

Behavior of Heavy Metals in Sewage Sludge during Hydrothermal Treatment

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Abstract

A huge amount of sewage sludge is produced annually worldwide, which is regarded as a kind of solid waste and at the same time as a kind of resource. Conventional treatment methods (including land filling, incineration and land application) are facing two problems which are vital to their sustainability: (1) secondary pollution and (2) high cost. From a long run, land application may be the best alternative for sewage sludge disposal. Pretreatment is of crucial demand to stabilize the sludge before soil application. Recently, hydrothermal treatment (HTT), especially HTT at temperatures lower than 300 °C, is widely recognized as a promising method for the pretreatment of sewage sludge because of its simplicity and cost effectiveness. However, the risk of heavy metals (HMs) must be controlled. This study aims to test the feasibility of using HTT to treat sewage sludge and examine the extent of HMs immobilization and the risk of HMs in the treated sludge.

After applying HTT for sewage sludge treatment, the risk of HMs in sludge before and after HTT was evaluated based on the total concentration, fractionation, and leaching test. The results showed that:

(1) The dewaterability of sewage sludge was greatly improved, and the volume of sludge was sharply decreased by 42%, 61% and 74% when the sludge was treated at 170 °C, 200 °C and 280 °C, respectively. Also, decomposition of some organic matters (such as carbohydrate, protein and amino acids) through dehydration and decarboxylation resulted in the stabilization of sludge. The treated sludge exhibited excellent adsorption capacity for HMs, which can be used for soil remediation.

(2) The behavior of HMs in sludge during HTT was reflected by the solid - liquid redistribution and fractional transformation. The result showed that the mobility and bioavailability of HMs was decreased because of fractional transformation during

HTT process. The highest risk reduction of HMs was achieved after HTT at 280 °C, with the content of metals in the weakly bound fractions decreased by 68.48%, 78.78%, 91.10%, 75.62%, 98.93% and 74.29% for Cr, Ni, Cu, Zn, Cd and Pb, respectively. This observation shows that the risk of HMs can be greatly reduced. Furthermore, the leachable content was decreased by 97.46%, 93.91%, 86.14%, 73.33%, 71.93% and 10.71% for Cu, Cd, Zn, Cr, Ni and Pb, respectively. This immobilization effect of HTT on HMs may result from the “release - precipitation” process, by which the weakly bound metals are transformed into more stable forms.

(3) Lignocellulosic materials in sludge was found to play a significant role on the behavior of HMs. Rice husk (RH) was selected to act as a kind of lignocellulosic material and added into the HTT process. The effect of RH addition was different for different metals at different treatment temperature. At 200 °C, RH addition can enhance the transformation of Cr, Cu and Cd from all fractions to F5 while adverse effect was detected for Zn and Pb. At 280 °C, RH addition favors the transformation of all tested metals except for Pb from F3 and F4 to F5, but all the metals in the weakly bound forms (F1+F2) increased with RH addition. The leachability of all the metals except Pb was decreased after RH addition. The results implied that some metals in sludge was encapsulated into the RH matrix and also adsorbed on the surface.

(4) Phosphorus in sludge was found to play a crucial role in the fractional transformation of HMs during HTT process. Results showed that after HTT almost all the other forms of phosphorus were completely converted into apatite phosphate. When hydroxyapatite (HAP) was added into HTT systems, it was found that the stability of HMs was changed, especially for Cr, Cu, Zn and Cd, and their leachability was decreased with the increase of phosphorus content in the sludge. More specifically, increasing phosphorus content can reduce the leachability and

bioavailability of Cd. A synergistic effect was observed and proposed between HTT process and HAP addition on Cd risk reduction, implying the immobilization effect of HTT on Cd could be partly attributed to the strong binding capacity of phosphorus with Cd.

This study will be valuable for controlling the risk of HMs in sludge, and can provide basic knowledge for improving the efficiency of HMs immobilization in sewage sludge.

Key words: Sewage sludge; hydrothermal treatment; heavy metals; immobilization; risk evaluation.

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Abbreviations

AP:	apatite phosphorus
HAP	hydroxyapatite
HMs:	heavy metals
HTT:	hydrothermal treatment
IP:	inorganic phosphorus
NAIP:	non-apatite inorganic phosphorus
OP:	organic phosphorus
PW:	process water
RAC:	risk assessment code
RH:	rice husk
SRC:	solid residue as control
SRs:	solid residues
TN:	total nitrogen
TCLP:	the standard Toxicity Characteristic Leaching Procedure
TP:	total phosphorus
WWTPs:	wastewater treatment plants

Chapter 1 Introduction

1.1. Sewage sludge production and environmental issues

Sewage sludge is a by-product of biological wastewater treatment process, and every year very huge amount of sludge is produced, which poses a big problem for the environment worldwide. Finding some appropriate, safe and cost-effective treatment methods for sewage sludge becomes one of the most serious and emergent challenges for the sustainable operation of wastewater treatment plants (WWTPs). The difficulty in dealing with the excess sewage sludge can be attributed to the following characteristics:

(1) Huge amount of generation. Generally, the generation of sludge is increased with the amount of wastewater treated in WWTPs. In recent years, the generation of sewage sludge has increased dramatically all over the world because of the elevating rate of wastewater treatment, especially in developing countries. For EU, in 2005, the sludge generation was 2.17×10^6 tons/year (dry solids) in Germany, 1.77×10^6 tons/year (dry solids) in United Kingdom, and 1.12×10^6 tons/year (dry solids) in Spain (Kelessidis and Stasinakis, 2012). In China, the sludge production was amount to 9.0×10^6 tons/year (dry solids) in 2005 (He et al., 2007) and about 3.0×10^7 tons/year (dry solids) in the coming years. This huge amount of sludge results in not only difficulties in management but also huge investment and operating costs for dealing with it.

(2) High moisture content. WWTPs usually produce sewage sludge with high water content ($> 99\%$). Dehydration should be conducted to reduce the water content and thus the volume of sludge before discharge. After common mechanical processes, the water content of sludge can be reduced to 80% and even to 70%. Still the water

content is very high, and its further dehydration process is very costly. Generally, sewage sludge treatment accounts for 50-60% of the total operational costs in WWTPs (Campos et al., 2009; Davis et al., 1997).

(3) Complexity of composition. Sewage sludge is formed by a variety of microorganisms' zoogloea and their adsorbed organic and inorganic matters which are originated from the wastewater. The organic matters include carbohydrates, proteins, and some trace organic matters (such as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins/dibenzofurans (PCDD/F), polycyclic aromatic hydrocarbons (PAHs), pesticide, herbicide, detergent, surfactant, preservative, and so on) (Stevens et al., 2001; Clarke et al., 2010; Wilson et al., 1997), and the inorganic matters include soil particles, inorganic salts, inorganic nutrients (N, P, K, etc.). The most important inorganic component is heavy metals (HMs) which can be adsorbed on to the sludge from wastewater during the treatment process (Karvelas et al., 2003; Al-Qodah, 2006). Therefore, the complex composition of wastewater determines the complexity of the sewage sludge components. Meanwhile sewage sludge is usually regarded as a kind of solid waste on one hand and nutrient sources on the other hand. Because of this controversial property, the treatment and ultimate disposal of sludge faces many problems and difficulties.

(4) High level of pollutants and potential environmental risks. Because of the complexity of composition, the sludge can not only provide nutrients to improve the productivity of soil, but also cause high potential environmental risks due to the high level of trace organic pollutants and HMs in sludge (Navas et al., 1998; Barzegar et al., 2002). Specifically, if not being stabilized, the sludge can bring about problems of secondary pollution. Firstly, without disinfection process, the sludge can spread disease and cause health risks because of the contained infectious pathogens which

are originated from wastewater (Lloret et al., 2013). Secondly, the organics in sludge can be released into water bodies with surface water flow leading to water pollution, and also the unstable organics in sewage sludge can be easily decomposed to produce odorous gases causing air pollution (deLuca et al., 1996). Therefore the organics in sludge should be stabilized before being discharged into the environment. Thirdly, and more importantly, is the high content of HMs in sludge can be dissolved into water bodies or transferred into plants and finally threat human health indirectly. Therefore, a safe, effective and sustainable treatment and disposal method is of urgent demand. The required method should meet the requirements of efficient recycling of resources and at the same time without delivery of harmful substances to humans or the environment (Commission of European Communities, 1998).

1.2. Sewage sludge disposal methods

In order to minimize the risk of sewage sludge to the environment, a sound way must be adopted to handle the sludge. Traditionally, there are 4 main methods including land filling, incineration, land application and comprehensive utilization (Pavšič et al., 2014; Wang, 1997; Kelessidis and Stasinakis, 2012).

Land filling was widely adopted in the world in the past decades because of its simplicity, but from a long run it is not sustainable (Mininni et al., 2004) because it is not only a waste of resources but also can result in water pollution, air pollution and some other sanitary problems. Furthermore, the leachate from filling sites is very difficult to treat, and the leachate production could always last for years resulting in much difficulty in treatment. Now, in many developed countries, the sludge disposed by this method is decreasing every year (Kelessidis and Stasinakis, 2012), but in some developing countries, land filling is still the main disposal method, although this method is not sustainable.

Incineration is now very popular, by which the sludge can be completely converted into carbon dioxide and minerals with energy production. However, much energy should be consumed for dewatering and water evaporation before incineration, and some toxic pollutants are formed in the exhaust (such as dioxins and HMs) during incineration (Mininni et al., 2004; Deng et al., 2009a). More importantly, after incineration, the produced fly ash is usually changed into a kind of hazardous material because of the accumulated HMs and some undestroyed organics (such as polycyclic aromatic hydrocarbons, PAHs) (Han et al., 2008; Chen and Yan, 2012; Pazos et al., 2010). Therefore, incineration method is still facing secondary pollution problems and at the same time not cost effective.

In recent years some comprehensive utilization methods have been adopted for handling sewage sludge, such as using sludge as additives for cement production, bricks making, and so on. This method now is still on developing.

Land application of sewage sludge is now very attractive, because the sludge can improve not only the properties of soil (Aggelides and Londra, 2000) but also its productivity. HMs contained in the sludge, however, should be controlled because it can increase the environmental risk (Kidd et al., 2007; Jamali et al., 2009), and HMs can be transferred to human body indirectly through food chain if not being dealt with properly. Therefore, the controversial problem requires land application method to be applied with great caution. In EU-15, land application of sludge now is the predominant choice for sludge management (53% of total amount), followed by incineration (21% of total amount) (Kelessidis and Stasinakis, 2012).

From a long run, land application of sewage sludge appears to be an economical and promising option for the future due to the following reasons: (1) Sewage sludge can provide many easily available nutrient sources like N, P, K and organic matters

(Table 1-1). Because of the shortage of phosphorus resources in the world, the sewage sludge with high content of phosphorus (Table 1-1) will be very important for agricultural production. (2) The application of sewage sludge can replace the inorganic chemical fertilizers to improve the structure and property of soil, and to prevent soil impoverishment caused by the frequent use of chemical fertilizers. (3) With the stringent management of wastewater drainage system, the content of HMs in sludge can be controlled and reduced by channeling different kinds of wastewater into different treatment plants and strictly limit the flow of industrial wastewater into the municipal WWTPs. (4) The risk of HMs in sludge can be reduced by pretreatment before land application, and the method will be introduced in the following Section 1.3.

1.3. HMs in sewage sludge and environmental risk control

1.3.1. Environmental risk of HMs in sludge

High level of HMs in sludge is now the major obstacle for land application (Fuentes et al., 2004; Wang et al., 2005a). Table 1-2 shows the concentrations of HMs in sewage sludge from different countries, which shows that Zn and Cu are generally existed at very high concentrations in different types of sludge. High level of HMs can damage the metabolic process and inhibit the growth of plants, and HMs can also be transferred from plants and then to human bodies and ultimately cause HMs poisoning or chronic diseases (Cheng, 2003; Charlet et al., 2012). In the past decades, the health damage caused by HMs has been widely reported, for example excessive lead in blood caused by lead pollution. The most tragic lessons learned from the HMs pollution were the “Minamata Disease” and the “Itai-itai Disease”, which were resulted from mercury (Hg) polluted water and cadmium (Cd) contaminated soil, and then Hg and Cd were transferred to human body by fish and rice, respectively. Now,

with the development of science and technology, the understanding of the risk of HMs to environment and human health is deepened, and more attention has been paid to the secondary pollutions caused by HMs in sludge. Therefore, before land application, the risk of HMs in sludge must be controlled to avoid this kind of secondary pollution to the environment.

To control the risk of HMs in sludge before land use, a lot of research work has been done. Generally, there are mainly two types of methods can be adopted for reducing the risk of HMs in sludge, *i.e.* HMs removal from sludge and HMs immobilization in sludge.

1.3.2. Risk control of HMs by removal from sludge

After being removed from sludge the total concentrations of HMs can be reduced, resulting in the decrease of potential environmental contamination. This approach includes various extraction methods such as chemical extraction (Deng et al., 2009b, Fuerhacker et al., 2012), bioleaching (Liu et al., 2012) and electrokinetic remediation (Hanay et al., 2009), etc.

(1) Chemical extraction

Chemical extraction of HMs has received extensive attention due to its simple operation, short extraction time and high removal efficiency (Deng et al., 2009b). It is mainly based on the addition of chemical agents to elevate the redox potential or decrease the pH value of sludge mixture so that HMs can be dissolved or released into solution, and then be separated from sludge solids (Ito et al., 2000). The efficiency of this extraction process depends on pH value, temperature, contact time, and extracting agent type and dosage. Previous studies reported that extraction under low pH value, long contact time, and high temperature conditions can improve the extraction efficiency (Veeken and Hamelers, 1999).

