RESEARCH ARTICLE
doi: 10.2306/scienceasia1513-1874.2022.120

ScienceAsia 48 (2022): **782–787**

Transformation of heavy metals via sludge composite conditioning

Sen Wang[a,b,*], **WanKun Xu**[a], **Pei Yi**[a,b], **JiaoJiao Yuan**[a], **Meng Li**[a], **Fang Su**[a], **Wen Shen**[a,c]

[a] School of Environmental Science and Engineering, Shaanxi University of Science and Technology, Xi’an 710021 China
[b] China Light Industry Water Pollution Control Engineering Center, Xi’an 710021 China
[c] Shaanxi Research Institute of Agricultural Products Processing Technology, Xi’an 710021 China

[*]Corresponding author, e-mail: wangsen@sust.edu.cn

Received 2 Aug 2021, Accepted 10 Jun 2022
Available online 10 Aug 2022

ABSTRACT: To investigate the distribution of heavy metals and their morphological transformation during sludge treatment, sludge was conditioned by the persulfate method and combined with papermaking sludge. The removal rates, distribution and morphological transformation of the heavy metals Cd, Cr, Cu, Pb and Zn were analyzed. The results showed that the concentrations of heavy metals in residual sludge were all reduced to different degrees after persulfate conditioning. The Zn removal rate was highest, reaching 33.90%. After compound conditioning, the heavy metal removal rate was reduced, mainly because of the heavy metals contained in papermaking sludge. Heavy metal removal followed the order Zn > Cu > Cr > Pb > Cd. After compound conditioning, heavy metals were mainly concentrated in the filter cake; Cd and Zn mainly occurred in unstable forms and Cr, Cu, and Pb in stable forms.

KEYWORDS: persulfate, papermaking sludge, heavy metals, morphological transformation, compound condition

INTRODUCTION

Sludge is the solid, semi-solid, and liquid waste produced in the process of urban sewage treatment [1]. It generally contains large amounts of organic matter, refractory substances, and heavy metals, as well as, high numbers of pathogenic microorganisms, parasite eggs [2–4]. Inadequate treatment results in risks to human health and causes secondary environmental pollution. The sludge contains large amounts of nitrogen, phosphorus, and other nutrients and can therefore be used as fertilizer and soil conditioner after composting [5]. However, the heavy metals in the sludge may form complexes with other substances and cause serious pollution [6] or may threaten human health by enrichment in the food chain [7]. For example, the “pain sickness” [8] in Japan in the early 20th century was caused by the heavy metal cadmium, whereas lead affects the central and peripheral nervous system, the cardiovascular system, and the reproductive system, among others [9]; excessive lead levels have also be linked to a lower intelligence in children and to hyperactivity disorder [10].

The main methods for the removal of heavy metals in sludge are bioleaching [11–14], chemical method [15], pyrolysis [16, 17], and electrokinetic remediation [18, 19]. Xiong et al [20] studied the migration of heavy metals during electric dehydration and found that heavy metals were basically retained in the mud cake after electric dehydration; in addition, heavy metal migration mainly depended on the forms of heavy metals. Zhang et al [21] studied the effect of persulfate on the removal of heavy metals; the Pb, Zn, Cu, and Cd removal rates from sludge reached more than 60%. In another experiment, Qi et al [22] bioleached municipal sludge with *Thiobacillus subtilis* oxide and obtained Cu, Zn, Ni, and Cr removal rates of 55.97%, 47.66%, 26.10%, and 2.10%, respectively. The transformation of heavy metals in sludge resource use and energy conversion are crucial, and numerous studies [23–25] have shown that the bioavailability of heavy metals in sludge mainly depends on the distribution of the heavy metal forms.

In this context, it is particularly important to study the morphological distribution of heavy metals during sludge conditioning. According to the five-step extraction method proposed by Tessier et al [26], heavy metal forms can be divided into exchangeable, carbonate-bound, iron-manganese oxide-bound, organic-bound, and residue forms. Among them organic-bound and residue forms are stable in sediments and more stable under natural conditions, are not easily absorbed by plants and not easily released, and have little effect on the food chain. The stability follows the order: residue form > organic-bound form > iron-manganese oxide-bound form > carbonate-bound form > exchangeable form [27].

