

Modification of MSW fly ash by anionic chelating surfactant

Guangren Qian^{a,*}, Houhu Zhang^a, Xiaolan Zhang^a, Peng-Cheong Chui^b

^a College of Environmental Engineering, Shanghai University, Shanghai 200072, PR China

^b School of Civil and Environmental Engineering, Nanyang Technological University, Singapore

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Abstract

This paper elucidates a study on the re-utilization and stabilization of municipal solid waste (MSW) fly ash in producing a high value-added product by the surface modification of anionic chelating surfactant on the particles. After modification, MSW fly ash can be expected using as a filler of ultra-high molecular weight polymers. The effects of anionic chelating surfactants (ACS) on surface modification of MSW fly ash and fixing capacity for heavy metals were explored. Meanwhile, the interaction mechanism between surfactants and MSW fly ash was suggested. The results showed that anionic chelating surfactants can be used to effectively modify MSW fly ash particles and achieve a high active ratio. At the same time, they also exhibited a strong fixing capacity for heavy metals. Of the two modified MSW fly ash, ED3A-modified MSW fly ash has a much higher active ratio than MAP-modified MSW fly ash at over 95%, although its fixing capacity for heavy metals was a shade lower than MAP-modified MSW fly ash.

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Keywords: MSW fly ash; Surface modification; Anionic chelating surfactant; Heavy metals

1. Introduction

MSW fly ash generated from municipal solid waste incinerators is often classified as an industrial hazardous material because of its high concentrations of heavy metals and potential dioxins [1–4]. Accordingly, MSW fly ash must be detoxified prior to landfill or utilization. Currently, the most popular methods for MSW fly ash treatment are the immobilization of heavy metals by chelating agents before landfilling [2], the extraction of dioxins by using surface active agents was reported as well [4].

The possible applications of MSW fly ash have been extensively studied. MSW Fly ash can be used in many fields, such as in construction materials, geotechnical applications, and agriculture [5]. These applications of MSW fly ash generally resulted in low value-added products with high potentials in the leaching of heavy metals.

MSW Fly ash has a fine particle size distribution and a large specific surface area with main mineralogical constituents of SiO₂ and CaCO₃, which suggests that MSW fly ash possesses similar properties as non-metallic inorganic minerals, such as limestone and wollastonite powder. At present, these natural non-metallic powders are processed and used as filler in ultra-high molecular weight polymers through surface modification [6,7]. Hence, if the physical properties of MSW fly ash are carefully re-evaluated, high value-added utilization of MSW fly ash may be a potential.

The key to utilizing MSW fly ash as a high value-added filler is surface modification. Hence, the selection of the right surfactant is vitally important. As opposed to natural mineral powders, the fixing or stabilization of heavy metals in MSW fly ash has to be considered on top of the effectiveness of active filler-surface modification. Conventional surfactants usually comprise the hydrophilic and hydrophobic groups, by which they act as a bond combining mineral particles and host polymers [8]. However, such surfactants have little fixing capacity on heavy metals. On the other hand, chelating

* Corresponding author. Tel.: +86 21 5633 8094; fax: +86 21 5633 8094.
E-mail address: grqian@mail.shu.edu.cn (G. Qian).

agents, such as ethylenediaminetetraacetate (EDTA) and phosphate can act in the stabilization of heavy metals but possess no active function of surface modification due to a lack of hydrophobic groups in their structures [9,10]. It is obviously advantageous to have a single chemical agent that can accomplish both surface-modification and the stabilization of heavy metals. Anionic chelating surfactant has the priority according to the requirements by combining the surface activity of surfactants and the sequestering action of chelating agents in a single molecule.

In this study, the effectiveness of anionic chelating surfactant on the surface modification of MSW fly ash and fixing capacity of heavy metals were investigated in order to produce high value-added filler.

2. Material and methods

2.1. Properties of raw MSW fly ash

The MSW fly ash used in the experiments was collected from the Shanghai Yuqiao MSW incinerators. The raw MSW fly ash has the appearance of a gray fine powder. In the laboratory, the MSW fly ash was sieved, and the fraction smaller than 125 μm in diameter was subjected to the subsequent experiments. The average equilibrium pH of the MSW fly ash suspensions (solid-to-liquid ratio of 1:10) was 12.90 by a PHS-3C pH electrode.

2.2. Selected anionic chelating surfactant

In this study, two types of anionic chelating surfactant were selected: ethylenediaminetriacetic acid lauryl-ED3ANa₂ (ED3A) and monolauryl phosphate (MAP). They were obtained from the Hampshire Chemical Co. Ltd. and the Shanghai Goodway Chemical Co. Ltd., respectively.