The traditionally used extraction agents include acid (organic or inorganic) (Naoum et al., 2001; Deng et al., 2009b; Veeken and Hamelers, 1999) and chelating agent (EDTA, etc.) (Hanay et al., 2009; Nair et al., 2008). The extraction of HMs can also be realized by ionic liquids extraction (Fuerhacker et al., 2012), and solid - liquid - solid extraction (Sprynskyy, 2009). Although a very high removal efficiency of HMs can be achieved by this kind of method, practically these methods are limited by the requirement of high dosage of agent which inevitably results in high processing cost and high salts content in sludge which causes another kind of pollution from sludge. Furthermore, the low pH value leads to difficulty in pH adjustment which needs vast amount of alkalis. Therefore, this method still needs to be improved so that the dosage of agent can be reduced.

(2) Bioleaching

Recently, many researchers have tried the bioleaching method for removing HMs from sludge. It is based on the mechanism that, some microorganisms, such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, can catalyze the oxidation of sulfur to sulfuric acid causing bioacidification and solubilize metal sulfides into metal sulfates (soluble) by their metabolism, and therefore the metal sulfides can be released into the liquid phase of sludge and then be separated (Tyagi et al., 1988). Bioleaching is now regarded as a low cost and environment friendly process for the removal of HMs from sewage sludge (Peng et al., 2011). During bioleaching process, some energy sources should be provided, such as Fe^{2+} , and S^0 (Liu et al., 2012; Pathak et al., 2009). The efficiency of HMs bioleaching from sludge depends largely on the dosage of energy substances, the chemical forms of HMs, temperature and contact duration (Zhang et al., 2009; Pathak et al., 2009). Wong et al. (2004) reported that the leaching efficiency of HMs from sludge reached up to 99%, 65%, 74%, 58% and 84% for Zn,

Cr, Cu, Pb and Ni, respectively by using FeS₂ as an energy source after 16 days of bioleaching at 28 °C and initial pH of 3.0.

Although having many advantages like simplicity and cost effectiveness, the practical application of bioleaching is still under testing because of the relatively low specific growth rate of the bioleaching bacteria, the instability of bioleaching efficiency and the long contact time as well. These problems add some difficulty in the large-scale application of this method.

(3) Electrokinetic remediation

Electrokinetic technology for HMs removal from sludge is based on the application of direct electric current field across two electrodes to dissolve or remove charged metals. This method is considered as a promising method with the advantages of high efficiency, short processing time and removing different metals simultaneously.

Wang et al. (2005b) reported that the removal efficiencies of HMs from acidified sewage sludge were: 95% for Zn, 96% for Cu, 90% for Ni, 68% for Cr, 31% for As and 19% for Pb. Peng et al. (2011) investigated the HMs removal by combination of bioleaching with electrokinetic remediation method, and they found that after the 10 days' treatment, Cu and Zn could be reduced by 88.73% and 99.11% in the solid phase of sludge.

Electrokinetic remediation, though with a high removal efficiency being achieved for HMs from sewage sludge, is still new for sewage sludge treatment and all the previous works were just done in laboratory. More research should be done to make this technology more practical.

Generally, HMs can be greatly removed from sludge by using the above mentioned methods. However, practically these methods are limited by the production

of high amount of residue resulted from the extracting agent, the requirement of long contact time or the difficulty in controlling the removal efficiency.

1.3.3. Risk control of HMs by immobilization in sludge

Immobilization of HMs in sludge provides another method for reducing the environmental risk of HMs. Being different from the methods aiming at removing HMs from sludge by reducing the total concentrations in sludge, immobilization focuses on changing the existing forms of HMs in sludge. During immobilization, the total concentration of HMs in sludge probably may not be reduced, and sometimes its potential environmental contamination even increased if only assessed by total HMs content. However, the direct toxicity, mobility, bioavailability or leachable fractions of some HMs may be reduced, which is much more important for the decrease of environmental risk.

HMs immobilization has been widely utilized in soil remediation because of its simplicity and cost-effective management. Some commonly used materials for HMs immobilization are biochar, phosphate, carbonate, silicate and phosphate-, carbonate-, silicate- based minerals (McGowen et al., 2001; Mendez et al., 2012). The immobilization mechanisms are probably different for each metal, including precipitation with complex anions, surface adsorption, ion exchange, etc. (Basta et al., 2001; Theodoratos et al., 2002).

For the immobilization of HMs in sludge, many methods have been tried and tested, such as forming ceramsite by incineration (Xu et al., 2009), mixing with biochar produced from agricultural residues (Uchimiya et al., 2011; Debela et al., 2012), natural mineral adsorption (Kosobucki et al., 2008) and thermal treatment (Obrador et al., 2001). After these processes, HMs can be transformed into more

stable state, and therefore the mobility, bioavailability, and eco-toxicity are reduced. Specifically, these methods can be adopted for sludge treatment on a large scale.

1.4. HTT and HMs immobilization in sewage sludge

Recently researchers reported that thermal treatment, a new method for sewage sludge stabilization, can change the fractionation of HMs in sludge during heating process and some metals can be transformed into more stable fractions (Weng et al., 2014; Obrador et al., 2001; Li et al., 2012).

To date research works are mainly focused on the thermal treatment of sewage sludge through dry pyrolysis under high temperature conditions (usually higher than 300 °C) and the sludge drying process before pyrolysis requires large amount of energy. Recently, hydrothermal treatment (HTT) has been investigated and used for solid waste treatment and is recognized as an environmentally friendly and sustainable method (Lu et al., 2012; Weiner et al., 2013; Parshetti et al., 2013). Before HTT process the dehydration and drying process is not required. Furthermore, the dehydration performance can be greatly improved after HTT process.

Recent works reported that the toxicity and leaching characteristics of HMs could be greatly changed after thermal treatment at 300-400 °C (Li et al., 2012; Yuan et al., 2011a). Up to now, the related research works were conducted at temperatures higher than 300 °C resulting in higher energy consumption and lower organic matter content left in the sludge, and also the collected sludge residue may not be suitable for direct land application.

HTT conducted at lower temperature is probably more suitable for sludge treatment because of low energy consumption and the sequestration of organic carbon can be achieved. Moreover, the produced coal-like materials (hydrochar) (Berge et al., 2011) can be adopted for soil improvement and remediation with its easily available

nutrients (P and K) and strong adsorption capacity (Gajic et al., 2012; Rillig et al., 2010).

At present little information could be found on the behavior of HMs in the sludge that be hydrothermally treated at lower temperatures ($< 300\text{ }^{\circ}\text{C}$), and the related environmental risk evaluation of the treated sludge is also scarce.

1.5. Research objective

HTT can provide a promising method for sludge stabilization before land application, but the risk of HMs in the produced hydrochar is still unknown. Therefore, the objective of this research is to evaluate and control the environmental risk of HMs in the hydrothermally treated sludge, and make sure the sludge is safe before land application. Based on this consideration, the investigation on the behavior of HMs in sludge and the influence factors during HTT will be of great importance for risk control of HMs in sludge and can help to improve the risk reduction effect of HTT on HMs. In general, this study is expected to provide some fundamental knowledge for HMs risk control in order to realize the practical application of HTT method under relatively lower temperatures ($< 300\text{ }^{\circ}\text{C}$).

1.6. Structure of the thesis

The structure of the thesis is illustrated by the experimental framework shown in Figure 1-1.

First of all, HTT was conducted by using sewage sludge in order to investigate the behavior of HMs in sludge during this process and to find ways for enhancing the immobilization effect on HMs in sludge. The risk of HMs in sludge was evaluated by total concentration, fractionation, and leaching test. The effect of HTT on fractional transformation and immobilization of HMs in sludge was analyzed in detail.

Next, the influencing factors were investigated to make clear the behavior of HMs during HTT. By studying these factors, the mechanism of immobilization of HMs in sludge during HTT was partially clarified.

Besides the environmental problems caused by sewage sludge and the importance of HMs control for soil application of sludge introduced in Chapter 1, the main research contents are included in the following chapters.

Chapter 2 was the selection of environmental risk evaluation methods.

Chapter 3 focused on the effect of temperature on behavior of HMs in sludge.

Chapter 4 investigated the effect of rice husk (a typical lignocellulosic material) on immobilization of HMs during HTT.

Chapter 5 interpreted the interaction between phosphorus and HTT and its effect on immobilization of HMs in sludge.

After the repetitive experiments, the risk of HMs in the hydrothermally treated sludge was evaluated and the effect of HTT on immobilization of HMs was further analyzed under different HTT operation conditions.

Table 1-1 Concentrations of organics, N, P and K in sewage sludge (Unit: %)

No.	OC	TN	TP	K	Country	Source
1	32.2	3.11	2.04	1.08	China	Liu and Sun (2013)
2	60.60	3.01	1.70	1.91	China	Liu and Sun (2013)
3	27.31	2.29	0.98	6.66	India	Hait and Tare (2012)
4	32.20	2.97	1.00	0.28	Brazil	Nogueira et al. (2013)
5	25.10	1.93	0.72	N.D.	Argentina	Torri and Lavado (2008)
6	33.51	5.09	2.03	N.D.	Italy	Contin et al. (2012)
7	N.D.	4.66	1.91	N.D.	Spain	Nieminen and Räsänen (2013)

OC, organic carbon; N.D., no determination; TN, total nitrogen; TP, total phosphorus;

K, potassium.

Table 1-2 Concentrations of HMs in sewage sludge from different countries (Unit: mg/kg)

No.	Cu	Pb	Ni	Mn	Cr	Zn	Cd	As	Hg	Country	Source
1	4567±143	81.2±2.8	148±6	1844±66	121±4	785±32	5.99±0.18	N.D.	N.D.	China	(1)
2	146±2	69.9±1.2	78±2	394±9	51.9±2.7	609±22	3.72±0.20	N.D.	N.D.	China	(1)
3	28.81~4532	5.23~740	1.6~569	N.D.	2.58~1067	13.76~9138	0.27~51	0.38~71	0.11~24	China	(2)
4	131.2~394.5	57.5~109.3	49.3~95.5	N.D.	45.8~78.4	783.4~3096	5.9~13	16.7~26.0	17.0~24.0	China	(3)
5	415	52.8	44.8	516	N.D.	1242	2.95	N.D.	N.D.	Japan	(4)
6	195±6	91±7	37±1	204±4	22±1	423±9	3±1	N.D.	N.D.	Japan	(5)
7	23.4 ± 6.5	31.8 ± 6.8	138.3 ± 3.7	N.D.	17.5 ± 1.2	N.D.	4.3 ± 1.2	N.D.	N.D.	Poland	(6)
8	410±120	N.D.	N.D.	80±20	770±210	610±130	N.D.	N.D.	N.D.	India	(7)
9	304.1±63.2	201.6±30.0	65.6±5.3	N.D.	277.7±34.0	1869.9±251.5	14.0±1.1	4.2±0.5	1.0±0.1	Brazil	(8)
10	258	326	41	150	552	1739	2	N.D.	N.D.	Greece	(9)
11	1491±533	146±24	314±111	N.D.	694±102	1840±1030	<1	N.D.	N.D.	Singapore	(10)
12	151	136	25	N.D.	N.D.	900	1.28	N.D.	N.D.	Spain	(11)
13	520	66.4	110	N.D.	76.7	1027	1.31	N.D.	1.61	Italy	(12)

(1) Liu and Sun (2013); (2) Ma et al. (2011); (3) Dai et al. (2007); (4) Ito et al. (2000); (5) Matsumoto et al. (2007); (6) Kosobucki et al. (2008); (7) Hait and Tare (2012); (8) Nogueira et al. (2013); (9) Zorpas et al. (2008); (10) Lim et al. (2006); (11) Méndez et al. (2012); (12) Contin et al. (2012). N.D., no determination.

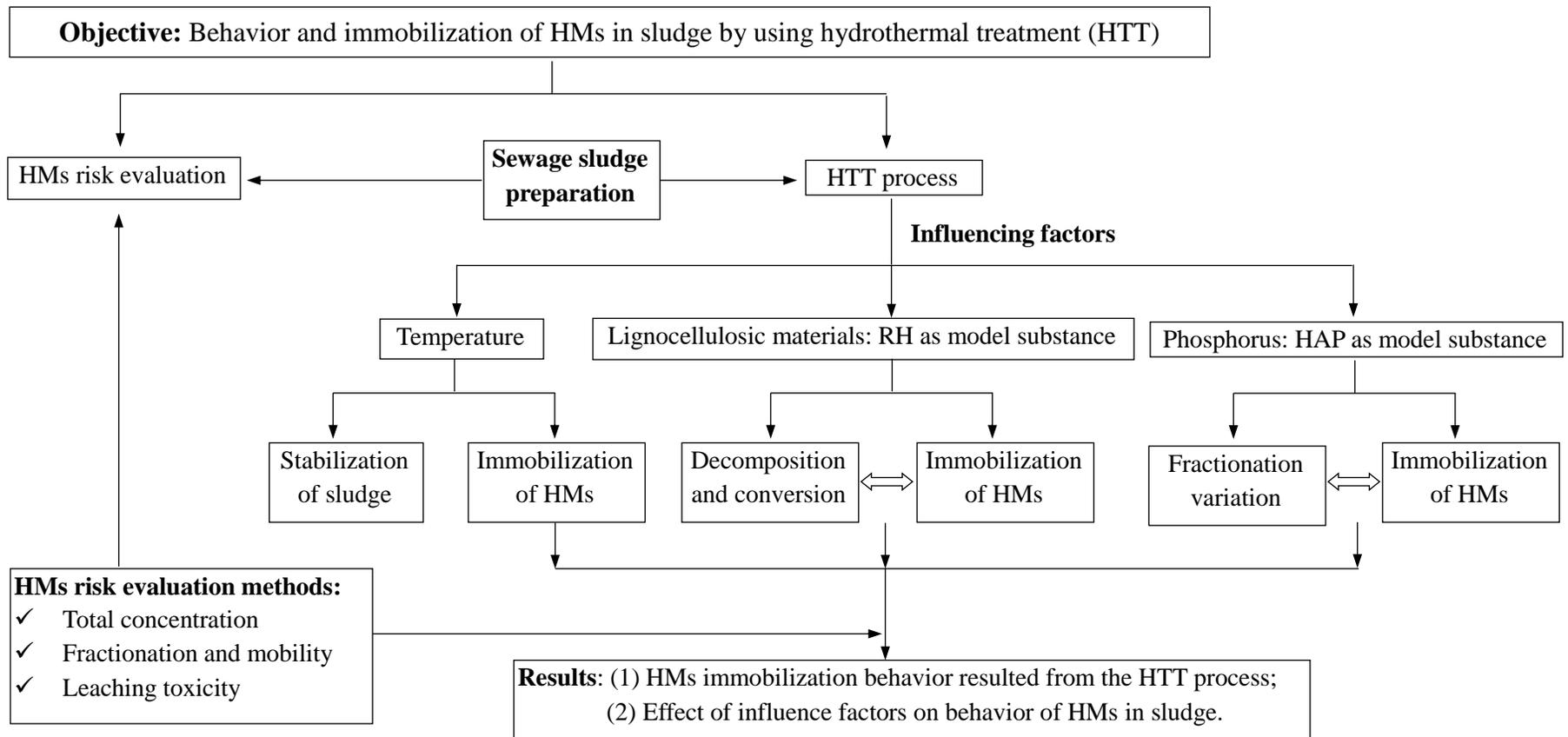


Figure 1-1 Experimental framework of this study. HMs, heavy metals; RH, rice husk; HAP, hydroxyapatite.

