

Study on Dechlorination of MSW Incineration Fly Ash using Fermentation Broth

Chuanfu Wu*, Xiaona Wang, Menglu Wang, Teng Li, Qunhui Wang

Department of Environmental Engineering, School of Energy and Environmental Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, China

*Corresponding author: Email: wucf@ustb.edu.cn

Summary

High amount of chlorine content is the bottleneck for direct use of municipal solid waste incineration fly ash as additive in Portland cement. Therefore, washing process is usually applied prior to the recycling of fly ash. To remove water insoluble chlorine, this study tends to investigate the impacts of various organic acid and dechlorination strategies on leaching behaviour of chlorine from fly ash. The results revealed that, compared with other organic acid, lactic acid is a suitable organic acid for dechlorination of fly ash in terms of the higher chlorine removal rate and less TS loss during the dechlorination process. The results multiple leaching experiment using fermentation broth of yeast (dominated by lactic acid) and anaerobic sludge (contained multiple types of organic acid) demonstrated that both fermentation strategies yield similar dechlorination effect, and multiple leaching steps (i.e. five–steps) was more effective than the one–step leaching. According to the calculation, the dechlorination effect of bioleaching is 10% higher than the conventional water washing under the same water consumption and bioleaching can save 75–80% liquid consumption compared with traditional water washing process under the same dechlorination efficiency. Therefore, bioleaching with multiple leaching steps is an ideal countermeasure for dechlorination of fly ash.

Keywords: Municipal solid waste; Fly ash; Dechlorination; Bioleaching; Style; Fermentation broth

1. Introduction

As industrialization and urbanization developed in the world, municipal solid waste (MSW) treatment has become outstanding problems. Incineration technology currently is very popular in some developed countries, e.g. Japan and Singapore [1, 2] due to it can efficiently reduce the volume of the MSW and recovered of energy. However, MSW incineration produces large amount of fly ash (i.e. represents 2% to 4% of the total amount of waste incinerated), which is considered a hazardous material (i.e. containing heavy metals, dioxins, and other poisons) [3, 4]. Currently, many intermediate treatments, such as melting, cement solidification, chemical treatment and calcination, have been developed to reduce the amount and toxicity of fly ash [5, 6].

From the perspective of Reduce, Reuse and Recycle, fly ash should ideally be reused as mineral, fertilizers as well as soil conditioners in agriculture due to the rich elements contain. In addition, the unique microstructure of fly ash makes it become a good environmental adsorption material, which could adsorb a variety of elements and dyes, and it can also neutralize acid wastewater by its alkalinity [7]. In particular, a relatively suitable destination for fly ash is as a raw material for making cement because the composition of MSW fly ash is close to cement and the high combustion temperatures (1 100~1 500°C) and long residence times (the gas retention time is approximately 5s) in cement kilns, ensure the complete destruction of even the most stable organic compounds, e.g. PCB [8]. Additionally, the heavy metal in fly ash can either be stabilized during the calcining process or be recovered from the dust collectors of cement kilns. Notably, the reuse of fly ash as cement material can preserve natural sources and protects the environment.

However, the high chlorine content of fly ash (e.g. 25% by weight) is a severe issue for cement industry. It might accelerate the corrosion of embedded steel of cement kilns and steel in the concrete once high chlorine is introduced into the cement kilns [9]. Therefore, to maximize the reuse efficiency of fly ash, the chloride content in fly ash must be reduced as much

as possible. Currently, the most common countermeasure for dechlorination of MSW incineration fly ash is by water washing [10~12]. However, the water washing can only remove the water–dissolvable chlorine, e.g. NaCl and KCl. The water–dissolvable chlorine content was still markedly higher than the standard regulation for Portland cement. Therefore, development of an effective dechlorination method for MSW incineration fly ash is of great important.

This study optimized the fermentation broth leaching conditions for dechlorination of incineration fly ash. In addition, we study the impact of different organic acid and their concentration on the dechlorination effect and we also developed a stepwise leaching strategy to increase the dechlorination efficiency. The results thus obtained may lay the foundation for the development of reuse methods of fly ash and provide a scientific basis for further study.