Ethylenediaminetriacetic acid is an anionic chelating surfactant with the derivative structure of EDTA, in which one acetic acid radical is replaced by fatty acryl that makes ED3A be a surfactant, while the remaining three acetic acid radicals can chelate heavy metals as EDTA does.

Monolauryl phosphate is also an anionic chelating surfactant but with the derivative structure of phosphate, in which one hydroxyl is replaced by fatty acryl that makes MAP a surfactant, while the remaining two hydroxyls can chelate heavy metals as phosphate does.

2.3. X-ray diffraction (XRD) analysis

The mineral phases in the samples were identified by Dmax /RB X-ray diffraction with Cu K α radiation 34 kV, 20 mA. Once the diffraction patterns were obtained, both manual matching of the peak positions and a computer-aided search for the compounds were performed. The results were presented in an intensity -2θ format.

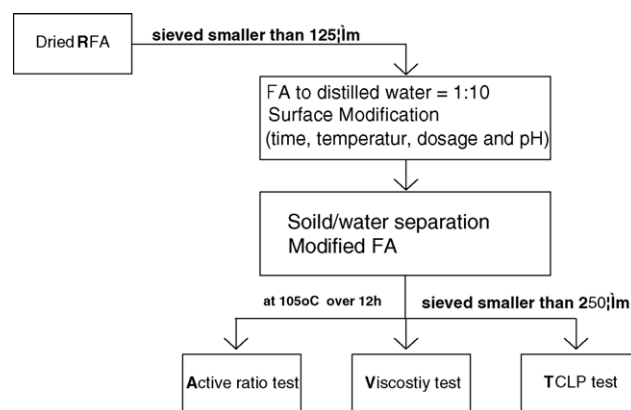


Fig. 1. Modification process of MSW fly ash.

2.4. IP-spectrophotometer

The spectra were recorded using a Perkin-Elmer 1725 \times IR Fourier transform spectrophotometer. For diffused reflectance spectra, the samples were prepared by dispersing 55 mg of the air-dried sample in 295 mg of KBr. The spectral measurement in the 400–4000 cm^{-1} region was made at 4 cm^{-1} resolution with the use of 120 scans.

2.5. Study methods

The whole modification process of MSW fly ash is shown in Fig. 1.

The modification processes of MSW fly ash consisted of three steps: (i) pre-sieving, (ii) surface modification, where anionic chelating surfactant is added into the raw MSW fly ash suspension and stirred at 1000 r/min, and (iii) milling and sieving, where the modified MSW fly ash is obtained after being dried.

2.6. Evaluation methods of surface modification

Two indices were employed in evaluating the surface modification effect: active ratio and viscosity.

2.6.1. Active ratio measurement

The effectiveness of the modified MSW fly ash in hydrolytic solvents, such as water can be evaluated by the active ratio:

$$H = \frac{G - W}{G} \times 100\%$$

where G is the pre-set weight of modified MSW fly ash and W is the weight of the precipitated portion in the bottom of container after the modified MSW fly ash had been dispersed into distilled water. Thus, $(G - W)$ is the weight of the floated MSW fly ash sample, and H is the value of active ratio. The active ratio shows the hydrophobic property of the sample with water: the higher the active ratio, the better the effectiveness of surface modification [11].

2.6.2. Viscosity measurement

Viscosity is the affinity characteristic of samples with organic solvents, such as liquid paraffin. The viscosity index manifests the hydrophobic property of the sample: the lower the viscosity, the better the effectiveness of surface modification [12].

The viscosity of the modified MSW fly ash was measured using a viscosimeter (Model NDJ-9S), which has four interchangeable spindles for different viscosity ranges. In this study, viscosity was determined using the second spindle at a rotational speed of 60 rpm for more than 10 min at room temperature.

A constant solid-to-liquid paraffin ratio of 1:4 was formed by adding 160 mL of liquid paraffin into a jacketed beaker containing 40 g of modified MSW fly ash. The beaker was then placed on a height-adjustable stand. Prior to viscosity determination, the liquid paraffin and the modified MSW fly ash in the beaker were mixed using a high-speed agitator for 5 min.