Chapter 2 Environmental risk evaluation of HMs in sewage sludge

2.1. Introduction

In the past, total concentration was a main index for assessing the risk of HMs in sludge, based on which many countries established their environmental standards for controlling the risk of sewage sludge to the environment. A lower total concentration is always considered to have lower potential toxicity. However, recent research works have reported that the toxicity, bioavailability and mobility of HMs in sludge depends not only on the total concentration but also on the existing forms (Xian, 1989; Angelova et al., 2004), especially the easily available fractions of HMs which may determine their direct toxicity (Huang et al., 2011; Singh et al., 2005). Therefore, the risk evaluation of HMs in sludge should focus on both the total concentration and their fractionation. Furthermore, the toxicity and mobility of HMs in sludge is closely related to their leachability which can be evaluated by leaching tests. The objective of this Chapter was to determine the risk evaluation methods in detail and to apply these methods for risk assessment on HMs in the sludge based on the above mentioned 3 aspects.

2.2. Materials and methods

2.2.1. Sewage sludge and sample preparation

The sewage sludge cake was sampled from a wastewater treatment center in Ibaraki prefecture, Japan where the sludge was firstly treated by anaerobic digestion,

and then dewatered by pressure filtration. The collected sludge was then kept in a refrigerator at 4 °C.

Before experiment, the sludge was diluted by adding deionized water so that the sludge could be homogeneously mixed, and then mixed with an appropriate volume of HMs mixture (containing Cr (VI), Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II)) because of the following two reasons: (1) very low levels of HMs were detected in the original sewage sludge, especially for Cd (2.07 ± 0.09 mg/kg) and Pb (17.51 ± 1.68 mg/kg), and (2) lower levels of these tested HMs were difficult to keep high accuracy during determination.

The HMs mixture was prepared by using the standard HMs solutions (1000 mg/L in 0.1 M HNO₃, respectively), and then adjusted its pH value to 7.0 with NaOH solution. The sludge was homogeneously agitated for 2 h and then kept in a glass beaker (enclosed by plastic wrap) in a refrigerator at 4 °C. During the following week the sludge was stirred manually once every day in order to let the supplemented HMs be completely dispersed or distributed into the sludge. The characteristics of the sludge used in this study is shown in Table 2-1.

2.2.2. Risk evaluation of HMs in sludge

According to the abundance, dosage - effect and eco-toxicity, 6 metals were selected as the target HMs in this study: Cr, Ni, Cu, Zn, Cd and Pb.

(1) Total concentration

Total concentration is a very simple and direct index for risk evaluation of HMs in sludge. In the past this index was regarded as the main limiting factor for HMs in sludge, especially for the application of sewage sludge to agriculture (Zorpas et al., 2008). After analyzing the concentration of each metal in sludge, the risk can be directly evaluated by comparing with the standard limits.

(2) Sequential extraction and fractionation of HMs

Recently, many researchers pointed out that only knowing the total concentration of each metal was not enough to assess the real environmental risk, because they found the risk and bioavailability of HMs was also determined by their fractionation and existing forms. The different existing forms of HMs could reflect their different binding strength and stability in sewage sludge and therefore their possible mobility, toxicity and bioavailability (Vela et al., 1993)

The fractionation of HMs in sludge depends on the sequential extraction procedure which comprises several extraction steps with different chemical extract reagents under different conditions. The sequential extraction procedure proposed by Tessier et al. (1979) is widely used in many fields. After using Tessier's method with 1.0g sample (Figure 2-1), HMs in sludge could be categorized into 5 fractions: Exchangeable metals (F1), metals bound to carbonates (F2), metals bound to iron and manganese oxides (F3), metals bound to organic matter and sulfide (F4) and metals in the residual state (F5). In each step (F1 to F4) the supernatant and residue were separated by centrifugation at 10000 rpm for 10 min. The collected supernatant from each step was then kept at 4 °C in a refrigerator after fixing the volume with 2% HNO₃.

HMs in F5 and their total concentration can be determined after acid digestion with acid mixture (HCl:HNO₃:HF=3:1:1) in PTFE beakers and heated on hot plates. After complete digestion, HNO₃ and hot water were used to dissolve the residue. The resultant clear solution was used for HMs determination.

HMs extracted into different fractions can reflect their binding strength in sludge, and their stability may be considered to increase from exchangeable to residual (Obrador et al., 2001). These 5 fractions of each metal can be used to reflect

their mobility, eco-toxicity and bioavailability after grouping them into 3 parts: (F1+F2), (F3+F4) and F5, representing direct toxicity/bioavailable (C_{bio}), potential toxicity/ potential bioavailable (C_{Pbio}) and no toxicity/non-bioavailable (C_{Nbio}), respectively (Table 2-2) (Vela et al., 1993; Li et al., 2012).

(3) Risk assessment code (RAC) and eco-toxicity

For quantitative evaluation of the eco-toxicity of HMs in sludge, RAC can be used based on the metals in the first two fractions (F1+F2) which are susceptible to changes of salt content and pH of sludge and the environment. Metals in these two parts can be easily released into aqueous phase and thus become more rapidly bioavailable (Sundaray et al., 2011). According to this consideration, the eco-toxicity of HMs can be evaluated by the risk index (RI) which is defined as the proportion of each metal in these two fractions (F1+F2) to the total concentration in the sludge ($RI = (F1+F2)/total \times 100$, Table 2-3) (Huang et al., 2011; Singh et al., 2005). Then, HMs in sludge can be classified by using RAC as no risk, low risk, medium risk, high risk and very high risk when the RI value ranges < 1 , 1-10, 11-30, 31-50 and > 50 , respectively.

Furthermore, the ratio of (F1+F2)/F5 can be used to describe the potential lability of HMs in sludge (Obrador et al., 2001).

(4) TCLP leaching test and leaching toxicity

Leachability is another important parameter for assessing the mobility and bioavailability of HMs in sludge. In this study, the standard Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1997) was used to evaluate the leaching toxicity of HMs in sludge. TCLP simulates landfill conditions by using acetic acid solution (pH 2.88, liquid/solid ratio was 20:1). The leaching tests were carried out in polyethylene tubes and shaken at 200 rpm for 18 h. The supernatant was harvested by

centrifugation, then filtered through 0.22 μm membrane, and then digested with H_2O_2 and concentrated HNO_3 for HMs analysis.

2.2.3. Analytical methods

The moisture or water content and solid content in sludge were analyzed by using weight loss after heating at 105 $^\circ\text{C}$. The organic matter (loss on ignition) and ash content were determined by burning at 550 $^\circ\text{C}$ in a muffle for 1 h. The pH value was analyzed with pH meter. The concentration of each metal was determined by using ICP-MS (ELAN DRC-e, PerkinElmer) after filtration through 0.22 μm membrane, and before analysis of HMs by ICP-MS the samples should be digested with H_2O_2 and concentrated HNO_3 to remove the dissolved organics. Each test was conducted in triplicate. The results were expressed as mean value \pm standard deviation in this study.

2.3. Results and discussion

2.3.1. Bioavailability and eco-toxicity of HMs in the sludge

The total concentration of each metal is shown in Table 2-1. Because the concentration was elevated by adding these metals into the sludge, it's meaningless to evaluate the risk of these metals by their total concentrations for the sludge used in present study.

After sequential extraction, the fractionation of HMs is shown in Figure 2-2. From this figure, the main existing forms were found to be different for the six metals in the sludge used in this study. About 65% of Cu was bound to organic and sulfide substances (F4), which may be attributed to its high stability of complexion with organic matter and sulfide (Staelens et al., 2000; Fuentes et al., 2008). Pb was found to be mainly existed in F4 (64%), and the majority of Ni (about 60%) was in the residual fraction (F5). Zn was found mainly in three forms in the sludge, namely F5

(39%), F4 (32%) and F3 (27%). Two forms, F5 (47%) and F4 (45%) were the main existing ones for Cr in the sludge. About half of Cd was bound to iron and manganese oxides (F3, 54%). It should be stated that all the six metals are very low at exchangeable (F1, < 5%) and carbonate bound (F2, < 2%) fractions in the sludge (except for Cd in F2, 13%).

Fractionation of HMs can be used to assess the bioavailability and toxicity. Table 2-4 shows that high percentages of Cd, Pb, Cu, Zn and Cr were found in the potential bioavailable fractions in the sludge, which were close to 77%, 72%, 65%, 59% and 52%, respectively. Therefore, these 5 metals maintained a high potential for eco-toxicity and bioavailability. The majority of Ni in the sludge was found in the non-bioavailable fraction, indicating its low mobility and availability to the environment.

2.3.2. Eco-toxicity of HMs in sludge based on RAC

The environmental risk of these metals in the sludge can be quantitatively evaluated by RAC mode based on (F1+F2) scales because these weakly bound fractions are easily affected by ionic strength and susceptible to pH changes in soil environment resulting in a very high mobility (Lasheen and Ammar, 2009; Yuan et al., 2011a). Based on the results of Figure 2-3, the high percentage of Cd (17%) in the first two fractions indicates a medium risk to the environment while the other metals (Cr, Ni, Cu, Zn and Pb) fell into the low risk level. Their RI values follow a descending order of Cd > Pb > Ni > Cu > Zn > Cr, which also represents a same trend of their mobility and toxicity. Generally, based on RAC result, this sludge was not suitable for soil application before reducing the risk and eco-toxicity of HMs, especially for Cd which is relatively more mobile and therefore more toxic.

2.3.3. Leachability of HMs in sludge

After TCLP test, the concentrations of all the tested metals in the leachate are shown in Table 2-5. The result showed that the concentrations of the leachable HMs were lower than the USEPA permissible limits (SW-846) except for that of Ni in CSR. The leachable concentration of Ni exceeded the limit value by about two folds. This implies the high leachability of Ni in the sludge used in this study and relatively lower leachability for other metals. Therefore, generally, the sludge may exhibit potential leaching toxicity to the environment.

2.4. Summary

In this part, the sludge samples were prepared and the HMs risk evaluation methods were selected and applied. The following results can be obtained:

(1) The risk of HMs in sludge can be evaluated by total concentration, fractionation, and leaching test from total control, bioavailability and leachability aspects. All these 3 aspects must be considered together for a comprehensive and practical risk assessment of HMs in sludge.

(2) After analyzing the HMs in the sludge prepared in this study, results showed that Cd, Pb, Cu, Zn and Cr were mainly existed in the potential bioavailable fraction in the sludge and at very low leachable level. Ni exhibited low mobility or bioavailability but the leachable content was very high. When evaluated by using RAC mode, Cd may exhibit medium risk to the environment while the other 5 metals may pose low risk.

Table 2-1 Physico-chemical characteristics of the sewage sludge

Parameters	Value*
Solid content (%)	14.53 ± 0.39
Moisture content (%)	85.47 ± 0.39
Loss on ignition (%)	46.09 ± 0.16
Ash (%)	53.91 ± 0.16
pH	6.43 ± 0.21
HMs (mg/kg, dry weight)	
Cr	150.18 ± 1.22
Ni	638.56 ± 96.15
Cu	415.00 ± 29.46
Zn	750.65 ± 59.59
Cd	73.02 ± 0.63
Pb	122.14 ± 9.06

* Mean ± standard deviation

Table 2-2 Relationship among fractions, eco-toxicity and bioavailability of HMs*

	Binding strength	Eco-toxicity	Bioavailability
F1+F2	Weakly bound	Direct toxicity	Bioavailable
F3+F4	Relatively stable	Potential toxicity	Potential bioavailable
F5	Stable	No toxicity	Non-bioavailable

* Vela et al. (1993); Li et al. (2012)

Table 2-3 Risk assessment code (RAC) for HMs in sewage sludge *

Category	RI= (F1+F2)/total ×100	Risk level
1	< 1	No risk
2	1-10	Low risk
3	11-30	Medium risk
4	31-50	High risk
5	> 50	Very high risk

* Singh et al. (2005)

Table 2-4 Concentrations of HMs in bioavailable (C_{bio}), potential bioavailable (C_{Pbio}) and non-bioavailable (C_{Nbio}) fractions in sludge used in this study (Unit: mg/kg)

	Cr	Ni	Cu	Zn	Cd	Pb
C_{bio}	1.60±0.35	24.38±0.82	12.20±0.26	14.98±3.10	12.25±0.44	5.95±0.92
C_{Pbio}	77.50±1.71	229.74±1.30	266.61±1.41	442.90±32.30	56.88±2.50	88.06±3.09
C_{Nbio}	71.08±2.41	384.44±0.48	137.28±1.93	321.11±10.17	4.58±1.82	29.05±0.33

Table 2-5 Concentrations of HMs released in TCLP test (Unit: mg/kg)

Metals	Leaching content	Permissible limits [*]
Cr	0.30 ±0.06	5
Ni	11.75 ±1.62	5
Cu	5.05 ±0.71	Not enlisted
Zn	2.25 ±0.43	5
Cd	0.72 ±0.09	1
Pb	0.03 ±0.001	5