2. Materials and methods

2.1 Fly ash and acid

The fly ash used in this study was obtained from an incineration plant located in Beijing, China. The fly ash was ground and dry at 105°C before used. The organic and inorganic acid used for the leaching experiment included citric acid, propionic acid, lactic acid, acetic acid, phosphoric acid, nitric acid and sulfuric acid. The leaching experiment with distilled water was used as a control. The hydrogen concentration of prepared acid equaled to 0.012mol/L, 0.023 mol/L, 0.047 mol/L, 0.093 mol/L, 0.187mol/L and 0.467mol/L.

2.2 Leaching experiment

To obtain the optimum leaching time and solid to liquid ratio for leaching experiment, five empty bottles was respectively filled with 3 g fly ash, then certain amount of deionized water was added according to the solid and liquid ratio of 1:5, 1:8, 1:10, 1:15 and 1:20. The leaching experiments were conducted in the shaker which operated at 25°C and 200 rpm. The liquid sample was taken regularly until the concentration of the chloride in solution did not change. For leaching experiment

with different acids, the conditions of shaker were the same with the one with deionized water.

2.3 Analytical methods

The TS and VS contents of the solid sample were determined following the water and wastewater monitoring analysis method of the Chinese State Environmental Protection Administration (2002). The chloride concentration in solution was determined by ion chromatography (yc3000 model, Qingdao Ailun Chromatography Technology Co., Ltd.). The mobile phase was 2.5mmol/L sodium carbonate and 1.7mmol/L sodium bicarbonate solution. The flow rate was set to 0.6mL/min.

3. Results and discussion

3.1 Optimum leaching condition

Fig. 1 shows the change of chloride removal rate with leaching time. The chloride removal rate rapidly reached 75% at the first 30 min and increased gradually till 2 h after the start of the experiment. The chloride removal rate became stable in 4 h. As there won't be much change of chloride removal rate when prolong the leaching time, the optimum leaching time for the fly ash was set to 2 h.

Fig. 2 shows the effect of solid to liquid ration on the chloride removal rate. In the light of the experiment result, the chloride removal rate of fly ash increased with the increase of solid to liquid ratio. Notable, the chloride removal rate increased rapidly at the solid to liquid ratios changed from 1: 5 to 1: 10. The chloride removal rate became stable at solid to

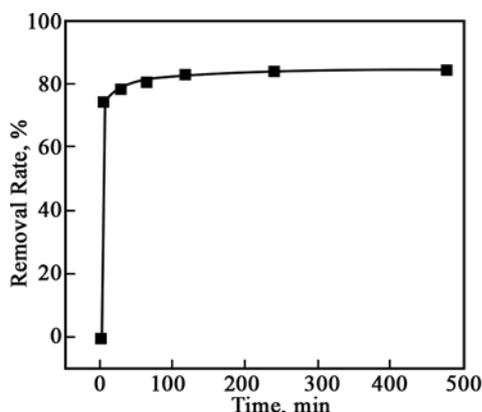


Figure 1. Relationship between leaching time and removal rate of chloride.

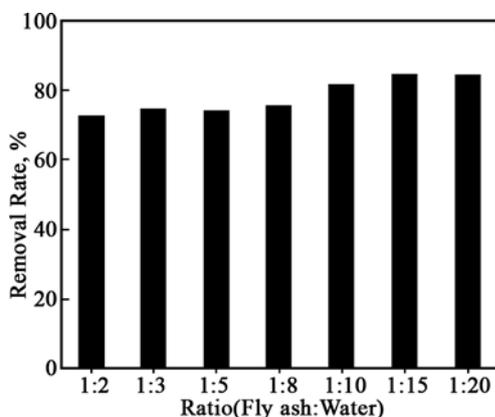


Figure 2. Effect of different solid to liquid ratio on chloride removal rate.

liquid ratio of 1: 15. In low solid to liquid ratio conditions, the chlorine removal rate was mostly affected by the solubility of the fly ash. However, with the increase of solid to liquid ratio, the dissolvable chlorine was exhausted. The dissolvable chlorine of total chlorine content of fly ash was ca. 84%. Therefore, solid to liquid ratio in 1:10 was considered the optimum ratio for the following leaching experiments.