At present, sludge conditioning is mostly performed using the advanced oxidation technology and skeleton construction. At first, extracellular polymeric substances (EPS) are cracked, generating free radicals with strong oxidation performance and thereby releasing water from inside the cells and removing heavy metals [28]. However, using this approach, the system can easily collapse and block the water channel during sludge dewatering. In papermaking sludge, fine fibers, $CaCO_3$, kaolin, and other substances can be used as skeleton for the formation of a rigid structure in the filter cake, to build a water channel, to reduce the compressibility of the filter cake, and to improve sludge dewatering. In this study, persulfate from papermaking sludge was used for sludge regulation, and the distribution relationship and morphological distribution of the heavy metals Cu, Zn, Pb, Cd, and Cr during compound conditioning were investigated to provide a scientific basis for sludge reduction and resource reuse.

MATERIALS AND METHODS

Experimental materials

The municipal sludge used in this study was excess sludge from a sewage treatment plant concentration tank in Xi'an, Shaanxi Province. The papermaking sludge was taken from the primary settling tank of a papermaking wastewater treatment plant in Shaanxi Province and contained small amounts paper fibers used for skeleton construction. Prior to use, the sludge was stored in a freezer at 4 °C. Table 1 shows the basic properties of the two sludge types at room temperature (20–25 °C).

Table 1 Basic properties of the two experimental sludge types.

Sludge type	Water content (%)	pH	Organic matter (%)	$SRF/10^{12}$ (m/kg)	CST (s)
Municipal	96.5	6.8	58.56	20.14	159
Papermaking	98.1	6.9	36.30	–	–

SRF = specific resistance of filtration; CST = capillary suction time.

Reagents

The agents used for deep dewatering included persulphate ($K_2S_2O_8$) and ferrous sulphate ($FeSO_4$-7 H_2O), which were of analytical grade and provided by Tianjin Damao Chemical Reagent Co., China. The reagents used for heavy metal determination and the extraction of heavy metal forms were perchloric acid ($HClO_4$), nitric acid (HNO_3), hydrogen peroxide (H_2O_2, 30%), sodium acetate (NaOAc), and glacial acetic acid (HOAc), all of which were of analytical grade and obtained from Sinopharm Group Chemical Reagent Co., China.

Experimental methods

We placed 100 ml of raw municipal sludge in a 250 ml beaker, which was mounted on six-link mechanical agitator (JJ-4A, Changzhou Wan He Instrument Manufacturing Co., Ltd., China); different conditioning methods were adopted. The specific scheme is shown in Table 2. The conditioned sludge was dewatered using a suction filtration device, the filtrate and filter cake of the dewatered sludge were used for digestion, and the contents of various heavy metals were determined. The dosage of fixed PDS (peroxydisulfate) was 30 mg/g DS (dry solid), that of $FeSO_4$ was 60 mg/g DS, and that of papermaking sludge was 100 mg/g DS. The reaction time was 10 min, and the initial pH was the original pH of the municipal sludge.

Analytical methods

The concentrations of heavy metals were determined according to the Monitoring and Analysis of Water and Wastewater (4th edn) [29], using inductively-coupled plasma emission spectrometry speciation (ICP-AES; American Thermoelectric icap6300, Shanghai Gold Casting Instrument Co., Ltd., China) for Cu, Zn, Pb, Cd, and Cr based on the five-step extraction method of Tessier et al [26].

RESULTS AND DISCUSSION

Effects of different conditioning methods on heavy metal concentration

The impact of municipal sludge, papermaking sludge, and the different conditioning methods on the concentration of five heavy metals in sludge are shown in Table 3. It was found that the levels of Zn in municipal sludge was highest, followed by Cu, Pb, Cr, and Cd, whereas the Zn content in papermaking sludge was highest, followed by Cr. This is because in China, pipelines are mainly galvanized [30], and the Zn in the pipeline enters the sewage treatment plant. In the follow-up treatment, Zn migrates to the sludge.

