Study on Heavy Metal Speciation Transformation and Stability during Anaerobic Digestion of Excess Sludge with Alkali Residue Addition

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Abstract [**Objectives**] This study investigated the transformation of heavy metals during anaerobic digestion of excess sludge with alkali residue addition. [**Methods**] Two types of solid waste, *i. e.*, excess sludge from a wastewater treatment plant and alkali residue from the ammonia-soda process, were selected as research objects. The effects of adding alkali residue calcined at 800 °C (AR800) on the speciation distribution and potential mobility of Zn, Cu, Cr, and As during anaerobic digestion were investigated. [**Results**] The speciation of heavy metals in the raw sludge varied significantly, and the stability ranked as Cr > As > Cu > Zn. After the addition of AR800, the stable fractions of all heavy metals in the digested sludge increased. The proportions of stable fractions of various metal reached their peak values on day 7 of anaerobic digestion. The differences in heavy metal fraction distribution were small under different dosages (2%, 5%, 8%). Considering both stabilization performance and economic cost comprehensively, 2% was selected as the optimal dosage. After digestion, the ratios of unstable-tostable fractions for Zn, Cu, Cr and As decreased from 2.17, 0.35, 0.08 and 0.16 to 0.69, 0.04, 0.02 and 0.05, respectively. It indicates that alkali residue addition can effectively reduce the potential mobility of heavy metals. Mechanistically, alkaline substances increase the surface charge of digested sludge and promote the transformation of heavy metals into more stable fractions. [**Conclusions**] This study provides a theoretical basis for the safe land application of digested sludge under the "treating waste with waste" mode.

Key words Excess sludge; Alkali residue; Anaerobic digestion; Heavy metal fraction; Potential mobility

DOI:10.19759/j.cnki.2164 – 4993.2026.04.005

With the urban sewage treatment capacity increasing continuously, the output of excess sludge keeps increasing. Heavy metals including Zn, Cu, Cr and As accumulated in sludge pose considerable environmental risks during land application, which has become a bottleneck restricting sludge resourceoriented disposal[1-2]. Anaerobic digestion is an important approach for sludge resource utilization, as it can not only realize sludge reduction and stabilization, but also recover biogas. The study of Chen *et al.*[3] showed that the proportions of stable fractions of Cu, Zn, Ni and Cr generally increased after anaerobic digestion, especially for Cr. Nevertheless, the decomposition of organic matter during digestion alters the pH and redox potential of sludge, and further affects the migrationtransformation behavior and bioavailability of heavy metals[4].

In recent years, Guan *et al.*[5] pointed out in their solidstate anaerobic digestion studies that the passivation of Cu and Zn is mainly achieved through complexation with humic acids, whereas the passivation of Pb and Cr is highly dependent on pH elevation. This finding provides direct evidence for enhancing heavy metal stabilization under alkaline conditions. A review of Kadam *et al.*[6] further systematically summarized the inhibitory and promoting effects of heavy metals including Cu, Zn, Cd, Fe and Ni on hydrolysis and acid-producing stages.

To enhance the hydrolysis and acid-production efficiency of sludge anaerobic digestion, alkaline reagents such as NaOH and $Ca(OH)_2$ are frequently dosed by scholars. Nevertheless, such treatments commonly suffer from high cost and deteriorated sludge dewatering performance[7]. As a largevolume solid waste generated from the ammonia-soda process, alkali residue features strong alkalinity, nontoxicity and abundant $CaCO_3$. Applying alkali residue to anaerobic digestion of excess sludge can realize "treating waste with waste", and its alkalinity can be utilized to promote sludge hydrolysis and acid production[8]. Li *et al.*[9] adopted refinery alkali residue to replace fresh alkaline agents for the pretreatment of refinery excess activated sludge, achieving a methane yield 5 times that of untreated sludge. Their subsequent study[10] further evaluated that alkaline fermentation-combined pretreatment yielded the maximum net benefit, and proposed a novel strategy for the cotreatment of waste sludge and alkali residue. The abovementioned studies have verified the feasibility of enhancing anaerobic digestion by alkali residue, whereas few studies have been conducted on its effects on the stability of heavy metal fractions in digested sludge.