Fig. 3 shows the influence of leaching temperatures on the chloride removal rate. Generally, the solubility of the chemical increased with the rising temperature. The results of this experiment were in consistent with the theory. As we can see from the figure, when the temperature increased from 15°C to 25°C, the chloride removal rate increased markedly. However, the chloride removal rate increased slowly when leaching temperature increased from 25°C to 45°C. The highest chloride removal rate (i.e. 85%) was observed at 60°C, which slightly higher than the dissolvable chlorine content of the fly ash. It probably attributed to the fact that high temperature accelerated molecular interaction, converting parts of the insoluble chloride changed into soluble state [13].

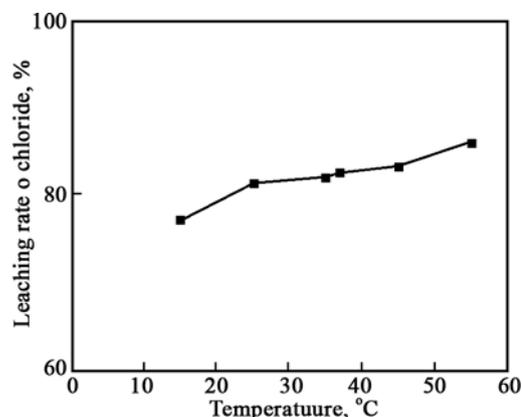


Figure 3. Influence of temperature on chloride removal rate from fly ash.

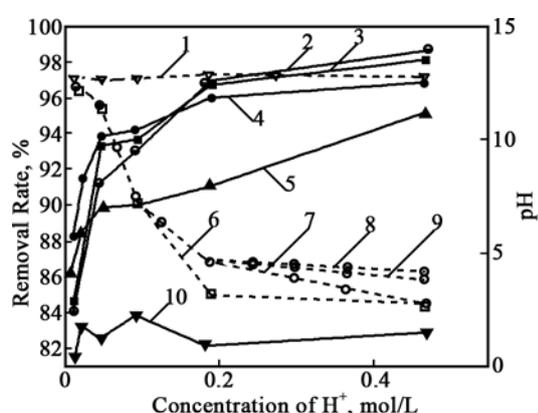
3.2 Comparison of acids leaching effect

Fig. 4 (a) and 4 (b) show the effect of different acids and their concentrations on the chloride removal rate in fly ash. In the light of the experiment results, the chloride removal rate increased with the increasing acid concentration (i.e. H⁺ concentrations). In addition, the chloride removal rate of different acid was markedly higher than that of deionized water. The acid can not only dissolved the soluble chloride, but also react with the insoluble chloride, converting it into soluble chloride. The improving effect to chloride removal rate was obviously at low acid concentrations. On the contrary, the improvement effect of acid to chloride removal rate became unconscious when the hydrogen ion achieved 0.187mol/L.

Fig. 4 also illustrated that the improvement effect of increasing hydrogen ion on chloride removal rate was much obvious for inorganic acid scenarios when the hydrogen ion concentration lower than 0.047mol/L, compared with the organic acids. At this point, the hydrogen ion concentration is the dominant factor regulating the chloride removal rate of the fly ash. However, at high hydrogen ion concentration, the effect between organic and inorganic acid on chloride removal rate became less different due to the hydrogen ion content in solutions is sufficient and the insoluble chloride could not be

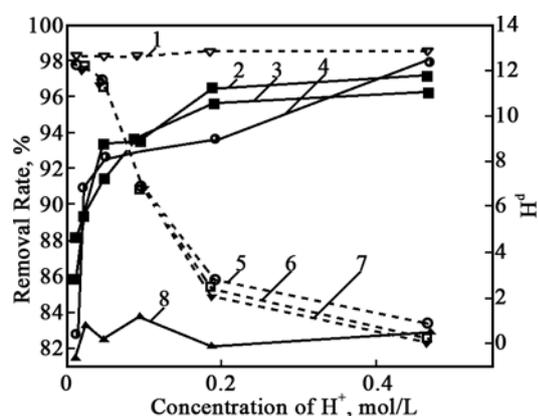
leaching out. In addition, fly ash contains a large number of calcium ions, adding lactic acid and sulfuric acid can react with calcium ions to form precipitation affecting the leaching effect. Therefore, the chloride removal rate in lactic acid and sulfuric acid is lower than that of other kind of acids.

