Study on passivation of heavy metals in sewage sludge with fly ash

D F Wang¹, X Q Wang¹, L X Li¹ and X Zhang¹,²

¹College of environmental science and engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, People’s Republic of China

E-mail: ahongjn@126.com

Abstract. The dewatering sewage sludge from the Wastewater Treatment Plant in the West of Jinan was chosen as the research object. Its physical and chemical properties were analyzed to investigate the passivation effect of fly ash on the four kinds of heavy metal (Cu, Ni, Zn and Pb) in sewage sludge. The results showed that the contents of organic matter, N and P were rich in the sludge and contents of the four heavy metals were accord with the standard “Disposal of sludge from urban wastewater treatment plant-Quality of sludge used in gardens or parks standard” (GB/T23486-2009). The four kinds of heavy metals could be passivated effectively by adding fly ash. The optimum effect could be obtained by adding 10-20% fly ash. It’s unfavorable to the passivation of Zn when the applied amount of fly ash exceeded 40%. The passivation effect of fly ash was mainly ion exchange and raising the pH to convert heavy metals into insoluble salts.

1. Introduction
Sewage sludge is a byproduct generated during the sewage treatment process. The total production of sewage sludge in China has been remarkably increasing as the increasing amount of treated wastewater. Its average growth rate was 13% per year from 2007 to 2013 [1,2]. The sludge way out has proved to be one of the main challenges that restricted the wholesome growth of wastewater treatment.

Sewage sludge is rich in nitrogen, phosphorus, organic matters and other trace elements which are necessary for plant growth. Land application is deemed to be an active and effective treated method for sludge. Sewage sludge in urban sewage treatment plants inevitably contains heavy metals, which has become a main barrier for land application of sludge [3]. The long-time application of sewage sludge would inevitably result in accumulating heavy metal in the soil.

Many methods have been used to stabilize the heavy metals in sewage sludge. During these processes, heavy metals in sludge were transferred from unstable state into stable state, reducing their mobility and bioavailability. Heavy metals could be immobilized via reacting with some chemical passivating agent by way of the processes of adsorption, precipitation and ion exchange. Lime was used to increase pH in sludge and form hydroxide precipitation with heavy metals [4]. Li et al added different amounts of lime to the dewatering sludge with a moisture content of 86.0%, and discovered that the highest passivation effect could be obtained through adding 7% lime [5]. In addition, the strong alkali condition could also kill some pathogenic microorganisms in the sludge. Zeolite was microporous aluminosilicate minerals and has a high specific area and a high cationic exchange capacity (CEC). Heavy metals could be immobilized by ion-exchange process and immobilized in
zeolite matrix [6]. Ashmawy et al believed that the optimum zeolite/sludge ratio was 10% and the retention percent of heavy metals was higher than 96% for Cu, Ni, Cd and Pb, and approximately 79% for Zn, respectively [7].

In this paper, the properties of sewage sludge and fly ash were analyzed to assess whether they were suitable for land use. The passivation effects of different amount of fly ash on the immobilization of heavy metals were analyzed. Scanning electron microscope (SEM) was used to determine the surface characteristics of fly ash and discuss the passivation mechanism of fly ash. It can help to provide a solution for the resource utilization of sludge and fly ash.

2. Materials and method

2.1. Materials

The dewatering sewage sludge was taken from the Wastewater Treatment Plant in the West of Jinan, where wastewater mainly originates from the domestic sewage and industrial wastewater of Changqing county and A²/O process was chosen as the biological wastewater treatment process. The sewage sludge was concentrated and dewatered by centrifugal machine to reach 20-30% solid content. The dewatering sewage sludge was air-dried, crushed by a grinder. The section passing through 100 mesh sieve was put in a sealed bag. The fly ash was taken from a coal-fired thermal power plant in Jinan and was screened through 60 mesh sieve.

HNO₃ and H₂O₂ was guaranteed reagent and all other chemicals were analytical reagent grade and can be used without further purification.