In this study, with four typical heavy metals including Zn, Cu, Cr and As selected as research objects, the BCR sequential extraction method was adopted to analyze their fraction variation patterns during anaerobic digestion, and the effect of alkali residue addition on heavy metal stability was investigated via the potential migration capacity evaluation system, so as to provide data support for the engineering application of alkali residueenhanced sludge anaerobic digestion.

Received: May 12, 2026 Accepted: July 15, 2026

Supported by Natural Science Foundation of Fujian Province (2026J0011857).

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Materials and Methods

Experimental materials

Excess sludge was collected from the secondary sedimentation tank of an urban wastewater treatment plant in Nanjing. The sludge was statically settled for 24 h and stored at 4 ℃ for subsequent use. The main properties of the sludge were as follows: pH 7.09, water content 97.06%, TSS 28 400 mg/L, VSS 13 500 mg/L, and SCOD 85 mg/L.

Alkali residue was obtained from the waste residue storage yard of an ammonia-soda plant in Shandong Province. Raw alkali residue powder (AR) was prepared through steps of crushing, water washing, drying at 60 ℃, grinding and sieving with a 100-mesh sieve. Part of the AR was calcined at 800 ℃ under air atmosphere for 2 h to obtain calcined alkali residue (AR800), which was stored in a sealed condition.

Experimental methods

Into 500 ml serum bottles, 400 ml of excess sludge was added, respectively. A blank control group and AR800 addition groups were set up, and the dosages for the AR800 addition groups were 2%, 5% and 8% based on the dry weight of sludge, respectively. High-purity nitrogen was purged for 5 min before sealing the bottles. The bottles were placed in a constant-temperature shaking incubator at (35 ± 1) ℃ with 180 r/min for 11-day anaerobic digestion, and samples were collected at regular intervals for analysis.

Analytical and determination methods

(1) Extraction of heavy metal fractions: The BCR sequential extraction method[11] was employed to fractionate heavy metal speciation into acid-extractable fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4), wherein F1 + F2 were defined as the unstable fractions and F3 + F4 as the stable fractions. Extraction procedure: For the acid-extractable fraction (F1), 40 ml of 0.11 mol/L HAc was added, followed by shaking and centrifugation. For the reducible fraction (F2), 40 ml of 0.5 mol/L $NH_2OH \cdot HCl$ (pH 1.5) was added to the residue from the previous step, followed by shaking and centrifugation. For the oxidizable fraction (F3), the residue from the previous step was sequentially treated with H_2O_2 for oxidation, and then 50 mL of 1.0 mol/L NH_4OAc was added for extraction, followed by shaking and centrifugation. For the residual fraction (F4), the residue was digested with 20 ml of distilled water and an HNO_3-$HClO_4$-HF mixture.

(2) Determination of heavy metal contents: The contents of heavy metals in sludge were all determined by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 7000DV).

(3) Evaluation of potential mobility of heavy metals: According to the method of Chen *et al.*[3], the ratio of the sum of unstable fractions to the sum of stable fractions was used as an indicator of the potential mobility of heavy metals. A higher R value indicates a stronger potential mobility of heavy metals.

$$R = \frac{m(F1) + m(F2)}{m(F3) + m(F4)}$$

Results and Discussion

Speciation distribution of heavy metals in raw sludge

The speciation distribution of heavy metals in the raw sludge is shown in Fig. 1. Zn predominantly existed in the acid-extractable fraction (33.40%) and the reducible fraction (37.25%), with the unstable fractions accounting for 70.65%, indicating that Zn was the most unstable heavy metal. Cu was mainly present in the oxidizable fraction (69.67%), exhibiting moderate stability. Cr showed relatively high contents in the residual fraction (53.44%) and the oxidizable fraction (38.41%), demonstrating the highest stability. As was dominated by the oxidizable fraction (46.93%) and the residual fraction (34.76%), showing stability ranking second only to Cr. In summary, the stability the four heavy metals ranked as Cr > As > Cu > Zn.

