Effect of salinity on the precipitation of dissolved metals in the wastewater that produced during fly ash disposal

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Abstract. In this study, a salinity wastewater was produced during the fly ash treatment in the waste incineration plant. Chemical precipitation method was applied for heavy metals removal in the salinity wastewater. The effect of salinity on the removal of dissolved heavy metal ions (Zn²⁺, Cu²⁺, Pb²⁺, Ni²⁺ and Cd²⁺) was studied, especially on the removal of Pb²⁺ and Cd²⁺. Because of the formation of [PbCl₄]²⁻ and [PbCl₃]⁴⁻ complexes, the residual concentration of dissolved Pb²⁺ increased from 0.02 mg/L to 4.08 mg/L, as the NaCl concentration increased from 0 % to 10 %. And the residual concentration of dissolved Cd²⁺ increased from 0.02 mg/L to 1.39 mg/L, due to the formation of [CdCl₄]²⁻ and [CdCl₃]⁴⁻ complexes.

1. Introduction

With the rapid growth of human needs and global population, a large number of municipal solid waste was generated each year. In order to dispose those solid wastes, incineration treatment was selected as a most common technology in many countries. Because of the effectively reduce of wastes’ volume and utilization of wastes’ heat value [1]. While the residues from the incineration treatment of municipal solid waste were fly ashes, which were classified as hazardous waste due to the high concentration of leachable heavy metals [2,3]. The environmental risk during the fly ashes’ disposal should be inhibited. The flue gas in the thermal plasma treatment of fly ash was usually scrubbed in spray tower by water. The composition of fly ash was reported by many researchers that calcium, chlorine, sodium and silicon were the major elements of fly ash, and zinc, copper, lead, nickel and cadmium were the major heavy metal elements of fly ash [3]. Zinc, copper, lead and cadmium were generally volatilized during the fly ash processing [4]. Ultimately, these heavy metals were present in the scrubbing wastewater.

The contamination of industrial wastewaters containing heavy metal ions had become a serious problem environmentally and ecologically [5,6]. For humans, extended exposure to heavy metals will result in damage to blood composition, mental and central nervous function, liver, lungs and other vital organs [7,8]. And for this reason, the treatment of dissolved heavy metal ions in water had received an extensive concern and become a hot topic in environmental researches. Methods applied in heavy metal ions removal from wastewater were chemical precipitation as sulfides or hydroxides [9], filtration [10], coagulation [11], inverse osmosis [12], electrolysis [13], and so on [14]. Among these methods, chemical precipitation as hydroxides was the one of the most widely used techniques.

Among these heavy metals, lead was a highly poisonous metal, which affected almost every organ and system in the human body [15]. Lead can cause severe damage to the kidneys and brain, and
finally death. Cadmium toxicity contributed to a great number of health conditions, including heart disease, diabetes and cancer [16].

During the thermal plasma treatment of fly ash, the chlorinum in fly ash was also all volatilized to flue gas and finally present in the scrubbing wastewater. As a result, a high salinity wastewater with various heavy metals was produced. The salinity of this wastewater was up to 50g/L, which was several times and even more than general high-salinity industrial wastewater. When hydroxide precipitation process was applied for removal of dissolved heavy metal from wastewater at optimum pH, it was found that the removal of dissolved heavy metal ions was so difficult.

The salinity was considered as a key factor for the difficulty of heavy metals removal. Therefore, it was significant to study the effect of salinity on the removal of dissolved heavy metals, in order to achieve the harmless treatment of fly ashes. In this paper, the effect of salinity on the removal of dissolved heavy metal ions was studied.

2. Experimental

2.1. Chemicals and materials

Analytical pure ZnCl₂, PbCl₂, CuCl₂·2H₂O, NiCl₂·6H₂O, CdCl₂·2.5 H₂O, NaCl and NaOH, were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The salinity wastewater produced in thermal plasma treatment of fly ash was supplied by China Tianying Inc. (China).

The composition of salinity wastewater produced in thermal plasma treatment of fly ash was measured by a Haiguang GGX-600 flame atomic absorption spectrophotometer (AAS), the concentration of zinc, copper, lead, nickel and cadmium were also measured by a Haiguang GGX-600 AAS, and the value of solution pH was monitored by the METTLER-TOLEDO FiveEasyPlus pH meter.