As seen in Table 3, the total metals in the sludge were removed to different degrees after persulfate conditioning. The highest removal effect was obtained for Zn, with a removal rate of 33.90%, followed by Cu with 26.65%. The heavy metals Zn Cu, and Cd mainly exist in the sludge system in an unstable form, and the redox potential of sulfate radicals produced after persulfate activation is $E_0 = 2.50–3.10$ eV [26]. When oxidizing the unstable heavy metals to achieve removal, the Cd removal rate was close to zero, which may be due to the low content of Cd. Both Pb and Cr existed mainly in a stable form in the sludge system, and were not easily dissolved, resulting in low removal rates of 9.63% and 9.27%, respectively. The effect of compound conditioning on the removal of heavy metals in sludge was lower than that of the use of persulfate alone, except for the removal of Zn and Cu, where removal rates of 29.24% and 5.89%, respectively, were obtained. However, the contents of Cd, Cr, and Pb were slightly higher than those in the original sludge, most likely because the papermaking sludge itself contained heavy metals; the amounts followed the order Zn > Cu > Cr > Pb > Cd. In addition, the contents of Cd, Cr, and Pb in the municipal sludge were lower.

Table 2 Sludge conditioning plan.

Experiment no.	Sludge sample	Conditioning method
1	Papermaking sludge	Stirring for 5 min
2	Municipal sludge	Stirring for 5 min
3	Papermaking sludge conditioning	Municipal sludge → stirring 5 min → papermaking sludge → stirring 10 min
4	Persulfate conditioning	Municipal sludge → stirring 5 min → potassium persulfate → stirring 5 min → ferrous sulfate → stirring 10 min
5	Compound conditioning	Municipal sludge → stirring 5 min → papermaking sludge → stirring 10 min → potassium persulfate → stirring 5 min → ferrous sulfate → stirring 10 min

Table 3 Heavy metal concentrations in the different experiments.

Experiment no.	Cd (mg/kg)	Cr (mg/kg) (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn
1	8.20	148.15	100.79	67.99	616.93
2	2.91	68.52	76.46	33.66	515.87
3	4.76	101.85	86.45	44.60	531.22
4	2.91	62.17	56.08	30.42	341.01
5	4.23	76.72	71.96	40.21	365.01

Effects of different conditioning methods on heavy metal distribution

Fig. 1 shows the distribution of the five heavy metals in the filtrate and the filter cake as a result of the different conditioning methods. The distribution of heavy metals in filtrate and filter cake was similar before and after conditioning, and heavy metals are mainly distributed in the filter cake [31]. According to the previous study, the larger the distribution of the metal in the filter cake, the less likely that metal is to migrate with the filtrate [18]. The heavy metals Cd, Cr, Cu, Pb, and Zn in the raw mud accounted for 15.38%, 35.86%, 19.15%, 30.32%, and 27.96%, respectively, of the total amount in the filtrate. After persulfate conditioning, the levels were 9.54%, 15.83%, 4.74%, 10.32%, and 8.26%, respectively. The main reason was that the Cu could combine with strong organic ligands to form stable compounds and was fixed in the filter cake; Pb forms a lead sulfate precipitate with SO_4^{2-} present in the system, which cannot easily be morphologically conversed.

After compound conditioning, the proportions of the five heavy metals in the filtrate were 3.16%, 6.76%, 0.88%, 1.73%, and 1.66%, mainly because the distribution of heavy metals in papermaking sludge in filter cake exceeded 99%, except for Cr, which would have a certain effect on the distribution of heavy metals in the original sludge after compound conditioning [32]. The concentrations of heavy metals in the dewatered sludge filtrate were reduced, thereby minimizing the load of wastewater treatment plants in practical applications. However, most of the heavy metals occur in the filter cake, which has an impact on the use of the sludge, and further research on the treatment and disposal of heavy metals in filter cake is needed.

Effects of different conditioning methods on heavy metal morphology

The environmental risk posed by heavy metals does not only depend on their total content but is also closely related to the form in which they are present [33, 34]. Fig. 2 shows the distribution of the five heavy metal forms in sludge by different conditioning methods. The percentages of the residual state of four heavy metals (Cu, Cr, Cd, Pb) in sludge increased to varying degrees.