^{*} USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

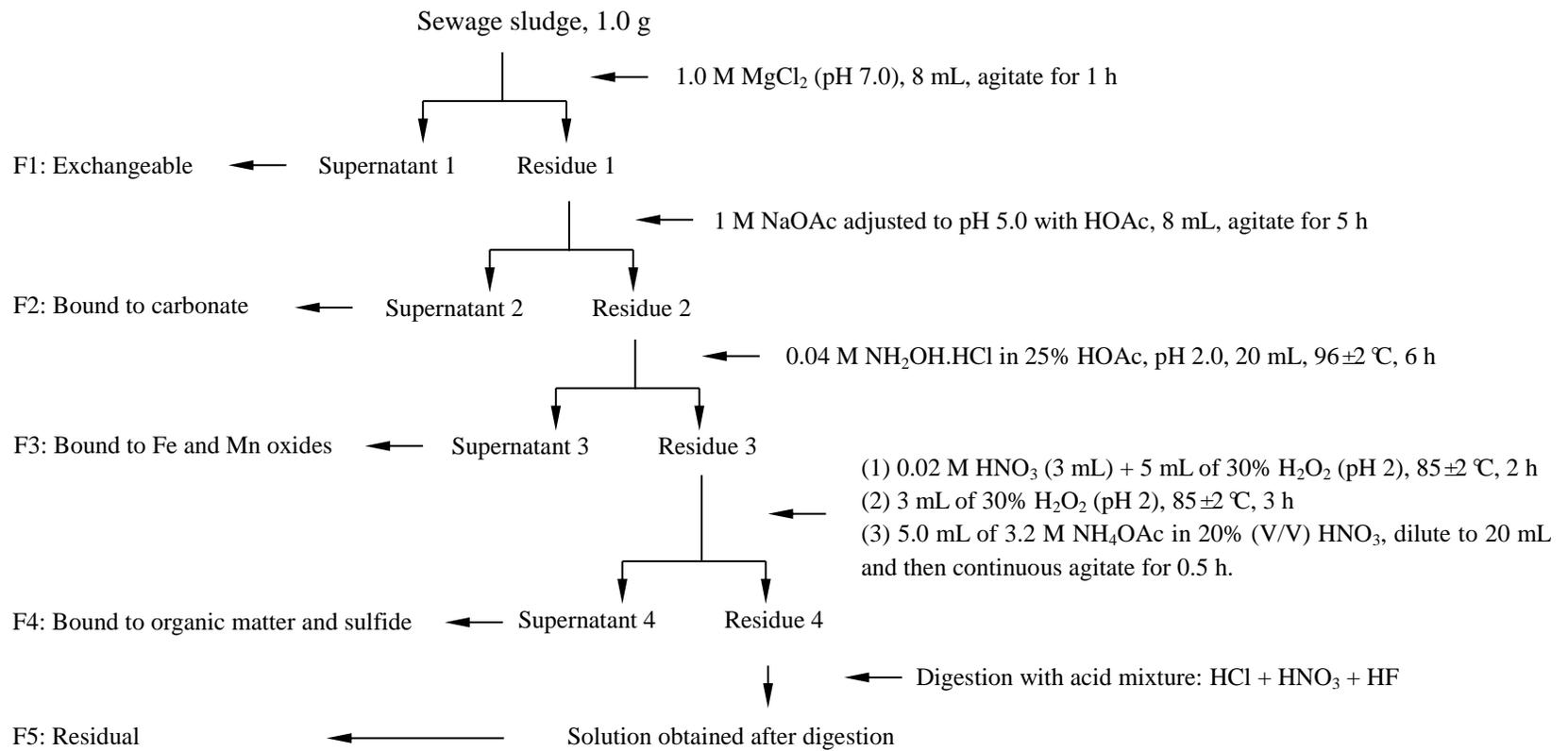


Figure 2-1 Sequential extraction procedure for the speciation of heavy metals in sludge (Tessier et al., 1979).

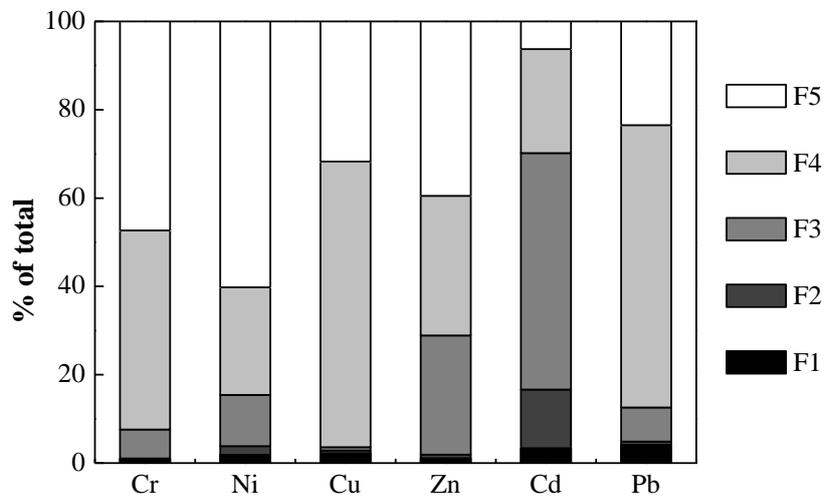


Figure 2-2 Speciation of HMs in the sludge used in this study. F1, exchangeable metals; F2, metals bound to carbonates; F3, metals bound to iron and manganese oxides; F4, metals bound to organic matter and sulfide; F5, metals in the residual state.

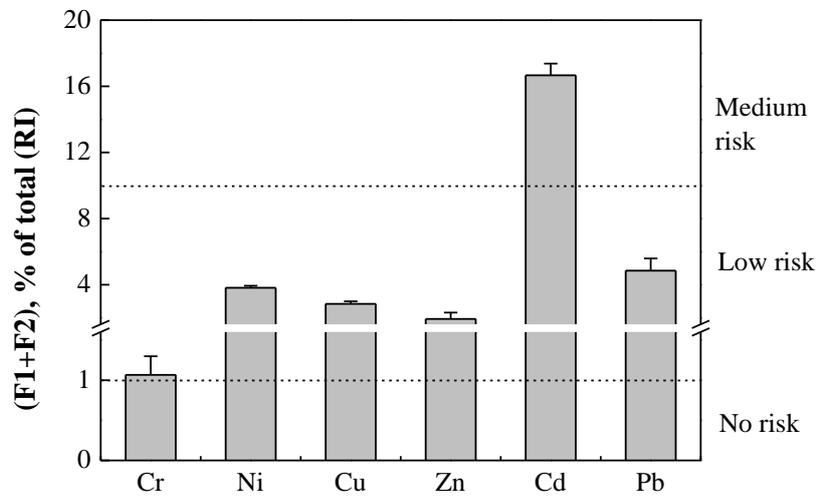


Figure 2-3 Eco-toxicity of HMs in the sludge evaluated by RAC mode based on the scale of metals in (F1+F2).

Chapter 3 Effect of HTT on sludge stabilization and behavior of HMs

3.1. Introduction

HTT provides a novel thermochemical conversion process which can be used to convert waste biomass into value-added products. HTT is very attractive due to its simplicity and effectiveness in dealing with organic solid waste disposal (Hu et al., 2012; Hwang et al., 2012; Theegala and Midgett, 2012). Recently it's widely recognized as an environmental friendly method for disposal of sewage sludge. When applied to sludge treatment, the sludge-derived hydrochar collected after HTT can provide organic matter and easily available phosphorous, potassium and micronutrients for improving the structure and productivity of soil, which also can be used as soil amendments to stabilize HMs in soil and improve the sorption capacity of soils towards many trace organic contaminants (PAHs, pesticides, herbicides, and etc.). Moreover, the sludge-derived hydrochar can be regarded as a kind of carbon sequestration (Gajic et al., 2012; Rillig et al., 2010; Khan et al., 2013).

Although sludge-derived hydrochar is a valuable source of nutrients and organics, the accumulated heavy metal in it is a constraint for soil application. In order to assess the potential environmental risk of hydrochar during soil application, it is crucial to make clear the mobility, bioavailability and leaching toxicity of the HMs. In this chapter, the risk of HMs in the sludge after HTT was evaluated based on their total concentration, fractionation and leachability before soil application.

Furthermore, investigating the behavior of HMs in sludge during HTT at different temperatures can help to understand the effect of HTT on the risk of HMs,

because the behavior of HMs in HTT will ultimately determine the risk of these metals.

3.2. Materials and methods

3.2.1. Sample preparation

The sludge sample used in this study was the sludge prepared in Chapter 2 (Section 2.2.). The characteristics of the sludge are also shown in Table 2-1.

3.2.2. HTT process

HTT of sewage sludge was carried out in an enclosed stainless steel reactor (Figure 3-1) with a volume of 200 ml and the maximal temperature of the reactor was 300 °C and the pressure cannot exceed 20 MPa.

The HTT procedure for sewage sludge treatment is shown in Figure 3-1. The prepared sludge was firstly loaded into the reactor with the same weight of 100 g to keep the same condition, and then the sludge was heated to 170 °C (HTT170), 200 °C (HTT200) or 280 °C (HTT280), respectively. After reaching the expected temperature, the HTT process lasted for 1.0 h. Then the power was turned off, and the sludge sample was cooled to ambient temperature by using an electric fan. After cooling, the process water (PW) and solid residues (SRs) of the treated sludge mixture were separated by vacuum filtration for 10 min. The collected PW was labeled as PW170, PW200 and PW280, respectively. The obtained SRs were then dried at 60 °C for 48 h, and ground into particle size smaller than 0.15 mm which was sufficiently fine to be homogeneously mixed, and then stored in enclosed plastic bags as samples of SR170, SR200 and SR280, respectively.

The solid residue samples from control experiment (SRC, without HTT process) were obtained by directly drying the prepared sewage sludge.

3.2.3. Adsorption capacity of sludge after HTT

In order to evaluate the impact of hydrochar on soil and on the behavior of HMs in soil, especially on the mobility of HMs in contaminated soil, this study focused on the binding capacity of hydrochar with HMs in soil solution. In this study, HM solutions were used to replace the soil solution to carry out the experiments. For the adsorption process, the dosage of sludge and sludge-derived hydrochar was 4.0 g/L. In the HMs solution (pH 5.6), the initial concentration of Ni, Cu and Zn was 1.0 mg/L, and that of Cr, Cd and Pb was 0.2 mg/L. The adsorption was conducted in 50 ml tubes in a horizontal reciprocating oscillator. The adsorption capacity was assessed by the removal rate of HMs from aqueous solution.

3.2.4. Fractionation of HMs in sludge-derived hydrochar

HMs and their speciation in sludge after HTT process were analyzed by the sequential extraction procedure proposed by Tessier et al. (1979) which has already been shown in Chapter 2. The difference in fractionation of HMs in sludges before and after HTT process was adopted to describe the effect of HTT process on fractional transformation of HMs. Based on the results of fractional transformation, it could be learned whether HMs was transferred from the weakly bound fractions (F1 and F2) into more stable forms (F3 and F4) or stable state (F5).

3.2.5. Analytical methods

The moisture or water content and solid content of the sewage sludge were analyzed by using weight loss after heating at 105 °C. The organic matter (loss on ignition) and ash content were determined after burning at 550 °C in a muffle for 1 h. The pH value was analyzed with a pH meter (Mettler Toledo SG8, Switzerland). Ammonia nitrogen ($\text{NH}_4^+\text{-N}$) was analyzed with Nessler's reagent spectrophotometry

method (APHA, 1998). The concentration of each metal was determined by using ICP-MS (ELAN DRC-e, PerkinElmer) after filtration through 0.22 μm membrane. Each test was conducted in triplicate. The results presented in this study were mean value \pm standard deviation.

Fourier transform infrared spectroscopy (FTIR) was adopted to identify the variation of functional groups, and the determination was done with the following process: Dried sample of sludge or hydrochar was mixed with dried KBr and then compressed under vacuum for 10 min. The pellets were analysed with a FT/IR-300E spectrometer (JASCO Corp.) covering a frequency range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

3.3. Results and discussion

3.3.1. Change in dewaterability of sludge

To reduce the volume of sewage sludge by dewatering process is of great importance before the final disposal, because the sludge with high moisture content is very difficult and costly to transport and dispose. In addition, the high content of carbohydrate and viscous substance (extracellular polymeric substances (ESP), etc.) in sludge usually becomes an obstacle for dewatering, and a great amount of energy is required which makes the dewatering process be very expensive. Therefore, a sound dewatering performance is very important for the specific sludge.

After HTT process, the separation of PW and SRs was conducted by vacuum filtration, and the moisture of the collected sludge residues was analyzed and the results are shown in Figure 3-2. It was found that, after this simple heating process, the water content in the sludge decreased from 85% to 75%, 62% and 45% after HTT process at 170 $^{\circ}\text{C}$, 200 $^{\circ}\text{C}$ and 280 $^{\circ}\text{C}$, respectively. It resulted in sludge volume

reduction approximately by 42%, 61% and 74%, respectively according to the relationship between sludge volume and water content. Especially for the sludge residue obtained after HTT at 280 °C, the moisture content (45%) was lower than 50%. Furthermore, the PW could be separated within 1.0 minute. That is, only 1.0 minute is enough for effective liquid - solid separation of the treated sludge. For the raw sludge used in this study (with a moisture content of 85%), no water could be separated and collected by the same vacuum filtration process, even after this filtration lasted for 30 minutes. Therefore, the dewatering performance can be greatly improved for sewage sludge after HTT process when evaluated by the ultimate moisture content, showing its excellent effect on sludge volume reduction.

3.3.2. Physicochemical characteristics variation

Figure 3-3 shows the content of solid residues (hydrochar) and organics remained after HTT process. It can be seen that, the weight of hydrochar was decreased with temperature because of the dissolution and decomposition of organics in the sludge during HTT. After HTT process, the content of organic matter decreased from 46% (SRC) to 35% (SR170), 29% (SR200) and 21% (SR280), respectively. Also, the loss of weight and destruction of organic matter were similar showing the decomposition of sludge was mainly resulted from the destruction and dissolution of organic matters.