2.7. Toxicity characteristic leaching procedure (TCLP)

The toxicity characteristic leaching procedure was used to determine the leaching of heavy metals from the MFA [13]. It is generally accepted that pH condition in the solution plays a key role in controlling the leaching of heavy metals from hazardous wastes. An elevated pH condition can cause a higher leaching of some amphoteric heavy metals [14,15]. Considering the fact that the modified MSW fly ash has a higher pH and a strong neutralizing capacity on the acidity of the leachate, pH-adjusted solutions (pH 1, 3, 5, 7, 9, 11, and 13) were used instead of acetic acid solution in evaluating the leaching of heavy metals from the modified MFA at different pH values.

In this study, Pb, Zn, and Cd were selected as targeted heavy metals according to their relative concentration in raw MSW fly ash. The concentrations of the leachate were analyzed by a Perkin-Elmer 5100PC atomic adsorption spectroscopy (AAS).

3. Results and discussion

3.1. XRD patterns of raw MSW fly ash and washed MSW fly ash

The mineral constituents of raw MSW fly ash (RFA) and washed MSW fly ash were analyzed by XRD. As shown in Fig. 2, the main mineral constituents of raw MSW fly ash are quartz (SiO_2), anhydrite (CaSO_4), sylvite (KCl), halite (NaCl), and calcite (CaCO_3).

Washed MSW fly ash treated with distilled water showed an absence of highly soluble species, such as sylvite (KCl) and halite (NaCl) (Fig. 2). After washing, quartz, anhydrite, and calcite were major mineral constituents, which is similar to natural mineral powders, such as limestone and sand powder [7].

3.2. Particle size distributions of raw MSW fly ash

The particle size distribution is known to have a strong influence on the hydrodynamics of surface modification and final modification effectiveness. In most cases, a fine size distribution is favored for effective cover of surfactant on the surface of particles in the wet-modification process.

The particle size distribution of raw MSW fly ash is determined by Beckman coulter sorption analysis. The curve shown in Fig. 3 is the shape of a normal distribution in the mathematics. The majority of the MSW fly ash particles are in the range of 10–100 μm , with the average size of 25.3 μm . The specific surface area of raw MSW fly ash was as high as 9.8 m^2/g , while that of wollastonite was only 1.1 m^2/g [7]. A larger specific surface area will make the MSW fly ash particle more easily grafted by the anionic chelating surfactant than wollastonite, making it more suitable to be modified as a filler [16].

3.3. Effect of process parameters on the modification of MSW fly ash

To determine the effects of different process parameters on the effectiveness of modification, all parameters are fixed

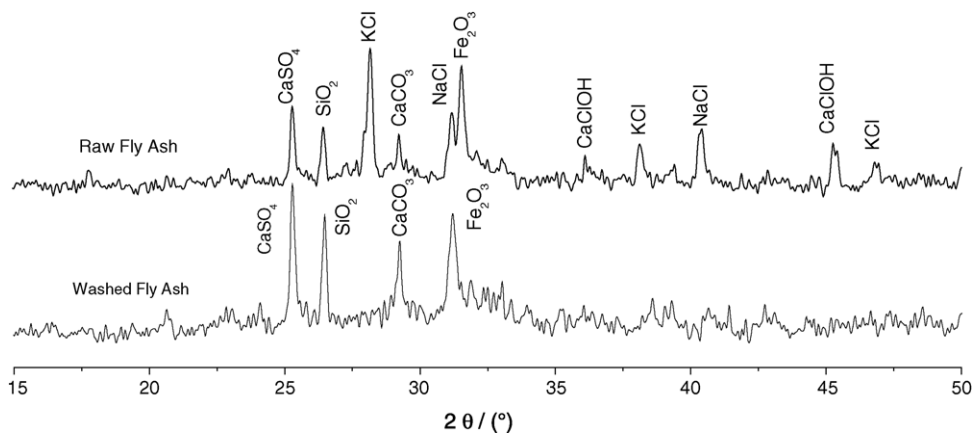


Fig. 2. X-Ray diffraction patterns of raw MSW fly ash and washed MSW fly ash.

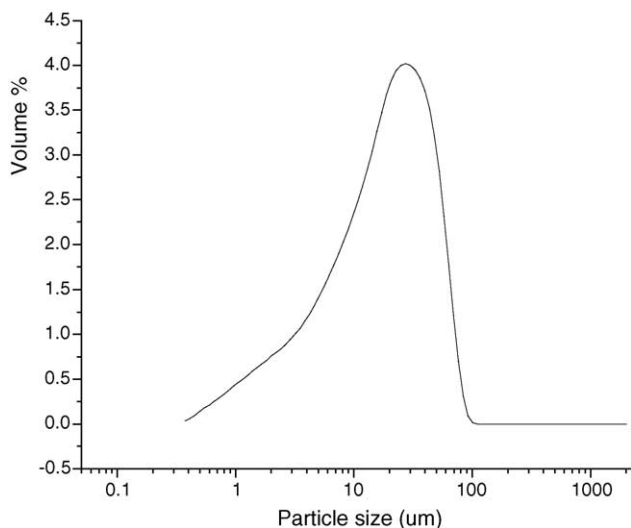


Fig. 3. Particle size distribution of raw MSW fly ash.

except for the parameter being tested. These parameters are stirring velocity (1000 rpm), solid-to-liquid ratio of MSW fly ash to distilled water (1:10).