2.2. Experimental methods

2.2.1. Analytical methods of physical and chemical properties. The basic properties of sewage, soil and fly ash were determined by “Determination method for municipal sludge in wastewater treatment plant” (CJ/T221-2005). PH was determined by electrode method and electricity conductivity (EC) and CEC were measured by 5:1 extraction-conductivity method and BaCl₂-H₂SO₄ method, respectively. Organic matter contents were measured with potassium dichromate volumetric method. Total nitrogen (TN) was determined by semi-micro Kjeldahl method. Sludge and soil were digested by H₂SO₄-HClO₄ to determine their total phosphorus (TP).

2.2.2. Analytical methods of heavy metals. The total content of heavy metals was determined by inductively coupled plasma emission spectrometry (ICP) after digested by HNO₃ and H₂O₂.

Heavy metals fraction was carried out according to the modified BCR method [8]. It involves successive treatment of sample with 0.11 mol. L⁻¹ HAC, 0.50 mol. L⁻¹ hydroxylammonium chloride at pH 1.5 and H₂O₂ followed by 1.0 mol.L⁻¹ ammonium acetate at pH 2. During the retrieval process, heavy metals in each sample are segmented into four fractions: exchangeable fractions, reducible fractions, oxidizable fractions, residual fractions. These four different fractions show different bioavailability. The exchangeable fraction is ccombined with carbonate, easily migrates into the soil solution. The reducible fraction and the oxidizable fraction are potentially bioavailable. The residual fraction is considered to be inaccessible to plants.

3. Results and discussion

3.1. Fundamental properties

It can be seen from table 1 that pH of the sludge was neutral, which was close to pH of the background soil. pH of the fly ash is as high as 10.88. This was related to the composition of fly ash, of which the main components are CaO, MgO, Fe₂O₃, etc. The pH value of fly ash has a linear relationship with the content of the CaO, or the CaO/SO₄²⁻. The high pH value is beneficial to transfer exchangeable fractions, oxidizable fractions and reducible fractions into the residual fraction [9]. Adding fly ash to
the soil will increase the pH of the mixture, which can reduce the biological availability of heavy metals.

Table 1. Fundamental properties of sewage sludge, background soil and fly ash.

|                | pH       | EC (mS/cm) | CEC (mmol/kg) | Organic matter (g/kg) | TN (g/kg) | TP (g/kg) |
|----------------|----------|------------|---------------|-----------------------|-----------|-----------|
| Sewage sludge  | 6.89±0.13| 1.92±0.064| 142.52±3.48   | 19.37±2.53            | 17.14±1.87|           |
| Background soil| 6.82±0.04| 0.11±0.004| 30±13         | 0.15±0.05             | 0.35±0.04 |           |
| Fly ash        | 10.88±0.02| 0.57±0.04 | 79.59±2.06    |                       |           |           |

EC is an important indicator to measure soluble salt content. High soluble salt content will inhibit the growth of plants, and lead to root burning. The EC of sewage sludge and fly ash were 1.92 mS/cm and 0.57 mS/cm, respectively, which were much higher than that of the background soil. If they were added into the soil, the EC of the mixture would be less than 2, which met the demand for EC in the national standard of China “Disposal of sludge from municipal wastewater treatment plant - Quality of sludge used in gardens or parks” (GB/T23486-2009) [10].

CEC is an important indicator of soil characteristics. The soil with high CEC has better buffering capacity and ability of preserving water and fertilizer. The CEC of the sludge and fly ash were 142.52mmol/kg and 79.59mmol/kg, which were higher than that of background soil. If they were added into the background, a mixture with high buffering capacity and high ability of preserving water and fertilizer could be obtained. The high CEC for fly ash showed that ion exchange might become one of the main mechanisms for heavy metals passivation.

The content of fertilizer components in sewage sludge is an important factor to measure its utilization value during land application process. The organic matter, TN and TP in the sludge were far higher than that in the background soil, which were 49.8, 129.1 and 48.9 times of that of the background soil. They met the requirement of the fertilizer efficiency index for sewage sludge for the garden greening in GB/T23486-2009.