In the raw mud, Cd mainly occurred in the form of a relatively stable residual form and an organic combination, accounting for 28.30% and 31.45% of the total amount, respectively. The proportion of the exchangeable form was 7.86%; after persulfate conditioning, the proportion of the exchangeable form increased, accounting for 12.67% of the total. The proportion of the iron-manganese oxide-bound form increased from 13.52% to 50.66% of the original sludge. After compound conditioning, the proportion of the residual form further decreased to 3.11%, whereas that of the carbonate-bound form increased from 18.87% to 54.12%. The Cd in the raw mud mainly occurs in a stable valence state, and after conditioning, Cd tends to be in an unstable valence state, mainly because the strong oxidizing SO_4^{2-} produced during conditioning can oxidize Cd from a more stable form to an unstable form. The morphological distribution of Cd in sludge with different properties in different regions also varies [35].

In raw mud, Cr mainly occurs in stable form, mostly as a residue, and organic combination, and an iron-manganese oxide-bound form; these forms accounted for more than 80% of the total, whereas the percentage of the exchangeable form was only 7.74%. The proportion of persulfate conditioning was 83.73%, among them, the proportion of the residual form increased to 31.38%. After compound conditioning, the proportion of the residual form was 34.53%, less than 20% of the exchangeable and the carbonate bound forms, most likely because Cr occurred in the sludge mainly in a stable form and could not easily be

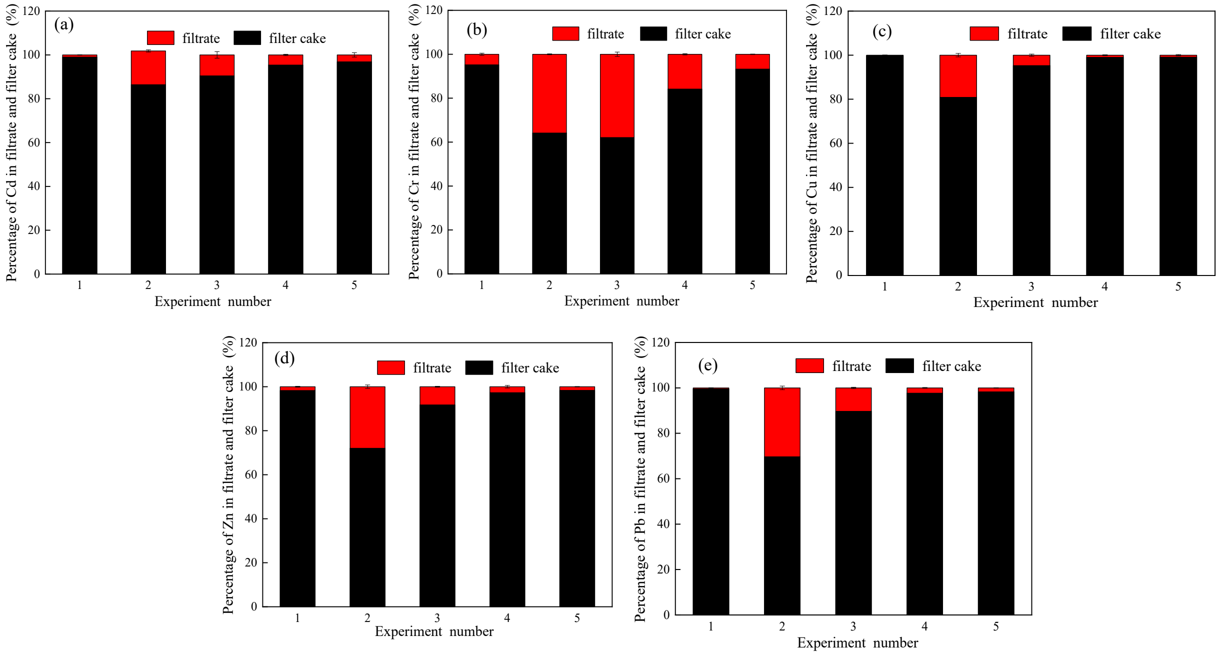

Fig. 1 Distribution of heavy metals in sludge as a result of different conditioning methods: (a) Cd; (b) Cr; (c) Cu; (d) Zn; (e) Pb.