Furthermore, the pH value of the sludge mixture (Figure 3-4a) and ammonia ($\text{NH}_4^+\text{-N}$) concentration in PW (Figure 3-4b) increased with temperature, which may be resulted from the decomposition of dead microbes, especially the decomposition of low-molecular weight organic acids, protein and amino acids contained in the raw sludge and treated sludge. This observation can also be partially confirmed by FTIR analysis (Section 3.3.3.).

The dissolution and decomposition of the labile organic matter during HTT process results in the stabilization of sewage sludge. Therefore, HTT can not only improve the dewatering performance to reduce the volume, but also can stabilize sludge.

3.3.3. FTIR analysis and evolution of functional groups

FTIR is widely used to determine the organic functional groups for characterization of organic substances. The FTIR spectra of raw sludge and the hydrochars obtained after HTT at different temperatures are shown in Figure 3-5. It shows that the FTIR spectra can be categorized into 6 regions based on the identified peaks for all the samples, and the difference in each peak can be adopted to illustrate the characteristic change of organics in sludge. The FTIR spectra shown in Figure 3-5 can be interpreted as follows:

(1) FTIR spectra for raw sludge

The broad band at about 3200-3500 cm^{-1} can be attributed to $-\text{OH}$ stretching vibration in hydroxyl or carboxyl groups and $-\text{N}-\text{H}$ stretching vibration (3275 cm^{-1}) in amine and amide groups (Gasco et al., 2007; Tian et al., 2002; El Fels et al., 2014). Bands around 2850 and 2925 cm^{-1} are associated with asymmetric and symmetric aliphatic $-\text{CH}$ stretching vibration in the CH_3 and CH_2 groups (Gasco et al., 2007; Silva et al., 2012). The band at about 1645 cm^{-1} can be attributed to stretching vibration of $-\text{C}=\text{O}$ in ketone and amide groups (Zhang et al., 2014; Gasco et al., 2007). The band around 1428 cm^{-1} is related to the $-\text{C}=\text{C}$ stretching vibration in aromatic ring carbons (El Fels et al., 2014). Band at about 1035 cm^{-1} can be attributed to the stretching of $\text{C}-\text{O}-\text{R}$ in aliphatic ethers (Öz çimen and Ersoy-Meri çoyu, 2010) or $-\text{Si}-\text{O}$ (Yuan et al., 2011b). The band at about 870 cm^{-1} is associated with the aromatic nucleus $-\text{CH}$ wag, which may relate to aromatic rings in lignin.

(2) Variation in FTIR spectra for the obtained hydrochar

After HTT process, the change in identified peaks of the hydrochar can be observed by comparing with the raw sludge (except the intensity of bands at about 2850 and 2925 cm^{-1} which showed no obvious change)

The intensity of band at 3358 cm^{-1} was decreased, possibly attributable to the decomposition of hydroxyl groups containing in protein and amino acids during HTT at elevated temperatures. This observation is probably related to the dehydration and ammonia release from sludge during HTT. The dehydration effect may contribute to the improved dewatering performance (Section 3.1.) of the treated sludge. The decomposition of protein and amino acids during HTT can also be partially evidenced by the high content of ammonia released into the process water from sludge (Figure 3-4b).

The intensity of band at about 1645 cm^{-1} was sharply reduced implying the decomposition of ketone and amide groups through decarboxylation during HTT. The dehydration, decomposition of protein and amino acids and decarboxylation implies the stabilization of sludge and the production of hydrochar after HTT process. Furthermore, the color of SR was changed from grey to black, indicating that some portion of organics has been converted into hydrochar (Hu et al., 2010).

Besides, the $-\text{OH}$ and $-\text{C}=\text{O}$ functional groups in sludge usually play a great important role on adsorption and stabilization of HMs and other contaminants. Thus the decrease of these two functional groups may have some negative effect on HMs adsorption, which needs further investigation.

The significant increase in relative intensity of band at about 1428 cm^{-1} in hydrochar, which relates to the $-\text{C}=\text{C}$ group in aromatic ring carbons, suggests that a high carbon aromaticity has been produced by aromatization during HTT process (He

et al., 2013). The intensity of band at about 1035 cm^{-1} was also significantly increased. An increase in SiO_2 content in the obtained hydrochar might bring about this change based on the decomposition of organics in sludge, resulting in an increase of SiO_2 (The content of inorganics in the hydrochar was relatively increased) in the sludge residues after HTT process (Figure 3-3). The real reason of this change is still under investigation.

3.3.4. HMs adsorption capacity of sludge and sludge hydrochar

Figure 3-6 shows the HMs adsorption results for sludge and the produced hydrochar, and Figure 3-7 shows the removal rate of HMs after adsorption for 12 hours. After reaching adsorption equilibrium, the removal rate of HMs from aqueous can be adopted to reflect the adsorption capacity of sludge and the collected hydrochar, because the initial concentration (C_0) for each metal was the same (for Ni, Cu and Zn, $C_0= 1.0\text{ mg/L}$; for Cr, Cd and Pb, $C_0= 0.2\text{ mg/L}$) during adsorption process with the same dosage of raw sludge and the obtained hydrochar (4.0 g/L).

It can be seen that, both sludge and sludge-derived hydrochar showed high removal rates for HMs (except for Cr) from aqueous. The adsorption process for all the metals can soon be completed within 2 hours. Hydrochar obtained at different temperatures showed different adsorption capacity for different metals, and SR280 showed the highest adsorption capacity for the tested metals except for Cr. After reaching equilibrium, more than 90% of Ni, Cu, Zn, Cd and Pb were adsorbed by the hydrochar obtained from HTT at $280\text{ }^\circ\text{C}$. The high adsorption capacity for HMs implies the feasibility of land application of the sludge-derived hydrochar for soil remediation.

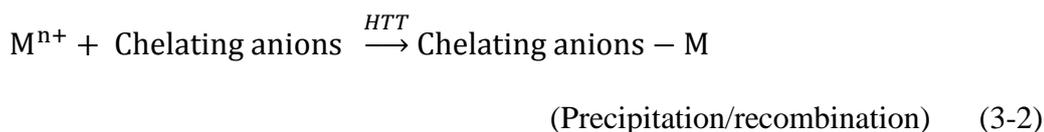
3.3.5. Redistribution of HMs in PW and SR after HTT

The organics in sludge is very important for binding HMs, and the decomposition of organics during HTT process will inevitably result in the redistribution of HMs in sludge liquid (PW) and solid (SRs) phases. After vacuum filtration, the PW and SRs were separated, and then HMs in these two phases were analyzed.

Figure 3-8 shows the redistribution of HMs in PW and SRs after HTT. It was found that, although the released content was very low (< 1.3% of the total), HMs could be dissolved from sludge particles into PW resulting in increased concentrations in liquid phase after the HTT process. Also, the HMs dissolved in PW can be seen as a kind of HMs removal from sludge. This observation might be brought about by the degradation of extracellular polymeric substances (EPS) and other organics, and thereafter some HMs bound to them were released into the liquid phase (Appels et al., 2010). During HTT process, different metals behaved differently. The amount of Zn, Cd or Pb released into PW increased with the increase of temperature, while the highest release was obtained at 200 °C for Cr, Ni or Cu (Figure 3-8a).

The effect of HTT on dissolution of HMs implies the binding state of the metals will be inevitably changed, and which can probably provide an opportunity to change the fractionation of HMs in sludge by first releasing (Eq. 3-1) and then recombining into a more stable state with some chelating anions (such as phosphate, silicate, carbonate, OH⁻, etc.) (Eq. 3-2) or be encapsulated into newly formed hydrochar during HTT process with high temperature and pressure. The feasibility of this speculation should be investigated in the following study.





where S represents sludge particle. Chelating anions include PO_4^{3-} , SiO_4^{2-} , CO_3^{2-} , OH^- , and phosphate-, carbonate-, silicate- based minerals, etc.

As for total concentration, although HTT process seemed to have some positive effect on HMs release from sludge particles into PW, the majority of HMs was remained and accumulated (> 98.7%) in SRs. The total concentration was detected to elevate with the increase of treatment temperature because of the decomposition of sewage sludge and reduced mass of SRs (Figure 3-8b). The elevated content of HMs in the hydrochar means the potential risk of these metals might be increased if only using the total concentration as an assessment index.

The release of HMs into PW and the accumulation in SRs may partly be ascribed to the dehydration effect of HTT, because the HTT process under high temperature and pressure may destroy the binding state of water, which includes interstitial, capillary and absorbed water in the sludge (Wang et al., 2007). The metals can exist in these 3 types of water, and the migration of water during HTT process will inevitably affect the distribution of metals. Therefore, after HTT, some metals were released into PW with water migration, while some metals were concentrated by the precipitation of minerals and then fixed into sludge particles (Weng et al., 2014). This precipitation phenomenon may be enhanced under the increased pH value of the sludge mixture in the HTT reactor (Figure 3-4a).

3.3.6. Fractional transformation of HMs after HTT

Though the total concentration of HMs in the collected hydrochar after HTT shows some possibly increased potential risk, practically it may not be the fact. Because it's widely known that the risk of HMs in solid waste depends not only on the

total content but also on their fractionation and existing forms. The existing forms of HMs are usually more important because they determine the bioavailability, mobility and eco-toxicity of HMs. By using the sequential extraction procedure proposed by Tessier et al. (1979), the HMs in sludge and sludge-derived hydrochar can be extracted into different fractions which can reflect their existing forms. The result is shown in Figure 3-9.

Figure 3-9 shows that, the contents of Cu and Pb were all sharply decreased in the first 3 fractions, while increased in F5 after HTT, especially for Cu in F1 and Pb in F2 with the contents decreased negatively with treatment temperature and for Pb in F5 increased positively with temperature. In addition, HTT exerted different effect on both Cu and Pb in F4. Cu in F4 decreased after treatment at 170 °C and 280 °C while Pb content in F4 was reduced at temperatures higher than 200 °C.

In the case of Zn, the contents decreased in F1 (except in SR170), F2 and F3 while increased in F4 and F5. A considerable reduction of Ni content was observed in F1 (except for treatment at 200 °C), F2, F3 and F4, and the corresponding content of F5 was significantly increased.

As for Cr and Cd, HTT showed some positive effect on the reduction of these metals in F1 and F2 fractions in the sludge. After treatment at 170 °C and 280 °C, Cr content was observed to decrease in F4 and increase in F5. The percentages of F3 (except for 280 °C) and F4 of Cd in the sludge increased after HTT treatment, while the F5 fraction firstly increased and then decreased with temperature. Still, the major form of Cd was F4 after treated at 280 °C, mostly contributed by the conversion from its F3 fraction.

From the above results, it can be concluded that the weakly bound forms (F1 and F2) of HMs are all decreased in sludge after HTT process except for F1 fraction of Zn

and Ni after treatment at 170 °C and 200 °C. The F5 fractions of HMs are all increased after HTT with the exception of Zn and Cr in SR200 and Cd in both SR200 and SR280. It can be inferred that HMs in sludge could be transformed from weakly bound fractions (especially F1 and F2) to stable state (F5) during HTT process showing the positive effect of HTT on immobilization of HMs in sludge.

This immobilization effect on HMs may have some association with the dehydration process. Some weakly bound metals (metals in F1 and F2) may transfer with the migration of water, resulting in partial release or dissolution into PW and partial fixation into sludge through precipitation and recombination. This fractional transformation and redistribution of HMs help to explain the proposed mechanism in Section 3.5.1, that is, first release/dissolution and then precipitation/recombination follows.

Furthermore, the reduction of HMs in the weakly bound fractions may have some relationship with the decomposition of some functional groups (Figure 3-5) and at the same time the increased concentration of related cations (such as $\text{NH}_4^+\text{-N}$, K^+ , Na^+ , Ca^{2+} , Mg^{2+} , etc.) in the sludge solution (PW) (Table 3-1), and especially the high concentration of $\text{NH}_4^+\text{-N}$ increased to 0.17, 0.18 and 0.25 mol/L in the PW170, PW200 and PW280, respectively. The high content of these related cations in PW can compete for adsorption sites with HMs and then resulted in some weakly bound metals be exchanged into PW. These two aspects may have some contribution to the content reduction of HMs adsorbed by sludge during HTT process.

3.3.7. Bioavailability assessment of HMs in sludge before and after HTT

After the 5 fractions of HMs being grouped into 3 parts, the concentration of each metal in F1+F2, F3+F4 and F5 can be used to reflect their stability and

bioavailability as bioavailable (C_{bio}), potential bioavailable (C_{Pbio}) and non-bioavailable (C_{Nbio}).

The significance of temperature on the fraction distribution of HMs is indicated by p- values obtained by one-way analysis of variance (ANOVA) with the experimental data (Table 3-2). Table 3-2 shows the variation of C_{bio} , C_{Pbio} and C_{Nbio} of HMs in the sludge after HTT. It was found that, all the metals in bioavailable fraction were decreased after HTT process, though the total concentration increased with temperature. Especially, when treated at 280 °C, HMs content in bioavailable fraction was the lowest (except for Pb), and the C_{bio} level was decreased by 53.75 %, 69.32 %, 81.15 %, 64.75 %, 98.37 % and 61.18% for Cr, Ni, Cu, Zn, Cd and Pb, respectively. The decrease of HMs in C_{bio} indicated the positive effect of HTT process on reducing the direct toxicity and bioavailability of these metals in sludge (Li et al., 2012; Huang et al., 2011).

Except that Ni was mainly existed in the non-bioavailable fraction, the other five metals were mainly found in the potential bioavailable fraction in SRC (Table 3-2). After HTT process, the C_{Pbio} values of Cu and Cd increased with temperature while C_{Pbio} of Pb remained relatively stable; the C_{Pbio} values of Cr and Zn slightly decreased at 170 °C and then increased at higher temperatures. Although having an increase trend, the C_{Pbio} values of Ni in SR were less than those in SRC. Generally, after HTT the potential bioavailability of Cr, Cu, Zn and Cd was increased, while that of Pb kept almost unchanged. Only the potential bioavailability of Ni was decreased after HTT. Considering the fact that the total concentration of Ni and Pb increased after HTT, the proportion ($C_{Pbio}/total \times 100, \%$) decrease (Figure 3-10) would be more meaningful to illustrate the transformation of HMs during HTT which implied the HTT process was more efficient on reducing the bioavailability of Ni and Pb.