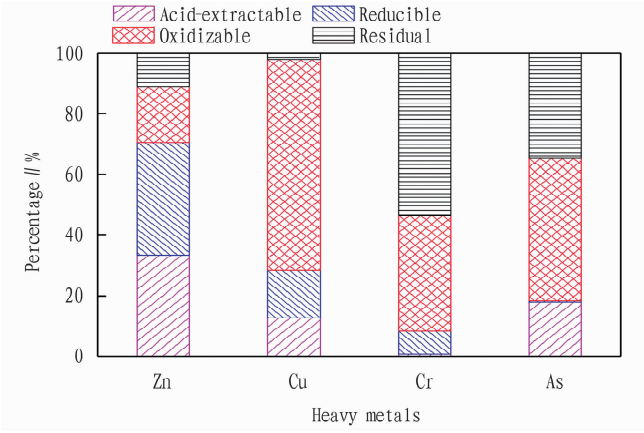

Fig. 1 Speciation distribution of heavy metals in raw sludge

Effect of calcined alkali residue dosage on heavy metal speciation after digestion

In this study, the addition of AR800 was found to enhance the hydrolytic acidification capacity of excess sludge, as it effectively reduced the richness and diversity of the microbial community during anaerobic digestion[8]. Therefore, the effects of different AR800 dosages on the stability of heavy metals during anaerobic digestion were investigated, as shown in Fig. 2. The results showed that the proportions of unstable fractions of Zn and Cu decreased with the dosage increasing, and Zn reached its lowest unstable fraction at a dosage of 5%. For Cr and As, the stable fractions predominated at all dosages, and the residual fraction contents increased slightly with the dosage increasing. The differences in speciation distribution among different dosages were relatively small. Considering both the stabilization efficiency and economic cost, the optimal dosage of AR800 was also determined as 2%. Since the main component of the alkali residue calcined at 800 °C was converted to CaO, the pH increased after its addition. The alkaline conditions promoted the dissociation of organic matter containing functional groups such as hydroxyl and carboxyl groups that coordinate with heavy metals in the sludge, thereby increasing the negative charge density on the sludge surface and enhancing the adsorption and immobilization of heavy metal ions[12].