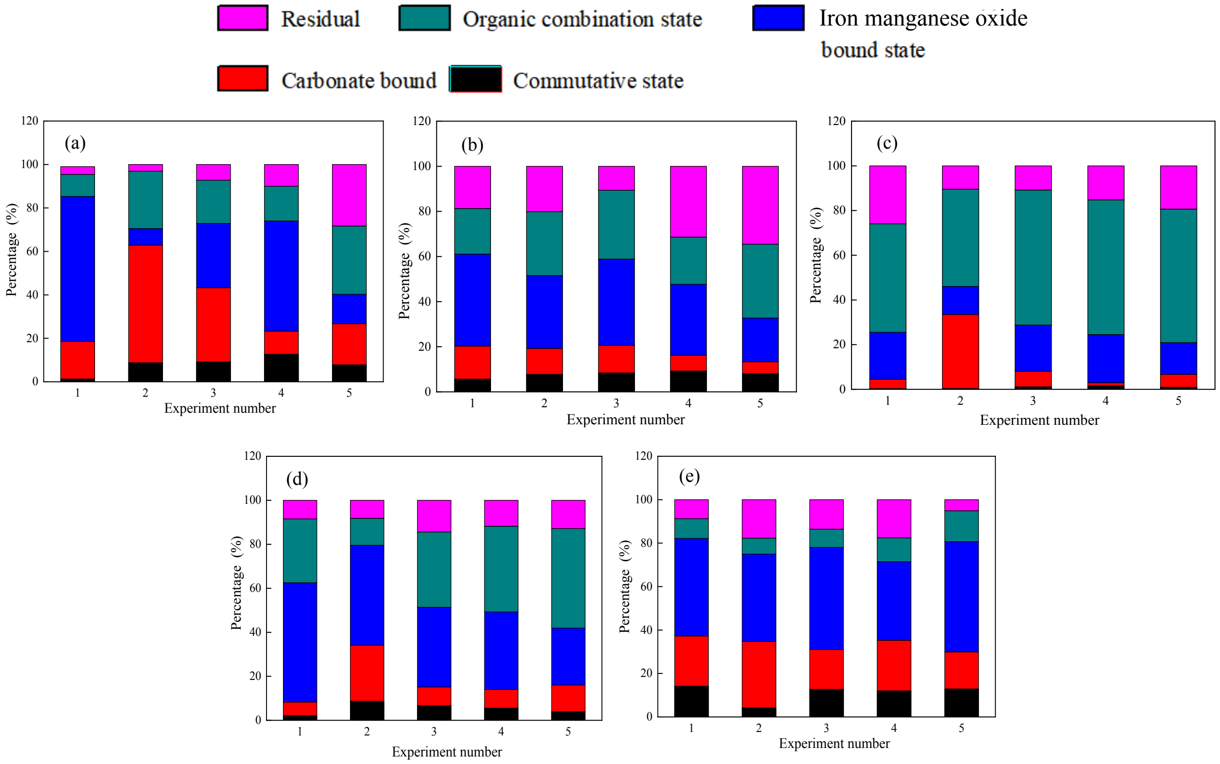

Fig. 2 Influence of heavy metal forms in sludge of different conditioning methods: (a) Cd; (b) Cr; (c) Cu; (d) Pb; (e) Zn.

dissolved.

Before and after conditioning, the main form of Cu was the organic-bound form, accounting for 43.51% in raw mud. With persulfate conditioning, it increased to 60.26%. After compound conditioning, it still occupied about 60%, and the proportion of the residual form increased slightly, from 10.44% to 19.35% of the sludge. This is because Cu can bind to organic ligands in the sludge, causing it to shift to an organic-bound form and form a more stable compound.

The iron-manganese oxide-bound form, the organic-bound form, and the residual form were three stable forms of heavy metals. The Pb was 65.85% more stable in raw mud, and the proportion of the carbonate-bound form was 25.45%. After persulfate conditioning, the proportion of the more stable form increased to 85.96%; that of the organic-bound form increased from 12.26% to 38.98% of raw mud, and that of the carbonate-bound form decreased to 8.53%. After compound conditioning, the proportion of Pb in the more stable form did not change significantly, but the organic-bound form further increased to 45.26%. The main reason is that the existence of SO_4^{2-} in the conditioning process facilitates Pb precipitation, resulting in a more stable form of Pb in the sludge.