2.2. Experimental procedure and setup

2.2.1. Sample analysis. The salinity wastewater, produced in thermal plasma treatment of fly ash, was analyzed. The dissolved heavy metal ions were the main pollutants of the scrubbing wastewater, whose concentrations were shown in table 1.

| Type of Metal Ion | Concentration, mg/L |
|------------------|---------------------|
| Zn²⁺             | 92.9                |
| Cu²⁺             | 20.08               |
| Pb²⁺             | 48.11               |
| Ni²⁺             | 12.47               |
| Cd²⁺             | 6.47                |

2.2.2. Preparation of synthetic wastewater.[18] The synthetic wastewater was prepared according to the data in table 1. In the synthetic wastewater, zinc, copper, lead, nickel and cadmium were added in the form of ZnCl₂, CuCl₂·2H₂O, PbCl₂, NiCl₂·6H₂O, CdCl₂·2.5 H₂O, respectively.

2.2.3. Experimental setup. The experimental setup was a simplified device used for studying the effect of salinity on the removal of dissolved heavy metal ions, whose outline was showed in figure 1. Thermostatic water baths were used to keep the temperature of NaOH solution storage tank and precipitation reactor at 25°C. A peristaltic pump was used to feed NaOH solution and an axial one blade stirrer was used to mix the solution, with speed of 100r/min. The pH value of the reaction solution was monitored by a pH meter.
2.2.4. Experimental procedure. Synthetic wastewater was added to the precipitation reactor with a volume of 500mL, keeping the temperature at 25°C in the thermostatic water bath. Then, 0.1 mol/L NaOH solution was slowly feed to the precipitation reactor by a peristaltic pump with the volumetric flow rate 5mL/min. The pH of the reaction solution should be monitored throughout the experiment. According to the completely precipitated pH of hydroxide, which shown in table 2, Zn(OH)$_2$, Cu(OH)$_2$, Pb(OH)$_2$ and Ni(OH)$_2$ were completely precipitated at the pH value of 9.5. Therefore, the experiments were stopped, when the solution’s pH value was adjusted to 9.5. Then, 30 minutes were needed for static settlement. After static settlement, the supernatant should be gotten for future determination.

While, the completely precipitated pH range of Cd(OH)$_2$ was 10.5 to 12.5, which greatly differed with the pH value of 9.5. For this reason, the pH value of supernatant should be adjusted to 11.0 by adding NaOH solution with a concentration of 0.1 mol/L. Then, settle 30 minutes to get supernatant for future determination.

In the experiments of the Pb$^{2+}$ removal, the precipitation reaction stopped at the pH value of 9.5. While in the Cd$^{2+}$ removal experiments, the precipitation reaction stopped at the pH value of 11.0.

Table 2. The beginning and completely precipitated pH of part hydroxide.

| Type of Metal Ion | pH: begin to precipitate (0.01 mol/L) | pH range: completely precipitated |
|-----------------|-------------------------------------|----------------------------------|
| Zn$^{2+}$       | 6.4                                 | 9 - 9.5                          |
| Pb$^{2+}$       | 7.2                                 | 9.2 - 9.5                        |
| Cd$^{2+}$       | 8                                   | 10.5 - 12.5                      |
| Cu$^{2+}$       | 6                                   | 9.0                              |
| Ni$^{2+}$       | 6.4                                 | 9.5                              |

2.3. Analytical methods

The concentrations of dissolved heavy metal-ions in the salinity wastewater, produced in thermal plasma treatment of fly ash, were measured by Haiguang GGX-600 flame atomic absorption spectrophotometer (AAS). The concentration of zinc, copper, lead, nickel and cadmium in the supernatant of precipitation solution were also measured by Haiguang GGX-600 flame AAS. AAS can be used to determine over 70 different elements in solution.