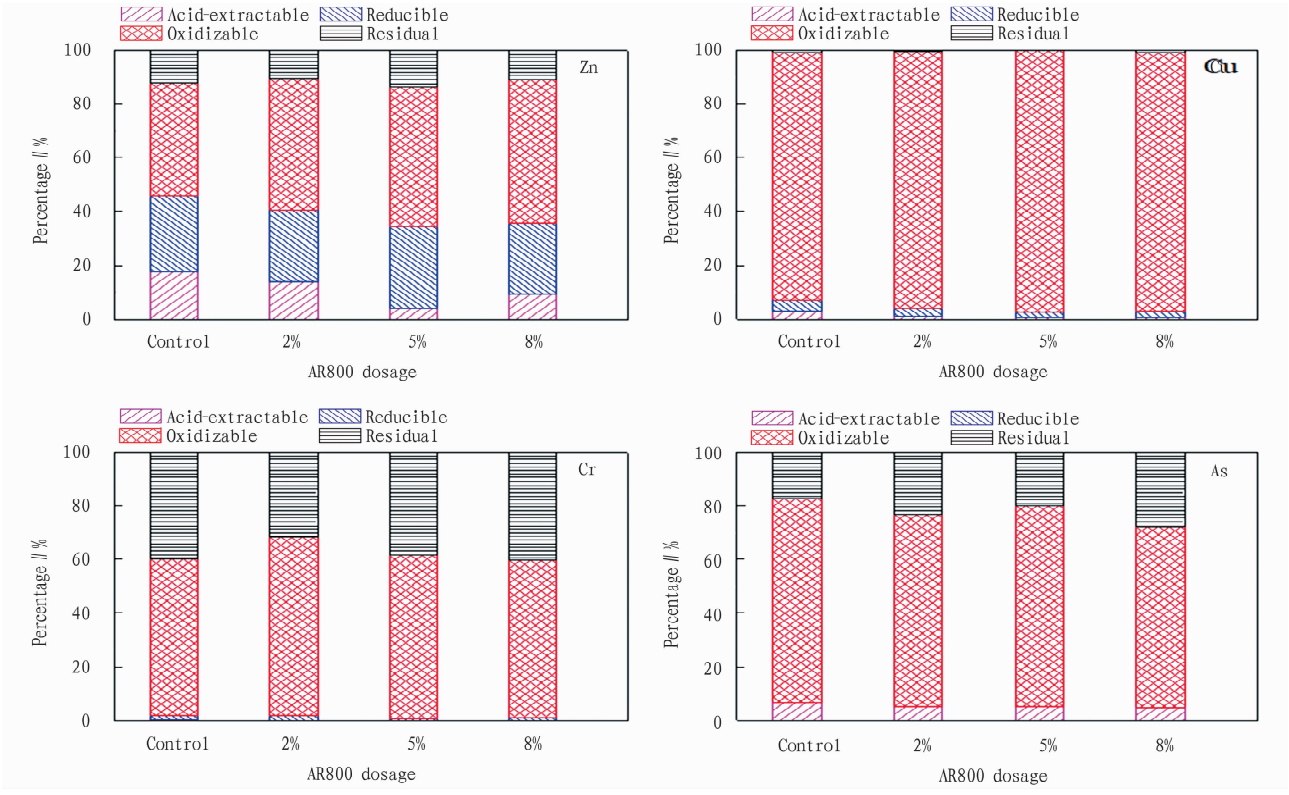

Fig. 2 Changes in speciation distribution of heavy metals at different AR800 dosages

Changes in heavy metal speciation during anaerobic digestion

At an AR800 dosage of 2%, the speciation changes of Zn, Cu, Cr, and As during the entire digestion process were further investigated, as shown in Fig. 3.