3.3.1. Dosages of anionic chelating surfactant

The dosage of surfactant can affect the effectiveness of surface modification significantly. Fig. 4 shows the variation of active ratio and viscosity with different dosages.

As shown in Fig. 4a, better modification effectiveness is achieved at higher dosages up to the optimum value. Beyond that, further increase in ACS dosages resulted in the decrease of active ratio of MFA moderately. This effect, at higher dosage, could be the sticking of modified particles due to multi layer adsorption of surfactant on the surface of MSW fly ash particles, thus weakened the modification treatment. The trends for viscosities of the two MFAs as shown in Fig. 4b also exhibited similar results.

The best surfactant dosage for modification was 7.0 vol.% for ED3A MFA and 5.0 vol.% for MAP MFA, respectively.

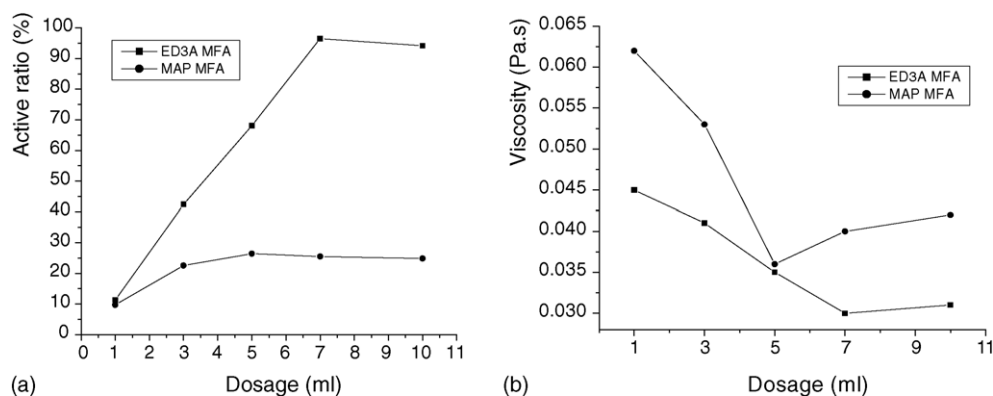


Fig. 4. Effects of surfactant dosages on active ratio and viscosity of MFA: (a) active ratio and (b) viscosity.

At these dosages, the MFAs have the maximum active ratios and the minimum viscosities.

3.3.2. Treatment time

The results on the variation of active ratio and viscosity with treatment times are shown in Fig. 5. The maximum active ratios for ED3A- and MAP-modified MSW fly ash were obtained at 15 min treatment time (Fig. 5a). At this treatment time, the viscosities of both MFA were also at its lowest (Fig. 5b). Thus, the best modification effectiveness of ED3A- and MAP-modified MSW fly ash was achieved at 15 min.

Although the reaction of anionic chelating surfactants with the surface of MSW fly ash particles may not be completely acted upon due to the shorter modification time, however, the results indicated that a longer modification time could lead to a decrease in the active ratio as well as an increase in the viscosity. This could be due to the stripping of the surfactant layers that had been grafted onto the MSW fly ash particle surfaces under prolonged treatment.

3.3.3. Treatment temperature

Temperature affects the modification of the MSW fly ash moderately as indicated in the active ratios and viscosities of MFA in Fig. 6. As shown in Fig. 6a, the active ratio of ED3A MFA increased only slightly with increase in the treatment temperature, although MAP MFA decreased significantly above 45 °C. This could be due to the enhanced dissolving activity of the surfactant at higher temperatures. However, an elevated temperature would weaken the surface grafting modification.

Based on the viscosity results in Fig. 6b, the optimum modification temperatures for ED3A- and MAP- modified MSW fly ash were found to be 75 and 15 °C, respectively.

3.3.4. pH value

The chemical reactions between MSW fly ash particles and the anionic chelating surfactants can be affected by pH. As such, 0.1N HNO₃ and NaOH were used in the pH-adjusted distilled waters throughout the study.