There were two jobs should be prepared before the determination. First, draw the standard curve of each heavy metal ions. Second, dilute the test samples to a proper concentration.
3. Results and discussions
Zinc, copper, lead, nickel and cadmium were the main pollutants of the salinity wastewater, produced in thermal plasma treatment of fly ash. The concentrations of zinc, copper, lead, nickel and cadmium analyzed by flame AAS, which were presented in table 1. Among the five types of heavy metal-ions, Zn$^{2+}$ and Pb$^{2+}$ were the most abundant metal ions. Except the five types of heavy metal-ions mentioned in table 1, the other metal ions were in lower concentrations which can be counted as minor and trace constituents.

Generally, the heavy metal ions can be removed by hydroxide precipitation process with adding alkaline. Unfortunately, during the water treatment process, it was found not easy to remove the dissolved heavy metal ions from wastewater that produced in thermal plasma treatment of fly ash.

3.1. Effect of salinity on the removal rate of dissolved heavy metal ions
Calcium, chlorine, sodium and silicon were the major elements of fly ash [9]. Among those, sodium would easily transport from solid phase to gaseous phase in the form of NaCl, during the fly ash processing. Sodium was analyzed by flame AAS, whose content was 2%. So that the wastewater produced in thermal plasma treatment of fly ash was a high salinity wastewater. As this reason, the effect of salinity on the removal of heavy metal-ions should be studied.

Synthetic wastewater without NaCl and with NaCl concentration of 5% should be prepared for experiments. The removal rates of zinc, copper, lead, nickel and cadmium were shown in figure 2. In figure 2, the removal rates of zinc, copper, lead, nickel and cadmium were found to reduce obviously, when the NaCl concentration of synthetic wastewater increased to 5%. The effect of NaCl concentration on removal of zinc, copper, lead, nickel and cadmium was significant, especially on removal of Pb$^{2+}$ and Cd$^{2+}$. The removal rate of Pb$^{2+}$ fell from 99.9% to 96.7%, when 5% NaCl was added to synthetic wastewater. Similarly to Pb$^{2+}$, the removal rate of Cd$^{2+}$ fell from 99.8% to 95.8%. While, the removal rate of Zn$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ were only descended 0.2%, 0.8% and 0.8%, respectively.

![Figure 2](image)

**Figure 2.** The removal rate of heavy metal-ions with the NaCl concentration of 0% and 5%.

Metal ions can be combined with Cl$^-$ to form complexes, such as [PbCl$_4$]$^{2-}$, [CdCl$_4$]$^{2-}$, [CuCl$_4$]$^{2-}$ and so on. The dissolved amount of metal ions in the solution was increased, because of the formation of metal-ion complexes.

The residual concentrations of zinc, copper, lead, nickel and cadmium in the synthetic wastewater with NaCl concentration of 0% and 5% were measured, as relevant data shown in figure 3.

In the figure 3, the residual concentrations of zinc, copper, lead, nickel and cadmium in synthetic wastewater with NaCl concentration of 5% were higher than in synthetic wastewater without NaCl, especially Pb$^{2+}$ and Cd$^{2+}$. The residual concentration of Pb$^{2+}$ increased from 0.02 mg/L in synthetic wastewater without NaCl to 1.57 mg/L in synthetic wastewater with NaCl concentration of 5%. And the residual concentration of Cd$^{2+}$ increased from 0.02 mg/L to 0.27 mg/L. While, the residual...
The concentration of Zn$^{2+}$, Cu$^{2+}$ and Ni$^{2+}$ were only increased by 0.12mg/L, 0.07mg/L and 0.10mg/L, respectively.

![Figure 3](image3.png)

**Figure 3.** The residual concentration of heavy metal ions with the NaCl concentration of 0 % and 5 %.

The effect of NaCl on the removal of Pb$^{2+}$ and Cd$^{2+}$ was significant. Therefore, the influence of NaCl concentration on Pb$^{2+}$ and Cd$^{2+}$ removal should be studied in future experiments.

3.2. Influence of salinity concentration on dissolved Pb$^{2+}$ removal

Lead was a highly poisonous metal, which affected each organ and system in the human body [15], because the lead can cross the blood-brain barrier by mimicking calcium. Lead degraded the myelin sheaths of neurons, interfered with neurotransmission routes, and decreased neuronal growth [17].