In raw mud, Zn mainly occurred as carbonate-bound form and iron-manganese oxide-bound form, accounting for 30.56% and 40.21% of the total, respectively; the proportion of the residual form was 17.71%. After persulfate conditioning, the proportion of the carbonate-bound form decreased to 23.25%, and that of the exchangeable form increased from 4.19% to 12.02% of raw mud. In contrast, the proportions of the other three forms did not change significantly, and after compound conditioning, the residual form decreased from 17.71% to 5.09% of the original sludge, and the iron-manganese oxide-bound form increased to 50.76%. The underlying cause is that Zn mainly occurs in an unstable form in sludge and can easily be oxidized and dissolved during conditioning.

CONCLUSION

After sulfate conditioning, the Cr, Cu, Pb, and Zn removal rates were 9.27%, 26.65%, 9.63% and 33.90%, respectively, whereas after compound conditioning, the removal rates somehow decreased. This can be explained by the inherent contents of heavy metals in papermaking sludge, which will have a certain impact on heavy metals in municipal sludge; heavy metal removal followed the order Zn > Cu > Cr > Pb > Cd. After conditioning, the forms of heavy metals in sludge changed, albeit in varying degrees; Cd and Zn tended to be unstable, whereas Cr, Cu, and Pb tended to be stable. The heavy metals were mainly concentrated in the filter cake, which has an impact of the use of sludge as a resource, making it necessary to improve heavy metal removal from the filter cake.

Acknowledgements: The authors would like to express heartfelt thanks to the financial support from Shaanxi Science and Technology Plan Project (2018SF-377), Technical Innovation Guidance Project of Shaanxi Province (2019CGXNG-039), Science and Technology Innovation Team of Innovative Talent Promotion Plan in Shaanxi Province (2021TD-35), and Shaanxi Science and Technology Key Project (2020SF-423).

REFERENCES

1. Gong XL, Chen Y, Du YN (2016) Research progress of Fenton reagent conditioning sludge. *Environ Eng* **36**, 107–112.
2. Wang Y, Wei Y, Liu J (2009) Effect of H2O2 dosing strategy on sludge pretreatment by microwave-H_2O_2 advanced oxidation process. *J Hazard Mater* **169**, 680–684.
3. Wei XY, Xiao XY, Zhang L (2010) Purification and land use of heavy metals and organic pollutants in urban sludge. *Environ Eng* **28**, 235–240.
4. Yan GY, Wu TP, Lu XQ (2019) Advances in deep dehydration technology of advanced oxidized sludge. *Environ Pollut Prevent* **41**, 1108–1113+1119.
5. Zhu SS, Chen N, Li JH (2018) Advances in the application of municipal sludge disposal technology and resource utilization technology. *Chem Ind Guangdong* **45**, 28–32.
6. Li B, Dai Y, Song W, Pan X (2021) Effects of alfalfa root exudates on the microbial remediation of nitrate-heavy metal complex pollution in groundwater. *ScienceAsia*, **47**, 366–373.
7. Ong SA, Toorisaka E, Hirata M (2010) Adsorption and toxicity of heavy metals on activated sludge. *ScienceAsia*, **36**, 204–209.
8. Jia WJ, Ke J, Hu HG (2017) Environmental reflection based on "Pain and Pain" in Japan. *Green Technol* **7**, 224–226.
9. Yang X, Feng B, Jia Q (2017) Advances in the study of cardiovascular toxicity of lead and its compounds. *China Voca Med* **44**, 224–226.
10. Li J, Li HB, Chang GF (2010) Relationship between ADHD and lead levels in children. *China Mat Child Health Care* **25**, 726.
11. Yu H, Qiu CS, Wang CC (2019) Effects of Fenton pretreatment on heavy metal morphology and bioleaching and dissolution of urban sludge. *Environ Eng* **13**, 725–731.
12. Zhu Y, Zeng GM, Zhang PY (2013) Feasibility of bioleaching combined with Fenton-like reaction to remove heavy metals from sewage sludge. *Bioresource Technol* **142**, 530–534.
13. Zeng XF, Twardowska I, Wei SH (2015) Removal of trace metals and improvement of dredged sediment dewaterability by bioleaching combined with Fenton-like reaction. *J Hazard Mater* **288**, 51–59.
14. Kang DJ, Kuang S, Tang H (2016) Application of microbial leaching technology in the removal of heavy metals from urban sludge. *Ind Water Wastewater* **47**, 11–15.
15. Yip TC, Yan DY, Yui MM (2010) Heavy metal extraction from an artificially contaminated sandy soil under EDDS deficiency: significance of humic acid and chelant mixture. *Chemosphere* **80**, 416–421.
16. Diao HJ, Zhang J, Wang MY (2019) Effects of high tem-

perature pyrolysis on carbon characteristics of sludge and changes of heavy metal morphology. *Environ Eng* **37**, 29–34.