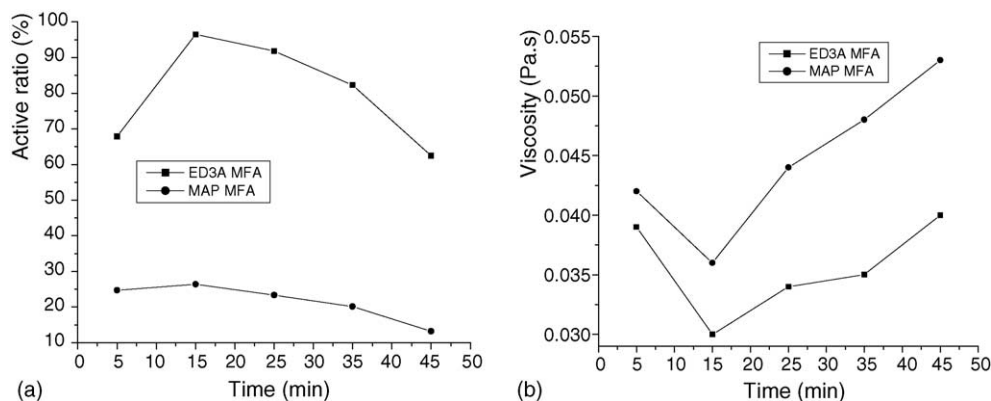


Fig. 5. Effects of modification times on the active ratio and viscosity of MFA: (a) active ratio and (b) viscosity.

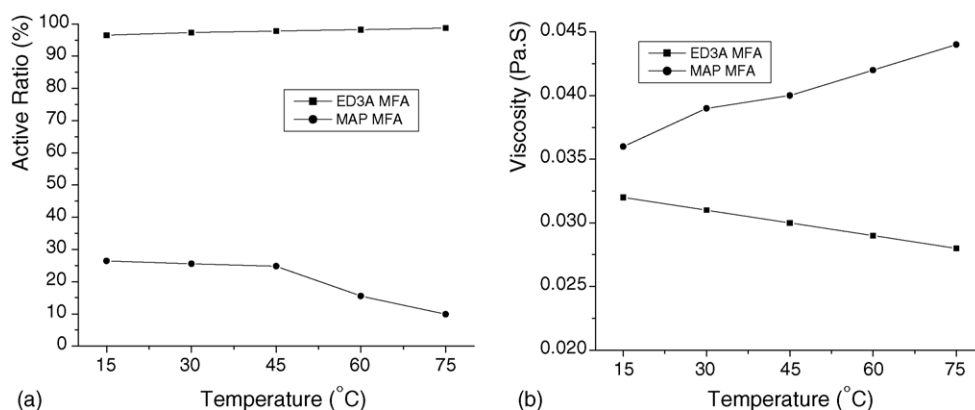


Fig. 6. Effects of modification temperatures on the active ratio and viscosity of MFA: (a) active ratio and (b) viscosity.

As shown in Fig. 7, the active ratios of the two chelating surfactants increased with pH. The highest active ratios and the lowest viscosities for both ED3A- and MAP- modified MSW fly ash were obtained at pH 11.

Based on above discussion, the optimum treatment parameters of surface modification by the two chelating surfactants can be summarized in Table 1. It can be drawn from the experiments that ED3A MFA has a substantially higher active ratio than MAP MFA with the optimal treatment parameter.

3.4. IR-spectras of modified MSW fly ashes

The diffused reflectance IR-spectra of MFA were recorded in order to evaluate the adsorption mechanism of ACS onto MSW fly ash using the Perkin-Elmer 1725× IR-spectrometer.

As shown in Fig. 8, the IR-spectra of two MFA have new absorption bands: at 2925.31 cm^{-1} (for ED3A) and 2922.77 cm^{-1} (for MAP) due to asymmetric C–H