3.2. Contents of heavy metals in sewage sludge and fly ash

The contents of Cu, Ni, Pb, and Zn in sewage sludge were 102.25 mg/kg, 184.75 mg/kg, 46.5 mg/kg and 1926.5 mg/kg, respectively. The contents of Pb, Ni, Zn and Cu in fly ash were 15.53 mg/kg, 13.83 mg/kg, 57.09 mg/kg, and 18.8 mg/kg, respectively (shown in table 2). All the contents of heavy metals in sludge and fly ash were lower than the maximum concentration of heavy metals from Disposal of sludge from urban wastewater treatment plant - Quality of sludge used in gardens or parks (GB/T23486-2009), so the sludge could be used for landscaping.

From the above discussion, it could be seen that the sewage sludge met the demands for sewage sludge used in garden and parks. At the same time, the sewage sludge is rich in organic matter, TN and TP. During the land application process, the nutrients would beneficial to the growth plants. The fly ash could also be added into the soil as the additive.

Table 2. Content of heavy metals in sewage sludge and fly ash (mg/kg).

|                | Cu  | Ni  | Pb  | Zn  |
|----------------|-----|-----|-----|-----|
| Sewage sludge  | 102.25 | 184.75 | 46.5 | 1926.5 |
| Fly ash        | 18.8  | 13.83 | 15.53 | 57.09 |
| In acid soil (pH<6.5)* | 800  | 100  | 300  | 2000 |
| In medium or alkaline soil (pH≥6.5)* | 1500 | 200  | 1000 | 4000 |

* Data came from Disposal of sludge from urban wastewater treatment plant - Quality of sludge used in gardens or parks(GB/T23486-2009).
3.3. Effect of fly ash on morphology of heavy metals in sludge

The fraction of heavy metal is more significant than total content in measuring their flowability, biological availability and hazards to environment. The modified BCR continuous extraction method provided a more circumstantial assessment method to determine the moving capacity of heavy metal in the environment. The passivation effect of fly ash with different ratio to the sludge was shown in figure 1.

![Graphs showing the passivation effect of fly ash on heavy metals in sludge](image-url)

**Figure 1.** Passivation effect of coal fly ash on heavy metals in sludge.

It can be seen from figure 1 that Cu in the sewage sludge were mainly in the residual fraction and the oxidizable fraction. The percentage of residual Cu increased after fly ash was added into the sludge. When the additional amount of coal ash is 10%, the residual Cu content increases from 30.3% to
48.4%. As the amount of fly ash added increased, the residual Cu increased little, but the exchangeable fraction continued to decrease. The exchangeable Cu gradually decreased with the increasing amount of fly ash. This might be due to the fact that pH of the fly ash is 10.88, when fly ash is mixed with sludge, it will have an impact on the humification of organic matter in the sludge. At the same time, fly ash is basically free of organic matter. Adding it to the sludge will reduce the organic matter content of the sludge and reduce the percentage of exchangeable Cu of the mixture [11]. When the addition of fly ash reach 40%, the exchangeable Cu could be reduced to 3.77%. The proportions of reducible Cu were less than 1%, and decreased with the addition of fly ash.

Ni mainly existed in the residual fraction, the oxidizable fraction and the exchangeable fraction. The residual Ni increased from 38.3% to 45.7% when 20% fly ash was added into the sewage sludge. The exchangeable Ni reduced with the increase of the amount of fly ash.

Pb was mainly in the exchangeable state and the residual state. Both the reduced fraction and the oxidizable fraction were lower than the detection limit. The exchangeable Pb decreased with the addition of fly ash and all of the reduced Pb was almost converted into the residual fraction. The exchangeable Pb decreased from 4.4% to 1.8% and the residual fraction increased from 95.6% to 98.2% when 10% fly ash was added into sewage sludge. Even if the addition of fly ash continued to increase, the residual Pb increased little. Therefore, the appropriate addition of fly ash for Pb immobilization was 10%.