17. Guan RN, Shi YF, Liang S (2017) Distribution of heavy metal form in pyrolysis residues of compound conditioning dehydration sludge. *Environ Sci Technol* **40**, 74–78.
18. Zhou BZ, Lv X, Zhao XH (2011) Electrodynamic remediation of heavy metals in excess sludge. *J Environ Eng* **5**, 1401–1404.
19. Yuan C, Weng CH (2006) Electrokinetic enhancement removal of heavy metals from industrial wastewater sludge. *Chemosphere* **65**, 88–96.
20. Xiong J, Zhang HQ, Wang YJ (2017) A study on heavy metal transport in sludge electrodehydration process. *Environ Sci Technol* **40**, 30–35.
21. Zhang WN, Xiao ZH, Ma B (2017) Effects of persulfate on dewatering of municipal sludge and removal of heavy metals. *China Environ Sci* **37**, 4605–4613.
22. Qi L, Mei ZS, Qiu CS (2018) Effects of biofiltration on heavy metal removal and morphological changes in urban sludge. *Environ Pollut Prevent* **40**, 1116–1121.
23. Han CM, Wang LS, Gong ZQ (2005) Analysis of middle grains in soil and its environmental significance. *J Ecology* **24**, 1499–1502.
24. Pueyo M, Rauret G, Lvck D (2001) Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimized three-step sequential extraction procedure. *J Environ Monit* **3**, 234–250.
25. Cao QY, Huang ZH (2017) Study progress of heavy metal morphology and influencing factors in contaminated soil. *Ecological Sci* **36**, 222–232.
26. Tessier A, Campbell PG, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* **51**, 844–851.
27. Wei YL (2019) Study on morphological characteristics of heavy metals in soil by continuous extraction. *Environt Develop* **31**, 117–118.
28. Marie CASF, Zhang YR, Yang JK (2017) Extracellular polymeric substances and sludge solid/liquid separation under *Moringa oleifera* and chitosan conditioning: a review. *Environ Technol Rev* **6**, 59–73.
29. Editorial Committee of Analytical Methods for Water and Wastewater Monitoring (2002) *Analytical Methods for Water and Wastewater Monitoring*, 4th edn, China Environ Sci Press, Beijing, China.
30. Huang MF, Wei Q, Ma XM (2021) Current status and outlook of research on corrosion of galvanized steel pipes in water supply networks. *Ecology Environ Monitoring Three Gorges*. Available at: https://kns.cnki.net/kcms/detail/50.1214.x.20210521.1447.013.html.
31. Shi YF (2014) Study on deep dewatering of activated persulfate-skeleton builder composite conditioning sludge. PhD thesis, Huazhong Keji Univ, China.
32. Xiong Q (2018) Research on the performance and mechanism of activated persulfate-biomass composite conditioning sludge dewatering. PhD thesis, Wuhan Univ, China.
33. Xiao Z, Yuan X, Li H, Jiang L, Leng L, Chen X, Zeng G, Li F, et al (2015) Chemical speciation, mobility and phytoaccessibility of heavy metals in fly ash and slag from combustion of pelletized municipal sewage sludge. *Sci Total Environ* **536**, 774–783.
34. Wang T, Xue Y, Zhou M, Yuan Y, Zhao S, Tan G, Zhou X, Geng J, et al (2016) Comparative study on the mobility and speciation of heavy metals in ashes from co-combustion of sewage sludge/dredged sludge and rice husk. *Chemosphere* **169**, 162–170.
35. Lombi E, Zhao FJ, Zhan G, Sun B, Fitz W, Zhang H, Mcgrath SP (2002) *In situ* fixation of metals in soils using bauxite residue: chemical assessment. *Environ Pollut* **118**, 435–443.