In the water treatment process of the salinity wastewater, produced in thermal plasma treatment of fly ash, dissolved heavy metals were removed by chemical precipitation as hydroxides. In the experiment, dissolved Pb$^{2+}$ was removed as the flocculation of Pb(OH)$_2$, by adding NaOH with a concentration of 0.1 mol/L. According to the completely precipitated pH value of Pb(OH)$_2$, the pH value of 9.5 was best for the removal of dissolved Pb$^{2+}$ from the synthetic wastewater.

\[
Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2 \downarrow
\]

(1)

If the pH value of synthetic wastewater above 9.5, the Pb(OH)$_2$ will dissolve again in wastewater as the formation of [Pb(OH)$_4$]$^{2-}$. When the pH value of wastewater above 13.0, the Pb(OH)$_2$ will completely dissolve in wastewater. Therefore, the pH value of precipitation reaction was a key factor for the removal of Pb$^{2+}$.

\[
Pb(OH)_2 + 2OH^- \rightarrow [Pb(OH)_4]^{2-} \downarrow
\]

(2)

While, Cl$^-$ abounded in the salinity wastewater, produced in thermal plasma treatment of fly ash. The Cl$^-$ was found to affect the precipitation reaction of Pb$^{2+}$.

![Figure 4](image4.png)

**Figure 4.** The removal rate and residual concentration of dissolved Pb$^{2+}$. 

The influence of NaCl concentration on the removal of dissolved Pb\(^{2+}\) was shown in figure 4. The removal rate of Pb\(^{2+}\) decreased from 99.9\% to 91.5\% with the NaCl concentration in synthetic wastewater increasing from 0\% to 10\%. And the residual concentration of Pb\(^{2+}\) in synthetic wastewater increased from 0.02mg/L to 4.08mg/L, when the NaCl concentration in synthetic wastewater increased from 0\% to 10\%. The result indicated that there was a negative influence of NaCl on the removal of Pb\(^{2+}\) from wastewater.

The emission standard of pollutants for lead industry (GB 25466-2010) shown that the emission limit of lead was 0.5 mg/L for new facility. According to this emission standard, the water treatment of heavy metals wastewater should be improved when the NaCl concentration in wastewater above 1\% for new facility.

In the wastewater with Cl\(^-\) abounded, Pb\(^{2+}\) will be combined with Cl\(^-\) to form complexes, such as [PbCl\(_3\)]\(^-\), [PbCl\(_4\)]\(^2-\) and so on. The formation of [PbCl\(_3\)]\(^-\), [PbCl\(_4\)]\(^2-\) complexes led to the decrease of Pb\(^{2+}\) in the solution, as the equation (3)-(5) shown. According to equation (1), the precipitate of Pb(OH)\(_2\) reduced with the Pb\(^{2+}\) decreasing in the solution. Ultimately, it led to the growth of dissolved amount of Pb\(^{2+}\) in the solution.

\[
Pb^{2+} + 2Cl^- = PbCl_2 \quad (3)
\]
\[
PbCl_2 + Cl^- = [PbCl_3]^- \quad (4)
\]
\[
[PbCl_3]^- + Cl^- = [PbCl_4]^{2-} \quad (5)
\]

As a result, for high salinity wastewater, the method of chemical precipitation as hydroxides for Pb\(^{2+}\) removal from wastewater was not appropriate, especially for the wastewater with a NaCl concentration above 3\%.

### 3.3 Influence of salinity concentration on Cd\(^{2+}\) removal

Cadmium was an extremely toxic metal, whose toxicity contributed to a great number of health conditions, including heart disease, cancer and diabetes [16].