Except for Cd, the other metals in C_{Nbio} increased to some extent (Figure 3-9), which means a part of metals in the weakly bound fractions or relatively stable fractions was transformed into stable state, especially for Ni and Pb.

Besides, the percentage increase in fraction F5 together with the decrease in the easily available fractions (F1 + F2), thus a lower ratio of (F1+F2)/F5 can be obtained, implying a reduced potential lability of HMs in sludge after the HTT process (Obrador et al., 2001).

Totally, HTT process is effective on immobilization of HMs, especially for Ni and Pb in the sludge. The HTT process at 280 °C is more effective on reducing the direct toxicity of the metals in sludge.

3.3.8. RAC analysis of HMs in sludge

The environmental risk of these metals in SRs can also be quantitatively evaluated by RAC mode based on the scale of metals in (F1+F2) to their total concentration, because these weakly bound fractions are susceptible to ionic strength and pH changes in soil environment resulting in a very high mobility (Lasheen and Ammar, 2009; Yuan et al., 2011a). Figure 3-10 shows the RI (Risk index, (F1+F2)/total × 100) value of each metal in sludge before and after HTT. It can be found that the RI value for all the tested metals in sludge was decreased after HTT process, especially when the sludge was treated at 280 °C. After HTT under 280 °C, the risk level of Cr, Ni, Cu and Zn all decreased by one grade from low risk to no risk, and that of Cd decreased by 2 grades from medium risk to no risk. Meanwhile, Pb remained at low risk level, though the RI value sharply decreased from 4.86 in SRC to 1.42, 1.83 and 1.25 for Pb in SR170, SR200 and SR280, respectively. After HTT at 280 °C, the RI value decreased by 68.48%, 78.78%, 91.10%, 75.62%, 98.93% and 74.29% for Cr, Ni, Cu, Zn, Cd and Pb, respectively. Therefore, after HTT, the risk and

direct eco-toxicity of HMs in sludge can be greatly reduced, showing the positive effect of HTT on HMs stabilization in sludge.

3.3.9. TCLP leaching test and leaching toxicity of HMs in sludge

The leaching toxicity of HMs in SRC and SRs was determined with the standard TCLP test shown in Table 3-3 and Figure 3-11.

The concentrations of leached Cu, Zn and Cd from sludge were declined after HTT process, while Cr and Ni behaved slightly different. The leached concentration of Cr and Ni from SR170 and SR280 decreased but increased from SR200. In the case of Pb, although the leachable contents increased in SR170 and SR200 to some extent, the concentrations were very low (0.045 and 0.081 mg/kg, respectively), and the leachable content was decreased in SR280. Briefly, all the lowest concentrations of leachable HMs were detected in SR280, and their concentrations in the leachate decreased by 97.46%, 93.91%, 86.14%, 73.33%, 71.93% and 10.71% for Cu, Cd, Zn, Cr, Ni and Pb, respectively, indicating the release of HMs (except for Pb) was significantly decreased. The HTT process at 280 °C exhibited the most significant effect on reducing the leaching risk of HMs to the environment.

The leaching rates of the six HMs are shown in Figure 3-11. This indicator is defined as the ratio of each metal concentration in the leachate to the total concentration of this metal (Huang et al., 2011), which can be used to reflect the proportion of HMs in the leachable state. The decreased leaching rates of Ni, Cu, Zn and Cd indicate the decrease in the leachable fraction of these metals, which is in contrast to the leachability increase of Cr from SR200 and Pb from SR170 and SR200. From Figure 3-11 and Table 3-3, it's obvious that the HMs related to leachable fraction were at the lowest proportions in the sludge after HTT at 280 °C, clearly showing the reduced leaching toxicity and leachable fraction of HMs in sludge after

HTT process. This observation coincides with the declination trend of weakly bound fractions (F1+F2) shown in Figure 3-10.

3.4. Summary

In this chapter, HTT of sewage sludge was carried out under different temperatures to investigate the effect of this process on the characteristics of sludge and behavior of HMs in sludge. The results could be summarized as follows:

(1) By using HTT, the dewatering performance of sewage sludge was greatly improved, and the volume of sludge was sharply decreased. Therefore, HTT can be used as a promising method for sludge dewatering.

(2) The decomposition of some organic matter (such as carbohydrate, protein and amino acids) through dehydration and decarboxylation resulted in the stabilization of sludge, and after HTT process, the sludge was changed into hydrochar. The sludge-derived hydrochar exhibits excellent adsorption capacity for HMs which can be used for soil remediation.

(3) After HTT, HMs were partly released into process water, but the majority of HMs was accumulated in the hydrochar, resulting in increased potential risk of these metals based on total concentration. The metals in sludge were found to transform from weakly bound fractions into relatively more stable or stable state, and therefore the mobility and toxicity of HMs could be reduced after HTT.

(4) The risk of all the metals decreased after HTT, especially when the sludge was treated at 280 °C. The contents of metals related to direct toxicity were decreased by 68.48%, 78.78%, 91.10%, 75.62%, 98.93% and 74.29% for Cr, Ni, Cu, Zn, Cd and Pb, respectively. After being treated at 280 °C, Cr, Ni, Cu, Zn, Cd showed no toxicity while Pb showed low toxicity.

(5) The leachability of all the metals decreased in sludge after HTT process. When the sludge was treated at 280 °C, the concentrations of the metals in the sludge were decreased by 97.46%, 93.91%, 86.14%, 73.33%, 71.93% and 10.71% for Cu, Cd, Zn, Cr, Ni and Pb, respectively.

Generally, although the total concentration of metals in sludge increased to some extent after HTT process, the bioavailability, mobility, toxicity and leachability of the metals all decreased because the metals were transformed from weakly bound fractions into more stable state. This fractional transformation of HMs may result from the first release and then precipitation and recombination process during HTT. Therefore, the HTT of sludge is effective in heavy metal immobilization, and among the tested conditions, HTT at 280 °C is preferable for the final disposal of sludge.

Table 3-1 Concentration of related cations released into the process water after hydrothermal treatment process (Unit: mg/L)

	Na ⁺	K ⁺	Ca ⁺	Mg ⁺	NH ₄ ⁺ -N
PW170	127.24±10.38	152.01±8.73	53.25±5.11	47.15±6.31	2357.24±17.91
PW200	237.19±3.08	201.55±5.97	187.24±8.56	133.59±11.87	2586.24±8.99
PW280	192.68±18.51	219.42±10.89	106.66±1.84	36.50±3.74	3566.17±7.37

PW170, PW200 and PW280 denote the process water collected after HTT under 170 °C, 200 °C and 280 °C, respectively.

Table 3-2 Concentrations of HMs in bioavailable (C_{bio}), potential bioavailable (C_{Pbio}) and non-bioavailable (C_{Nbio}) fractions in sludge before and after HTT (Unit: mg/kg) (n=3, $\alpha < 0.05$).

		Cr	Ni	Cu	Zn	Cd	Pb
C_{bio}	SRC	1.60±0.35	24.38±0.82	12.20±0.26	14.98±3.10	12.25±0.44	5.95±0.92
	SR170	1.34±0.18	14.79±2.36	6.15±0.75	22.65±1.91	2.12±0.37	2.00±0.05
	SR200	1.59±0.24	19.67±0.55	4.36±1.18	10.90±0.51	1.36±0.02	2.82±0.88
	SR280	0.74±0.11	7.48±0.65	2.30±1.27	5.28±1.19	0.20±0.01	2.31±0.34
	p-value	0.007	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
C_{Pbio}	SRC	77.50±1.71	229.74±1.30	266.61±1.41	442.90±32.30	56.88±2.50	88.06±3.09
	SR170	70.86±6.08	165.24±18.75	274.50±33.04	432.41±55.27	79.59±1.78	96.17±18.16
	SR200	95.82±7.67	187.84±13.94	334.81±27.39	533.73±25.41	89.78±0.80	86.53±7.99
	SR280	102.44±10.55	210.04±23.06	384.53±34.30	633.32±76.07	108.92±1.35	91.65±6.57
	p-value	0.002	0.007	0.004	0.004	< 0.001	0.708
C_{Nbio}	SRC	71.08±2.41	384.44±0.48	137.28±1.93	321.11±10.17	4.58±1.82	29.05±0.33
	SR170	92.98±6.44	507.41±21.11	188.90±31.92	381.67±26.01	7.04±1.85	43.04±9.52
	SR200	81.80±7.91	539.38±13.39	177.22±27.86	377.82±59.45	2.05±0.27	65.78±8.60
	SR280	116.67±10.65	705.93±23.70	244.46±33.36	487.93±116.47	5.22±0.41	90.26±5.95
	p-value	< 0.001	< 0.001	0.018	0.04	0.011	< 0.001

SRC means solid residue in control experiment. SR170, SR200, and SR280 denote the solid residue after HTT under 170, 200, and 280 °C, respectively.

Table 3-3 Concentrations of HMs released in TCLP tests (Unit: mg/kg)

HMs	SRC	SR170	SR200	SR280	Permissible limits*
Cr	0.30 ±0.06	0.14 ±0.01	0.42 ±0.05	0.08 ±0.02	5.0
Ni	11.75 ±1.62	3.88 ±0.36	12.16 ±1.60	3.30 ±0.67	5.0
Cu	5.05 ±0.71	0.60 ±0.04	1.39 ±0.39	0.13 ±0.04	Not enlisted
Zn	2.25 ±0.43	0.39 ±0.05	1.43 ±0.30	0.31 ±0.05	5.0
Cd	0.72 ±0.09	0.07 ±0.001	0.17 ±0.05	0.04 ±0.01	1.0
Pb	0.028 ±0.001	0.045 ±0.002	0.081 ±0.005	0.025 ±0.002	5.0

* USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). SRC means solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively.

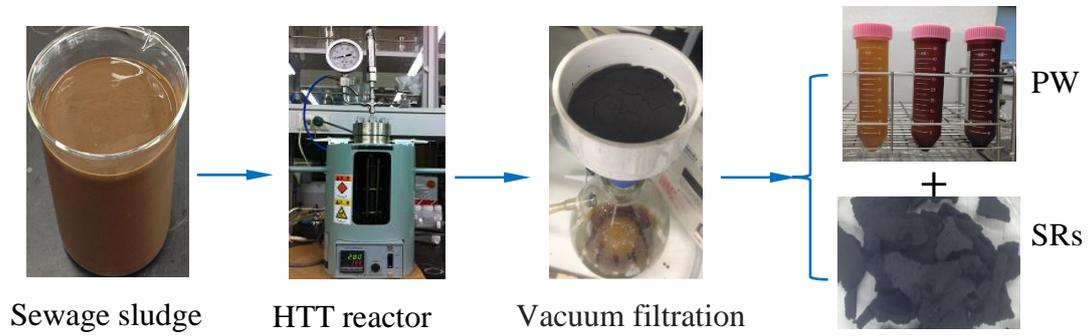


Figure 3-1 Schematic flow chart for sewage sludge treatment by using HTT procedure.

HTT, hydrothermal treatment; PW, process water; SRs, the collected solid residues.

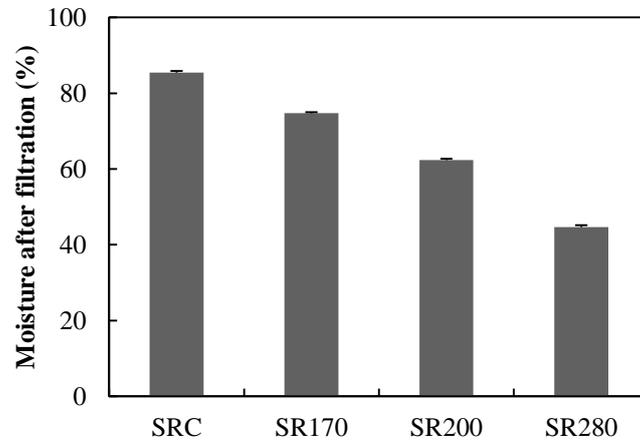


Figure 3-2 Moisture content of the sludge residues after vacuum filtration. SRC means solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively.

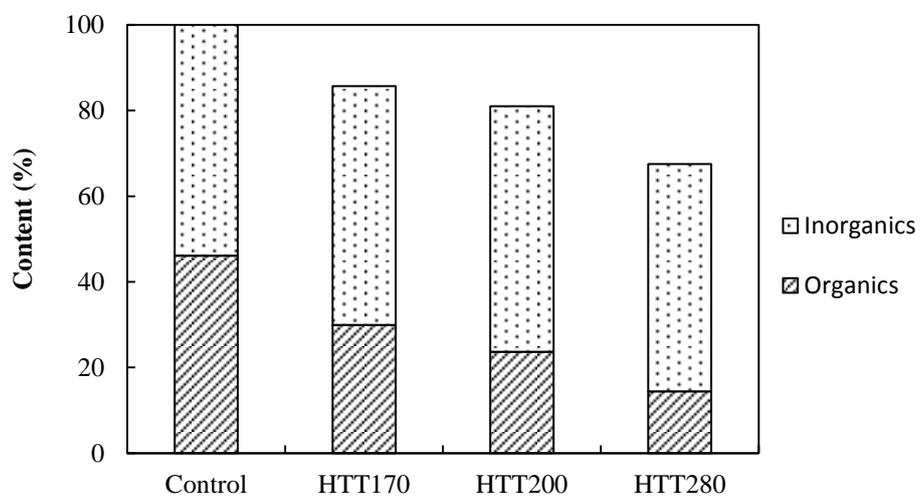


Figure 3-3 Content of mass remained after HTT treatment and the fractions of organics and inorganics. HTT170, HTT200, and HTT280 denote the hydrothermal treatment process under 170 °C, 200 °C, and 280 °C, respectively.