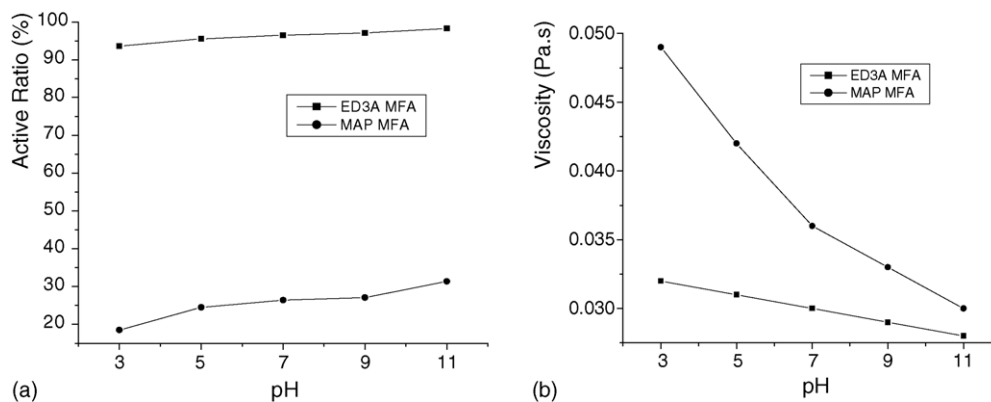


Fig. 7. Effects of pH on the: (a) active ratio and (b) viscosity of MFA.

Table 1
Optimum parameters for surface modification of MSW fly ash

Surfactant	Surfactant dosage (vol.%)	Modification temperature (°C)	Modification time (min)	pH of adjusted water
ED3A	7.0	75	15	11
MAP	5.0	15	15	11

stretching vibration, and at 2854.12 cm^{-1} (for ED3A) and 2853.21 cm^{-1} (for MAP) due to symmetric C–H stretching vibration, compared to raw MSW fly ash. These adsorption bands are evidence that ACS was grafted onto the surface of MSW fly ash particles.

3.5. Leaching characteristics of modified MSW fly ashes

The leaching characteristics of MFA were determined according to the US-EPA TCLP test procedure. The initial pH of the test sample was set ranging from 1 to 13 by using the pH-adjusted solutions. The final pH values of the different leachate samples were ranged between 8.5 and 12.6. Fig. 9 shows the concentrations of heavy metals in the leachates under the different initial pH conditions.

It is well known that the pH value has a significant influence on the speciation of heavy metals in aqueous medium with high alkalinity. The amphoteric behaviors of Pb and Zn have been extensively reported. They are either deposited as a metal hydroxide plumbite or re-dissolved in a basic medium as zincate [9,17]. As shown in Fig. 9a and b, Pb and Zn concentrations leached from MFAs were lower than RFA. Their concentrations remained at the same low level in the pH range 3–11 as Pb and Zn were fixed by the anionic chelating surfactant and remained stable. But beyond pH 11, their concentrations increased rapidly.

The leachate Pb^{2+} concentrations of ED3A- and MAP-modified MSW fly ash were mostly lower than the USA EPA

discharge standards ($\text{Pb}^{2+} \leq 5.0\text{ mg/L}$), except for pH 13. Although there is no regulatory limit for Zn, the concentration of Zn^{2+} was relatively low.

The leaching behavior of Cd was different from Pb and Zn as insoluble cadmium hydroxides can be formed with abundant OH^- and will not re-dissolve even in a high basic medium [9]. Hence, the leaching of Cd decreased with increasing pH. The concentrations of Cd from MFA were lower than RFA. It indicates that Cd could be fixed by both ACS and OH^- . As shown in Fig. 9c, the concentrations of Cd in leachates from RFA and MFA were much lower than the regulatory limit ($\text{Cd}^{2+} \leq 1.0\text{ mg/L}$).

Comparing the leachate concentrations of Pb, Zn, and Cd from RFA, it can be concluded that ACS shows a strong fixing capacity for heavy metals. As opposed to active effectiveness of surface modification, the fixing capacities of MAP for heavy metals Pb, Zn, and Cd were slightly better than that of ED3A.

4. Discussion

Based on the above results, the mechanism of the surface modification of MSW fly ash by anionic chelating surfactant can be assumed to be in two steps: (1) preferential adsorption of ACS on the surface of MSW fly ash particles and (2) interaction between heavy metals and ACS in an aqueous medium.

