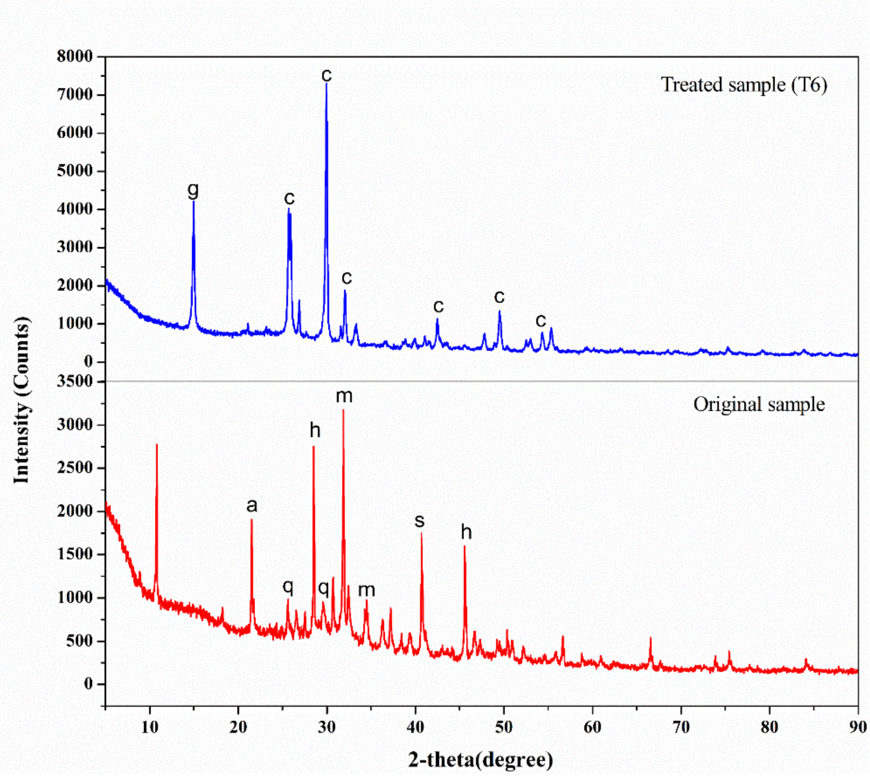

Figure 10. XRD diffractograms of original and treated MSWI fly ash samples. m-Calcium hydroxide, q-Calcite, h-Halite, s-Sylvine, a-Calcium methanolate, c-Calcium sulfate hydrate, g-Graphite.

4. CONCLUSION

This study systematically investigated the influence of different pretreatment solutions on the removal of HMs from fly ash during the EKR process. The main conclusions are as follows:

(1) The influence of different pretreatment solutions on the electrokinetic remediation of HMs from MSWI fly ash follows the order of HCl > HNO_3 > deionized water > HAc. Pretreatment with HCl facilitated the formation of the acid peak of MSWI fly ash during the EKR process.

(2) The leaching efficiency of HMs was positively correlated with HCl concentration within a certain range. The highest leaching efficiency was obtained by pretreatment with 6 mol/L HCl.

(3) By cathode acidification with citric acid and prolonging the proposing time, the HMs removal efficiency was boosted significantly. Sequential extraction of Pb, Zn, Cu and Cd indicated that

the oxidizable and reducible states were converted to a more stable compound after treatment.

(4) The maximum leaching efficiencies of Pb (94.23%), Zn (89.09%), Cu (88.21%) and Cd (84.97%) were obtained when the citric acid concentration was 0.05 mol/L, the voltage gradient was 2 V/cm, and the proposing time was 15 d.

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