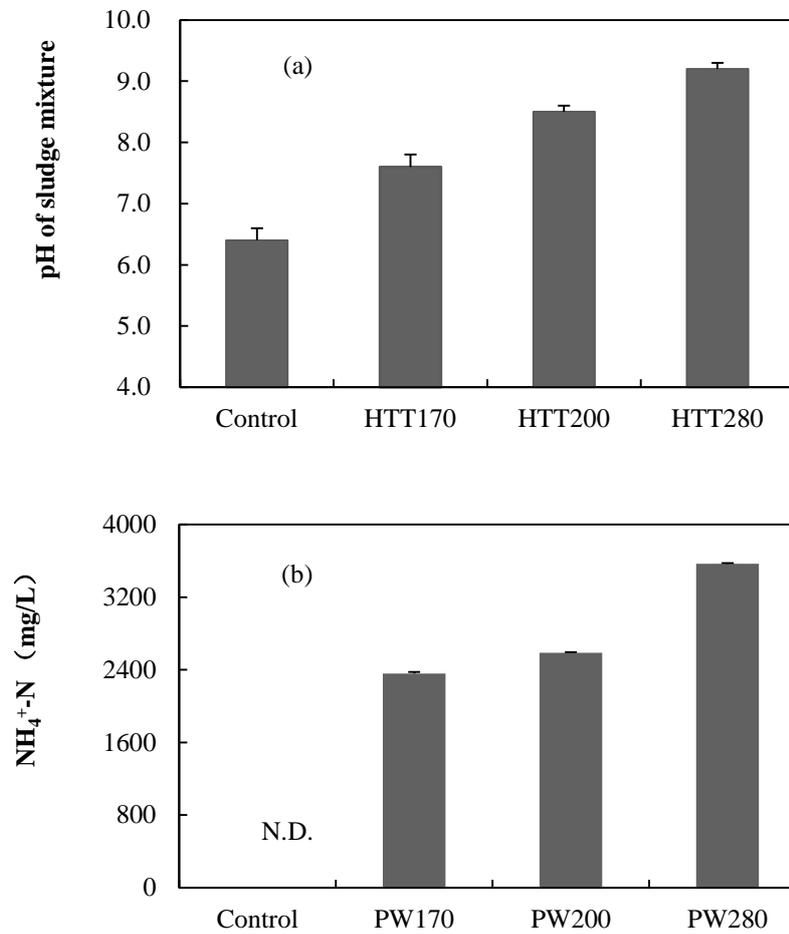


Figure 3-4 Effect of HTT process on pH value of sludge mixture (a) and ammonia release into process water (b). N.D. means not detected due to no process water was separated for control samples; HTT170, HTT200, and HTT280 denote the hydrothermal treatment process under 170 °C, 200 °C and 280 °C, respectively. PW170, PW 200 and PW 280 denote the process water collected after hydrothermal treatment under 170 °C, 200 °C and 280 °C, respectively. Control means sludge without hydrothermal treatment.

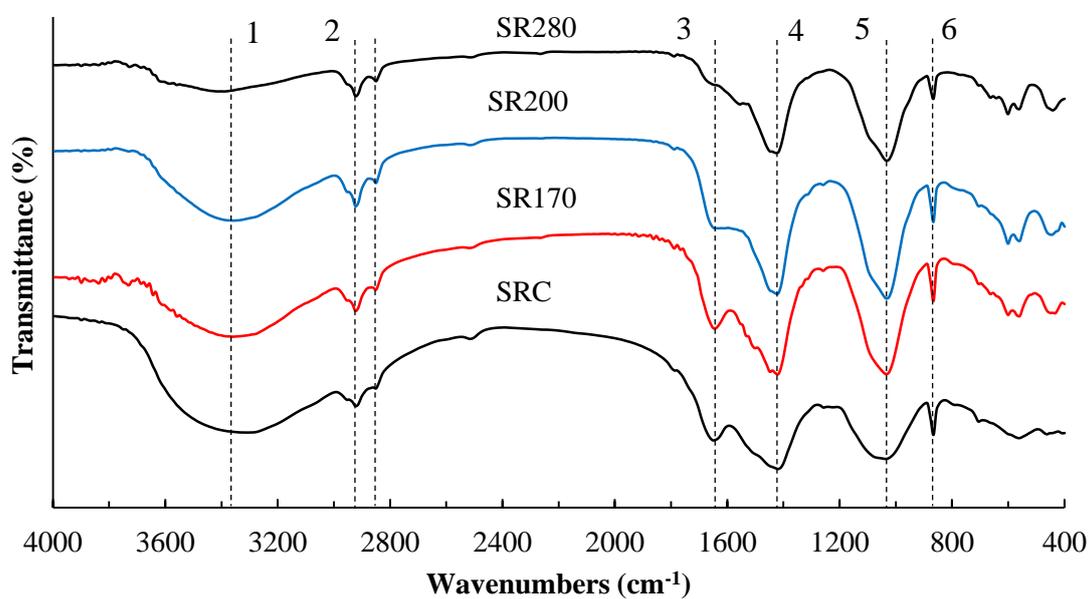


Figure 3-5 FTIR spectra of sludge and sludge-derived hydrochars obtained after HTT at different temperatures. 1: $-\text{OH}$ and $-\text{N}-\text{H}$ stretching; 2: aliphatic $-\text{CH}_x$ stretching; 3: $-\text{C}=\text{O}$ stretching; 4, aromatic ring $\text{C}=\text{C}$ stretching; 5, ethers $\text{C}-\text{O}-\text{R}$; 6, aromatic nucleus $-\text{CH}$. SRC means solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 $^{\circ}\text{C}$, 200 $^{\circ}\text{C}$ and 280 $^{\circ}\text{C}$, respectively.

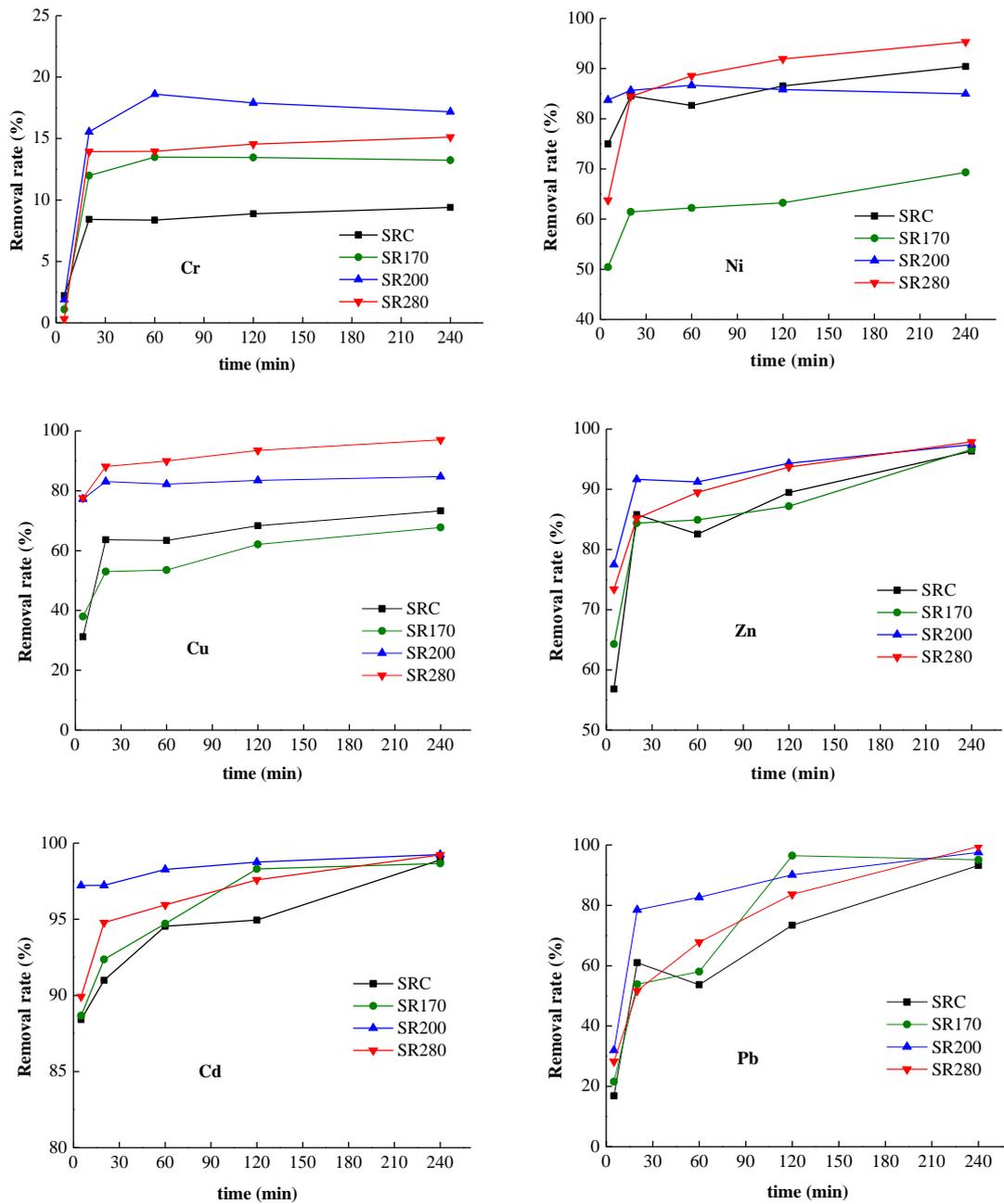


Figure 3-6 HMs adsorption efficiency by sludge and sludge-derived hydrochar. SRC means solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively.

(For Ni, Cu, Zn, the initial concentration $C_0 = 1.0$ mg/L; For Cr, Cd, Pb, the initial concentration $C_0 = 0.2$ mg/L; Sludge dosage was 4.0 g/L)

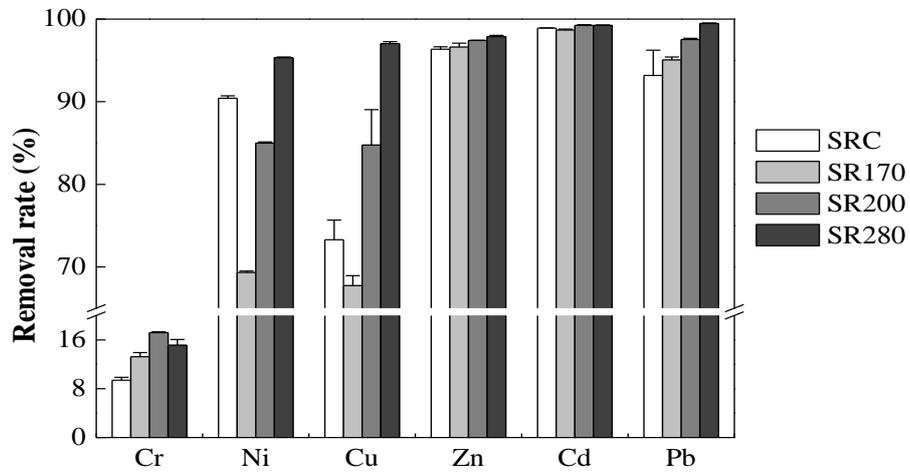


Figure 3-7 HMs adsorption efficiency by raw sludge and hydrochar. SRC means solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively.

(For Ni, Cu, Zn, the initial concentration $C_0 = 1.0$ mg/L; For Cr, Cd, Pb, the initial concentration $C_0 = 0.2$ mg/L; Sludge dosage was 4.0 g/L; Contact time was 12 h)

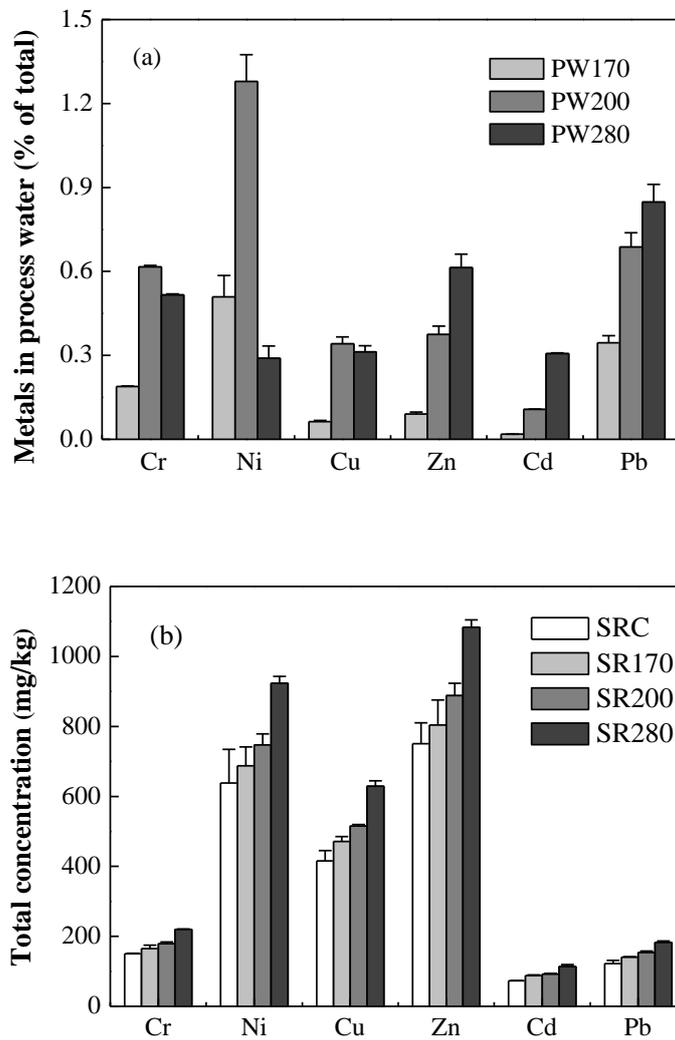


Figure 3-8 Redistribution of HMs in process water (a) and solid residues (b) after HTT of sewage sludge. PW, process water; SR, solid residue; 170, 200 and 280, treatment temperature (°C).