Fig. 4 also show the changes in pH value of the liquid after the leaching experiments with different kinds of acids. With the increase of acid concentration, the pH value of leaching solution decreases gradually. The trends of organic acids and inorganic acids are approximately the same. As we can see from the deionized water leaching experiment, the pH value of the liquid is about 12.6, indicating that 1 g fly ash contains about 0.001mol of hydroxyl. Under the same hydrogen ion concentration, the minimum pH of the solution in organic acids leaching experiments (i.e. ca. 4–5) was higher than in inorganic acids ((i.e. ca. 1)) due to the buffer property of organic acids.



(a) Organic

1–water pH, 2–acetic removal, 3–citric removal, 4–propionic removal, 5–lactic removal, 6–citric pH, 7–lactic pH, 8–propionic pH, 9–Acetic pH, 10–water removal



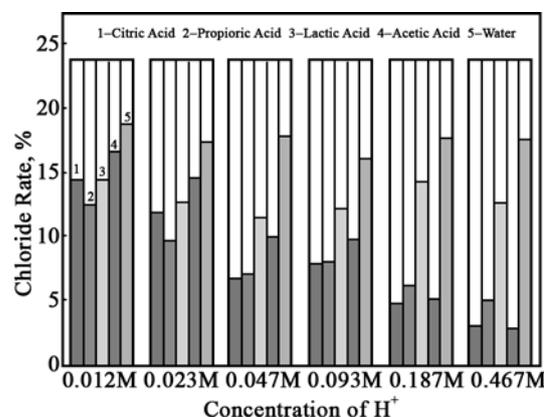
(b) Inorganic

1–water pH, 2–Nitric removal, 3–sulfuric removal, 4–phosphoric removal, 5–phosphoric pH, 6–sulfuric pH, 7–nitric pH, 8–water removal

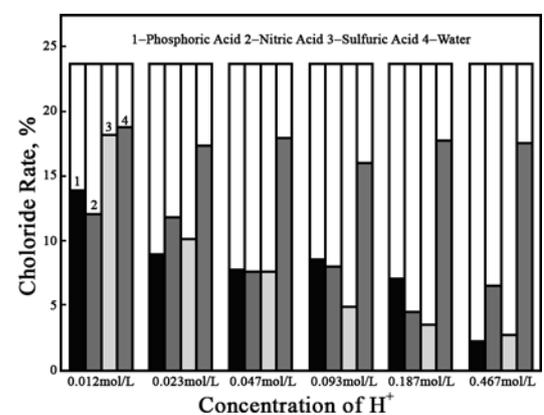
Figure 4. Influence of acids and their concentrations on the chloride removal rate.

Fig. 5 (a) and 5(b) show the amount of chloride (expressed by percentage) of the remaining solids after leaching by different acids with various concentrations. As shown in the figures, with the increase of acid concentrations, the chloride in the solid shows a clear trend of decline. In addition, the

chloride content of the remained solids was lower in inorganic acids treatments than that in organic acids. It could be attributed to the lower pH observed in inorganic acids treatments, converting part of the water insoluble chloride into soluble chloride.



(a) Organic



(b) Inorganic

Figure 5. Residual solid after acid leaching experiments.

4. Conclusions

This study investigated the dechlorination behavior of fly ash by water and different kinds of acids with various concentrations. The obtained results indicated that the optimum leaching conditions can be obtained in solid–liquid ratio of 1: 10, temperature of 25°C and leaching time of 2 h.

The dechlorination of fly ash by acids exhibited different phenomena. The dechlorination was improved with the increase of acid concentrations. Notably, inorganic acid showed higher dechlorination effect at a low concentration level, compared with organic acids. However, the dechlorination effect was similar when the concentration of the organic and inorganic acid increased to a high level.

Organic acids have good buffering effects on preventing pH drop in leaching solution. In addition, the weight losses of the fly ash in inorganic acids treatments were higher than that in organic acids treatments.

Acknowledgement

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