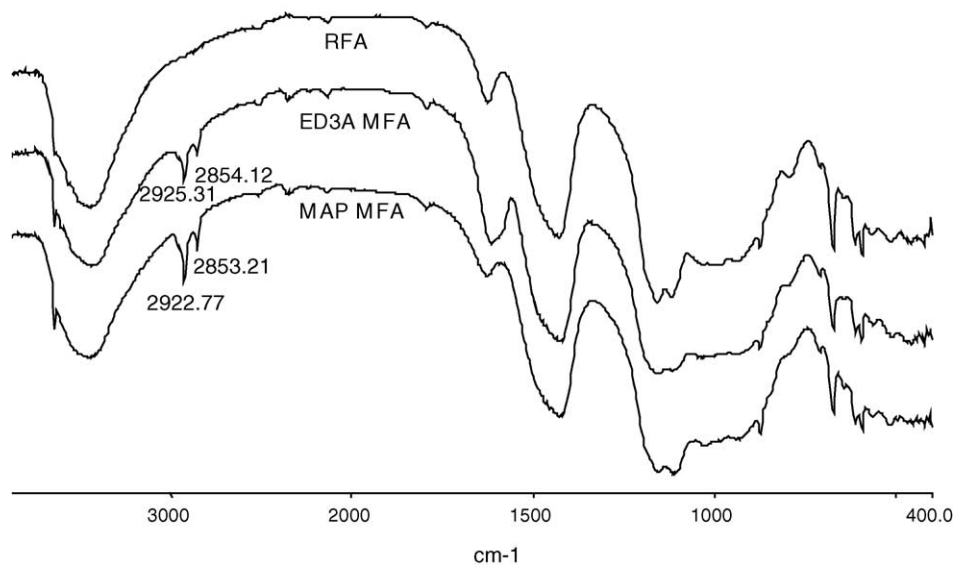


Fig. 8. IR-spectra of raw FA and modified FAs.

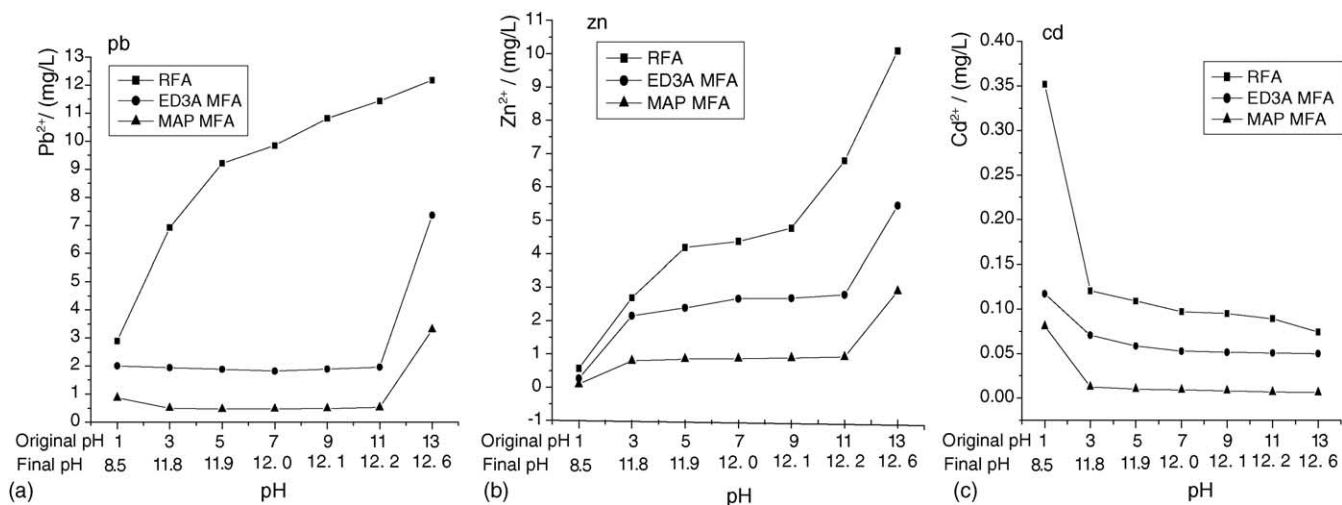


Fig. 9. Leaching of heavy metals from RFA and MFAs.

The high specific surface area of MSW fly ash (as high as 9.8 m²/g) will result in a strong adsorptive capacity of MSW fly ash to ACS in suspensions. The hydrophobic group, which is a long chain hydrocarbon with 12 carbons in the structure of ACS, is attached to the MSW fly ash particle, converting it from hydrophilic to a hydrophobic property [18].

It was also shown that ED3A and MAP used in this study have strong capacities to stabilize heavy metals. ED3A is a derivative of EDTA and can be chelated with heavy metals as EDTA does [19]. The possible interaction between ED3A and heavy metals (M²⁺: Pb²⁺, Zn²⁺, and Cd²⁺) is suggested as shown in Fig. 10 [20].

MAP is a type of organic phosphate in which one hydroxyl of phosphate is replaced by fatty acryl and the left two hydroxyls can be chelated with heavy metals (Fig. 11). The possible interaction between MAP and heavy metals (M²⁺: Pb²⁺, Zn²⁺, and Cd²⁺) is suggested in Fig. 11 [21].