Zn mainly existed in the reducible state, the oxidizable state and the residual state. The exchangeable Zn decreased with the increase of fly ash addition. The exchangeable state content reduces from 5.1% to 2.2% by adding 10% fly ash. With the increase of the amount of fly ash, the exchangeable Zn decreased little. When the addition of fly ash reached 40%, the exchangeable Zn tended to increase. This might be due to the fact that the passivation of metals by fly ash mainly depends on increasing the pH of the sludge [12]. The high pH helps to convert metal cations to hydroxide precipitates and form amphoteric hydroxide Zn(OH)$_2$, which could be dissolved in alkali condition. The excessive increase of the pH would cause Zn(OH)$_2$ to dissolve, leading to the increase of the exchangeable Zn. Therefore, excessive addition of fly ash was unfavorable to Zn fixation.

This result showed that fly ash had different passivation effects on different heavy metal in sludge. Overall, when addition amount of fly ash is 10~20%, the passivation efficiency on four heavy metal could obtained the best result.

3.4. Passivation mechanism of fly ash on heavy metals

The passivating effect of fly ash on heavy metals was investigated by SEM, shown in figure 2. It was shown in figure 2(a) that the particle shapes of sewage sludge were irregular, and most of them were flaky and bulk. Fly ash is produced by coal-fired power plants, which was predominantly amorphous aluminosilicate glassy spheres. They are different in size, smooth in surface and dense in texture, shown in figure 2(b). The specific area of the selected fly ash obtained by BET test was 2.1 m$^2$/g, less than that of the background soil (5.5 m$^2$/g). It means that the main passivation effect of the fly ash was not adsorption but the formation of hydroxide precipitation and ion exchange. Therefore, it is possible to modify the fly ash and increase its specific surface area, so as to improve its passivation effect on heavy metal in sludge. Figure 2(c) showed the SEM morphology of the sludge passivated with fly ash. Fly ash particles were wrapped and bonded together with the sewage sludge particles and they were fully contacted, which was beneficial to ion exchange process. The amorphous glassy spheres of fly ash showed a strong capacity for ion exchange. The selected fly ash had a high CEC of 79.59±2.06 mmol.kg$^{-1}$ (shown in table 1), which indicated for fly ash, ion exchange was one of the main immobilization mechanisms of heavy metals.

On the other hand, the selected fly ash was alkaline (pH=10.88). The high pH value is beneficial to transfer the other three fractions into the residual fraction. Heavy metals can be precipitated by forming metal hydroxide and carbonates with the increase of pH value. The increased pH also reduces the content of exchangeable fraction. What’s more, the increasing pH would increase the variable charges on the sewage sludge superficies, which would reduce the special capacity to adsorb heavy
metal onto the surface of sewage sludge. When the alkali fly ash was added into sewage sludge, the increasing pH was beneficial to the immobilization of heavy metals.

![Figure 2](image)

**Figure 2.** SEM morphology of fly ash and sludge (a) sewage sludge before passivation (×1500); (b) fly ash before passivation (×1500); (c) sewage sludge passivated by fly ash (×1500).

4. Conclusion
The selected dewatering sewage sludge had the good ability of water and fertilizer conservation. It is abundant in organic matters, nitrogen and phosphorus, which met the nutritional requirements of “Disposal of sludge from urban wastewater treatment plant - Quality of sludge used in gardens or parks standard” (GB/T23486-2009). The contents of the four heavy metals (Cu, Zn, Ni and Pb) were below the limits values of GB/T23486-2009. The passivation effects of fly ash on the four heavy metals were different. The optimum effect could be obtained by adding 10-20% fly ash. There was no obvious increasing passivation on the four heavy metals. Especially, it’s unfavorable to the passivation of Zn when the applied amount of fly ash exceeded 30%. The passivation effect of fly ash was mainly ion exchange and raising the pH to convert heavy metals into insoluble salts.

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