In the experiment, Cd\(^{2+}\) was removed by adding NaOH with a concentration of 0.1 mol/L. According to the completely precipitated pH value of Cd(OH)\(_2\), the pH range of 10.5 to 12.5 was best for the removal of dissolved Cd\(^{2+}\) from the synthetic wastewater.

\[
Cd^{2+} + 2OH^- = Pb(OH)_2 \downarrow \quad (6)
\]

![Figure 5. The removal rate and residual concentration of dissolved Cd\(^{2+}\).](image)

The influence of NaCl concentration on the removal of dissolved Cd\(^{2+}\) was shown in figure 5. The removal rate of Cd\(^{2+}\) decreased from 99.8\% to 78.5\% with the NaCl concentration in synthetic wastewater increasing from 0\% to 10\%. And the residual concentration of Cd\(^{2+}\) in synthetic wastewater increased from 0.02mg/L to 1.39mg/L, when the NaCl concentration in synthetic wastewater increased from 0\% to 10\%. In figure 5, it can be found that the removal rate of Cd\(^{2+}\) sharply dropped from 95.8\% to 78.5\%, and residual concentration of Cd\(^{2+}\) sharply increased from
0.27mg/L to 1.39mg/L, when the NaCl concentration in synthetic wastewater increased from 5% to 10%.

The result indicated that there was a negative influence of NaCl on the removal of dissolved Cd\(^{2+}\) from wastewater, which was more significant than Pb\(^{2+}\).

The emission standard of pollutants for electroplating (GB 21900-2008) shown that the emission limit of cadmium was 0.05 mg/L for new facility. According to this emission standard, the water treatment of heavy metals should be improved when the wastewater abounded NaCl (>1%) for the new facility.

In the salinity wastewater, Cd\(^{2+}\) will be combined with Cl\(^{-}\) to form complexes, such as [CdCl\(_3\)]\(^{-}\), [CdCl\(_4\)]\(^{-}\) and [CdCl\(_6\)]\(^{4-}\). The formations of [CdCl\(_3\)]\(^{-}\), [CdCl\(_4\)]\(^{-}\) and [CdCl\(_6\)]\(^{4-}\) were shown in equation (8)-(10). Similarly to Pb\(^{2+}\), the Cd\(^{2+}\) that dissolved in the solution was more than the wastewater without NaCl.

\[
\begin{align*}
Cd^{2+} + 2Cl^- &= CdCl_2 
\text{ (7)} \\
CdCl_2 + Cl^- &= [CdCl_3]^- 
\text{ (8)} \\
CdCl_2 + 2Cl^- &= [CdCl_4]^{2-} 
\text{ (9)} \\
CdCl_2 + 4Cl^- &= [CdCl_6]^{4-} 
\text{ (10)}
\end{align*}
\]

As a result, for high salinity wastewater, the method of chemical precipitation as hydroxides for Cd removal from wastewater was not appropriate.

4. Conclusions

In this study, the effect of salinity on the removal of dissolved heavy metal ions from wastewater, produced in thermal plasma treatment of fly ash, was investigated. When NaCl concentration in the wastewater was 5%, the residual concentration of zinc, copper, lead, nickel and cadmium increased by 0.12mg/L, 0.07mg/L, 1.55mg/L, 0.10mg/L and 0.25mg/L, respectively. The significant effect of salinity on Pb\(^{2+}\) and Cd\(^{2+}\) was further studied. The residual concentration of dissolved Pb\(^{2+}\) and Cd\(^{2+}\) in the wastewater increased due to complexation mechanism. Pb\(^{2+}\) was combined with Cl\(^{-}\) to form [PbCl\(_3\)]\(^{-}\) and [PbCl\(_4\)]\(^{2-}\), and Cd\(^{2+}\) combined with Cl\(^{-}\) to form [CdCl\(_3\)]\(^{-}\), [CdCl\(_4\)]\(^{-}\) and [CdCl\(_6\)]\(^{4-}\). The residual concentration of dissolved Pb\(^{2+}\) increased from 0.02mg/L to 4.08mg/L, when the NaCl concentration increased from 0% to 10%. And the residual concentration of dissolved Cd\(^{2+}\) increased from 0.02mg/L to 1.39mg/L. Therefore, there was a stronger inhibition of salinity on the removal of Cd\(^{2+}\) than Pb\(^{2+}\) by chemical precipitation as hydroxides. This paper shown and explained one of the difficulties in the fly ash treatment. The results of this paper would be helpful for the disposal of wastewater that produced during the thermal plasma treatment of fly ash.

Acknowledgement

The authors would like to express their sincere gratitude to Subsidiary company of China Tianying Inc, who permitted sampling collection for the present study.

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