Although the fixing capacities of heavy metals of the two anionic chelating surfactants were comparable, their active effectiveness on surface modification of MSW fly ash was significantly different. ED3A-modified MSW fly ash possessed a higher active ratio than MAP-modified MSW fly ash, which could be attributed to their different hydrophilic radicals. During the wet-modification process, the ED3A suspension produced a thick layer of foams of more than 2.0 cm in height, but there was no foam for the MAP suspension. According to the principle of surface physical chemistry, the modification effectiveness of surfactant on inorganic minerals can be related to the formation of foam layers. The thicker the foam layer, the better the modification effectiveness. However, the formation of foam layer is dependent on many factors, such as hydrophilic radical and electrolytic ions in the suspension. In the modification suspension of MSW fly ash, many superfluous electrolytic ions,

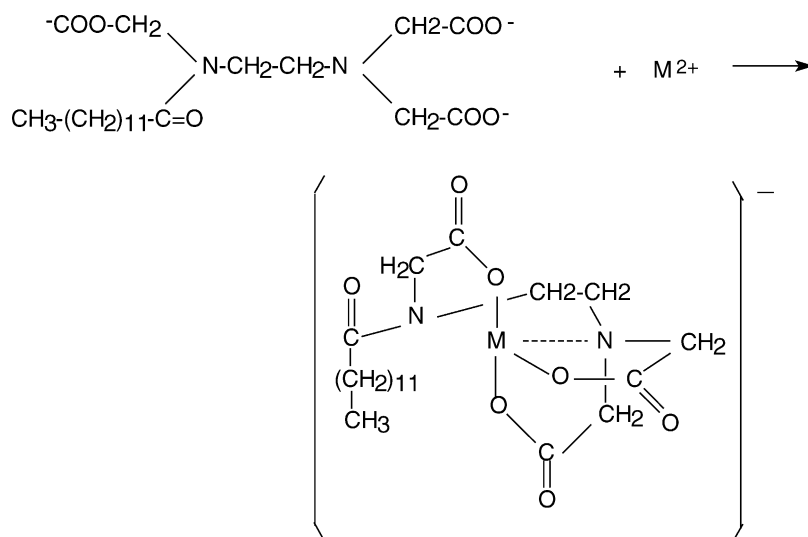


Fig. 10. Interaction between ED3A and heavy metals.

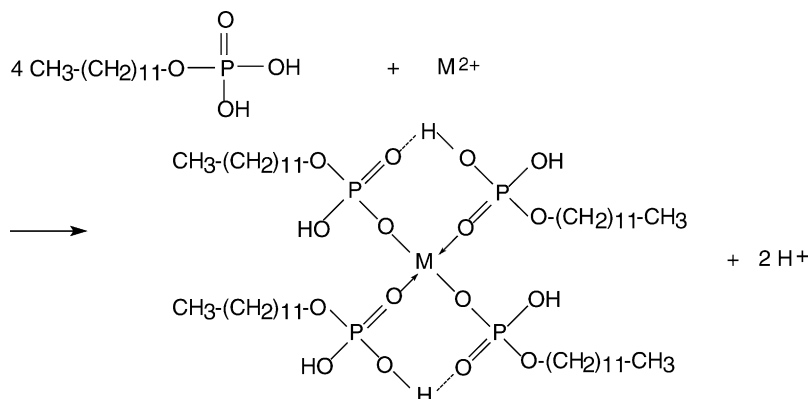


Fig. 11. Interaction between MAP and heavy metals.

especially polyvalent cations, will coexist with the hydrophobic radicals. In the case of superfluous electrolytic ions, the foams formed by common anionic surfactants will decrease tremendously. On the other hand, ED3A has a trivalent hydrophilic group, which provides linkage between the bivalent cations and the ED3A [20]. As a result, a more stable mucous membrane may be formed and cover the surface of the MSW fly ash particles. It is not certain if this had indeed resulted in ED3A MFA having a higher active ratio than MAP MFA.

5. Conclusion

This study shows that anionic chelating surfactants can be used to modify MSW fly ash particles effectively and achieved a high active ratio. At the same time, they also exhibited a strong fixing capacity for heavy metals. Of the two modified MSW fly ash, ED3A-modified MSW fly ash has a much higher active ratio than MAP-modified MSW fly ash at over 95%, although its fixing capacity for heavy metals was a shade lower than MAP-modified MSW fly ash.

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