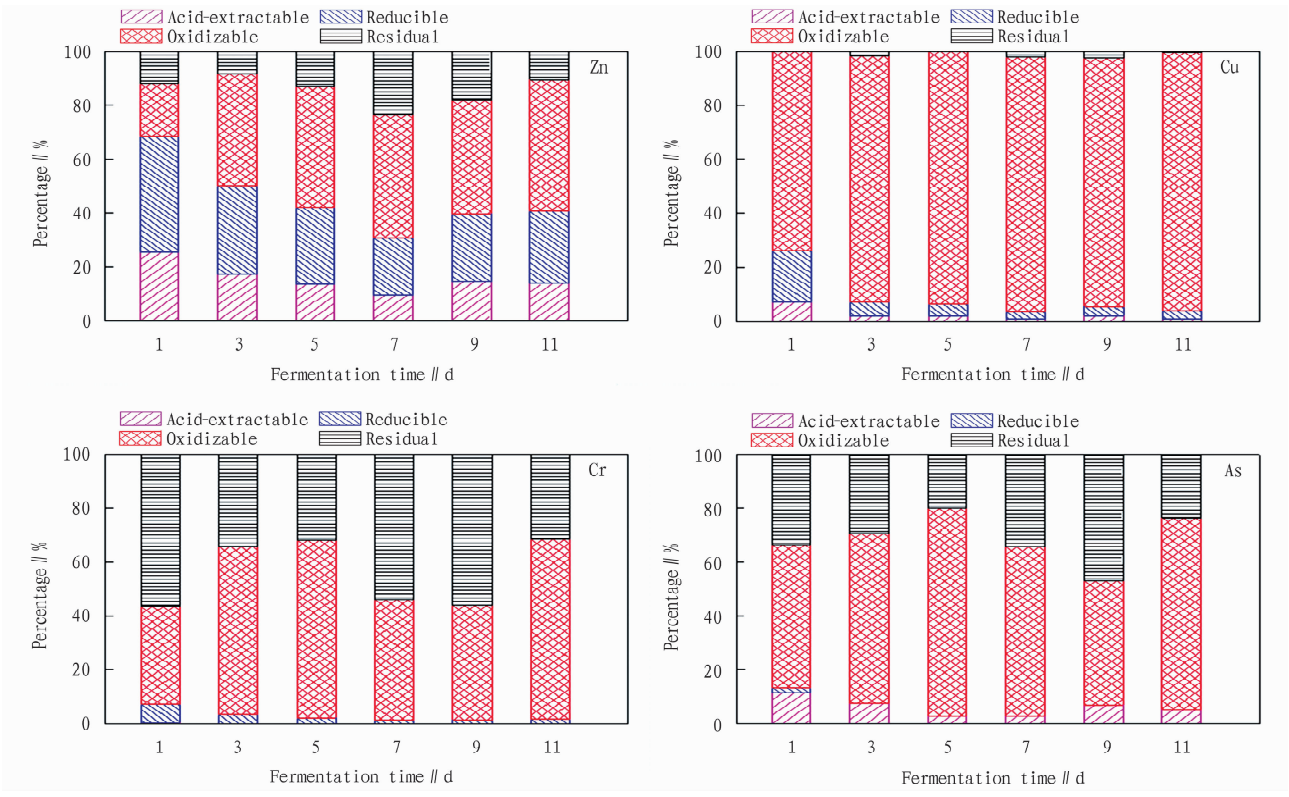

Fig. 3 Changes in speciation of heavy metals during sludge anaerobic fermentation process

During digestion, the unstable fraction content of Zn first decreased and then increased over time, reaching its highest stable fraction proportion of 69.25% on day 7. The acid-extractable and reducible fractions of Cu continuously decreased, while the oxidizable fraction increased and tended to stabilize in the later stage of digestion. For Cr and As, the oxidizable and residual fractions predominated throughout the digestion process, and stable fractions reached 98.74% and 97.27%, respectively, on day 7, representing the strongest stability of heavy metals during the entire digestion cycle. It might be attributed to the fact that the hydrolysis and consumption of organic matter such as proteins and polysaccharides during anaerobic digestion reduced the ligands that form oxidizable complexes with heavy metals, leading to a relative decrease in the oxidizable fraction and a relative increase in the residual fraction[2].

Evaluation of potential mobility of heavy metals

Based on the time-series data of *R* values (Table 1), the potential mobility of all four heavy metals decreased after the addition of AR800. Before digestion, the *R* value of Zn was as high as 2.17, much higher than those of Cu (0.35), Cr (0.08), and As (0.16), indicating that Zn had the strongest potential mobility. After 11 d of anaerobic digestion, the *R* value of Zn decreased to 0.69, indicating a reduction in its potential mobility. The *R* values of Cu, Cr, and As remained at low levels throughout the process. In particular, the *R* values of Cr and As in the later stage of digestion were only 0.02 and 0.05, respectively, suggesting extremely low bioavailability and manageable environmental risks.

Table 1 Effect of anaerobic digestion on potential mobility of heavy metals

Time of anaerobic digestion//d	[m(F1)+m(F2)]/[m(F3)+m(F4)]			
	Zn	Cu	Cr	As
1	2.17	0.35	0.08	0.16
3	1.00	0.08	0.03	0.08
5	0.72	0.07	0.02	0.02
7	0.44	0.04	0.01	0.03
9	0.66	0.06	0.01	0.07
11	0.69	0.04	0.02	0.05

Conclusions and Discussion

(1) The stability of Zn, Cu, Cr, and As in the raw sludge showed an order of Cr > As > Cu > Zn, and Zn was dominated by the unstable fractions.

(2) The addition of AR800 promoted the transformation of the four heavy metals from unstable to stable fractions, and the stabilization reached a peak on day 7 of digestion. The stable fraction contents were 69.25%, 94.49%, 98.74%, and 97.27%, respectively. The speciation distribution showed little difference among different dosages, and the optimal dosage was determined to be 2%.

(3) Zn exhibited the strongest potential mobility. After the addition of AR800, the *R* values of Zn, Cu, Cr, and As decreased from 2.17, 0.35, 0.08, and 0.16 to 0.69, 0.04, 0.02, and 0.05, respectively, effectively reducing the potential mobility risks of heavy metals.

(4) The alkali residue promoted the transformation of heavy metals from unstable to stable fractions by regulating the alkaline environment of the digestion system and synergizing with organic matter degradation, thereby providing a guarantee for the safe land application of digested sludge.

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Editor: Yingzhi GUANG Proofreader: Xinxiu ZHU