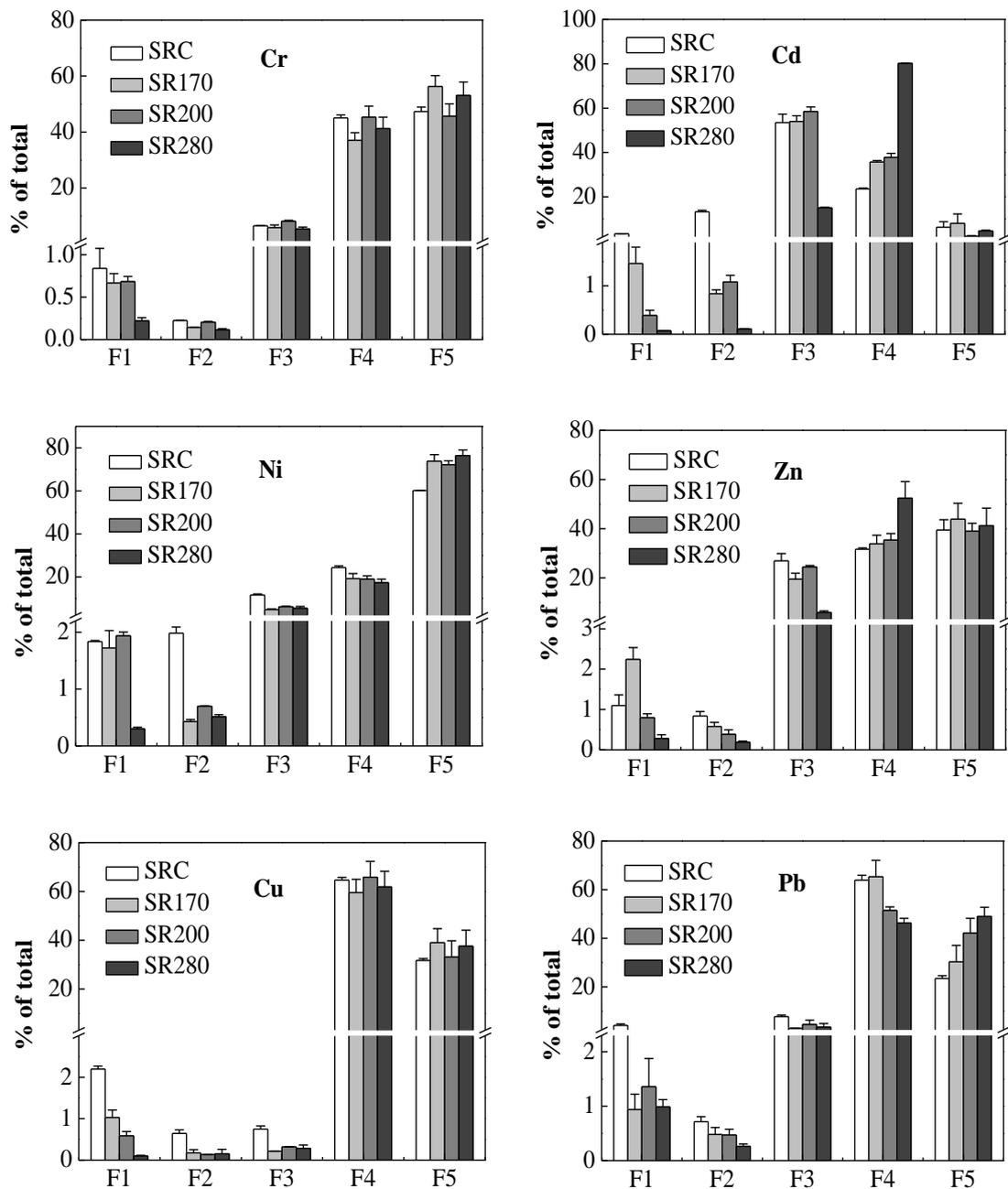


Figure 3-9 Fractional distribution changes of each metal in sewage sludge before and after HTT. SRC means solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively.

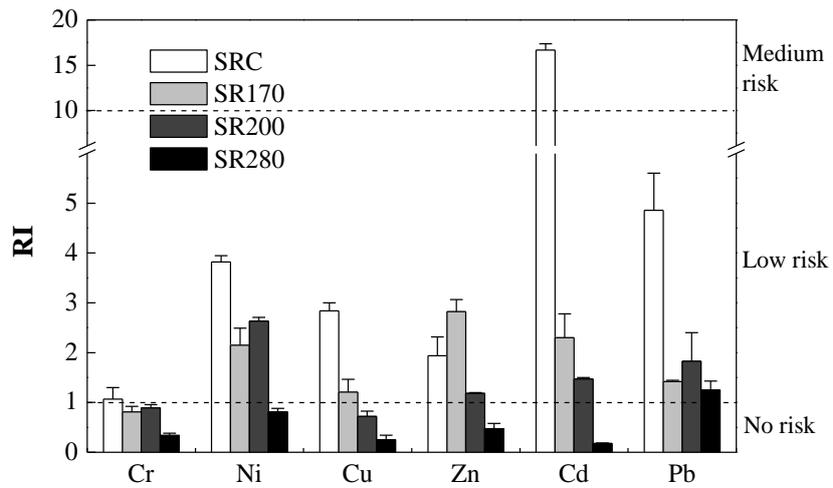


Figure 3-10 Eco-toxicity level of HMs in sludge assessed by RAC mode. SRC, solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively. $RI = (F1+F2)/total \times 100$.

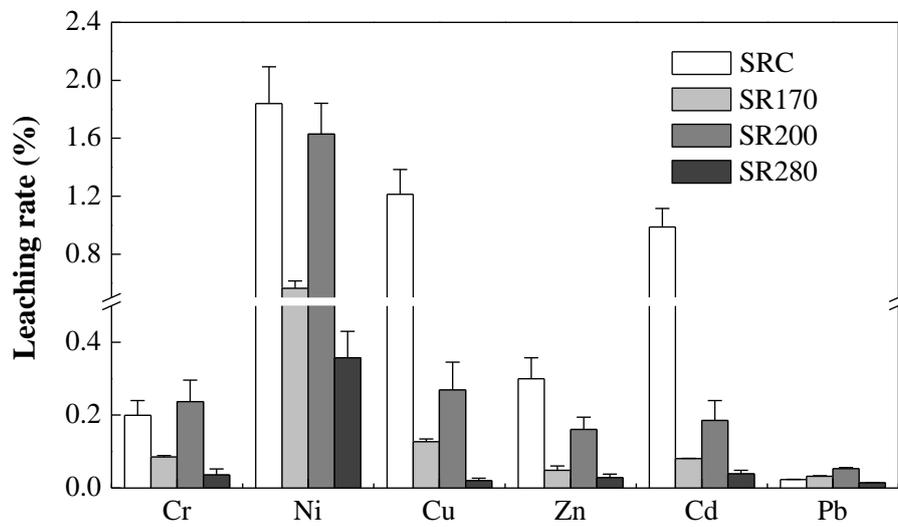


Figure 3-11 Leachable fractions of HMs in sludge before and after HTT process. SRC, solid residue in control experiment. SR170, SR200 and SR280 denote the solid residue after HTT under 170 °C, 200 °C and 280 °C, respectively.

Chapter 4 Effect of lignocellulosic materials on the behavior of HMs in sludge during HTT

4.1. Introduction

In the Chapter 3, HTT was applied for sewage sludge stabilization and dehydration, which facilitates the volumetric reduction and final disposal of sewage sludge. The results also indicate that HMs in sewage sludge could be redistributed in the process water and solid phases (produced hydrochar) after the HTT process. Moreover, the fractionation of HMs in the sludge residue can be greatly altered from weakly bound forms to a relatively more stable state resulting in the immobilization of HMs in the sludge after the HTT process. However, the mechanism of this immobilization and the influence factors are still unknown.

Besides the operational factors, the immobilization effect of HTT on HMs may be influenced by the components of sludge, which are organics and inorganics. Considering the organics in sludge, as presented before (Chapter 3, Section 3.3.), they can be converted into hydrochar during HTT process through decomposition and decarboxylation. This conversion of the organics in sludge will inevitably change the state of the bound metals (Appels et al., 2010).

It's well known that, in anaerobically digested sludge, the organics is basically some refractory organic substances, especially the lignocellulosic materials including lignin, cellulose and hemicellulose (Hao et al., 2013). Therefore, in this Chapter, the objective was to investigate the effect of these components on the behavior of HMs during HTT process. In order to make clear this kind of effect, rice husk (RH) was adopted as a kind of lignocellulosic materials based on the following reasons: (1) The

content of lignocelluloses are very high in RH; (2) RH is an agricultural by-product existed in large quantity, and its disposal also poses a big problem for the environment; (3) RH showed high capability for metallic cations fixation related with specific biomatrix and functional groups (Krishnani et al., 2008; Daifullah et al., 2003). After investigating the effect of the added RH on behavior of HMs during HTT process, the feasibility for enhancing HTT performance on sewage sludge treatment by RH addition can also be clarified.

Therefore, in the present Chapter, RH was selected as the model lignocellulosic substance and then added into the HTT system for investigating its effect on the behavior of HMs in sludge during HTT.

4.2. Materials and methods

4.2.1. Sewage sludge and rice husk

Dewatered anaerobically digested sewage sludge was prepared with the procedure presented in Chapter 2 (Section 2.2.1.), and the characteristics of the sludge is shown in Table 2-1. After being prepared, the sludge was kept in 4 °C.

Rice husk was dried at 105 °C for 2 h and then ground and sieved. The particles between 0.30 and 0.45 mm were collected and washed with deionized water, and then dried at 60 °C for 24 h for future use in the experiments. Table 4-1 lists the characteristics of RH used in this study, and its lignocellulosic components are shown in Table 4-2.

Before HTT process, RH was added into the prepared sewage sludge with different ratios (namely RH/sludge=0, 1/6, 1/3 and 1/1.75, respectively based on preliminary experiments, dry weight). The sludge and the added RH were then mixed manually and homogeneously to form RH-sludge mixtures.

4.2.2. HTT procedure

HTT experiments were conducted in an enclosed stainless steel reactor with a volume of 200 ml. As for the effect of RH addition on the immobilization behavior of HMs in sludge during the HTT process, 100.0 g of sludge or RH-sludge mixture was loaded into the reactor and hydrothermally treated under 200 °C (HTT200) and 280 °C (HTT280) for 1.0 h. After solid - liquid separation by vacuum filtration, the collected solid residue (SR), namely hydrochar was dried, ground and mixed homogeneously, and then stored in an enclosed plastic bag. The SRs obtained at RH/sludge ratios of 0, 1/6, 1/3 and 1/1.75 were labeled as SR0, SR1/6, SR1/3 and SR1/1.75, respectively. The collected process water (PW) was recorded as PW0, PW 1/6, PW 1/3 and PW1/1.75, respectively.

4.2.3. Evaluation methods and indices

The immobilization effect of risk reduction was evaluated from 3 aspects which were illustrated in detail in Chapter 2: (1) total concentration, (2) Fractionation of HMs which was used for assess the mobility and bioavailability, (3) Leachability of HMs in sludge.

After HTT with RH addition, the change of these 3 indices was used to explain the effect of lignocellulosic materials on the behavior of HMs during HTT process.

4.2.4. Analytical methods

The concentration of all the tested metals was determined by ICP-MS (Section 2.2.3.). The water content and then total solid was analyzed by weight loss after heating at 105 °C. The organic matter (loss on ignition) was determined after burning at 550 °C in a muffle for 1 h.

The lignocellulosic compositions (lignin, cellulose and hemicellulose) of sewage sludge and RH were determined by using the procedure proposed by Ververis et al. (2007). Based on this procedure, the lignin content was determined by gravimetric method after the hydrolysis process of cellulose and hemicellulose with 72% H₂SO₄ (w/w). The content of cellulose and hemicellulose in sludge and RH were calculated after determining the content of glucose and reducing sugar in the liquid phase after hydrolysis (Ververis et al., 2007). Glucose and reducing sugar in the solution were determined by the colorimetric method proposed by Mendel et al. (1954) and Miller (1959), respectively.

4.3. Results and discussion

4.3.1. Effect of RH addition on HMs redistribution in PW and SRs

As for the HMs control in solid waste, both extraction and stabilization effects may occur simultaneously during the HTT process (Escala et al., 2013; Jin et al., 2013), leading to a redistribution of HMs in the liquid (PW) and solid phases (SRs). This kind of redistribution provided a chance for the recombination of HMs in sludge, and the addition of RH during HTT process changed this redistribution process (Figures 4-2, 4-3).

Obviously, the vast majority of HMs were accumulated in the SRs after HTT process (Figure 4-3). After RH addition, the concentration of each metal decreased with the increase of RH/sludge ratio (d.w.). This decrease trend of HMs content in SRs was mostly brought about by a 'dilution effect' due to RH addition, depending greatly on the RH/sludge ratios applied.

Furthermore, the dissolution rate of these metals in PW was observed to decrease with the increase in RH dosage, which means RH addition changed the redistribution

of HMs. During the dissolution process, the newly formed hydrochar from RH showed strong capacity for combination with HMs which enhanced the accumulation of HMs in SRs during HTT process.

In addition, the redistribution of HMs in the two phases may also relate to the pH change during HTT process. After HTT process, the pH values of PWs were found to decrease slightly from 8.52 (PW0, single sludge) to 7.64(PW1/6), 7.35(PW1/3) and 7.21(PW1/1.75) under RH addition conditions, likely due to the decomposition of cellulose and lignin contained in RH during HTT (Y áñez et al., 2006) and subsequent production of some acidic substances. The latter needs further confirmation.

4.3.2. HMs fractional transformation and eco-toxicity assessment after RH addition

By sequential extraction, the fractionation of HMs in sludge after HTT process is shown in Figures 4-4, 4-5, and 4-6.

(1) Effect of RH addition on fractionation of HMs during HTT process at 200 °C

Figure 4-4 shows the fractionation of HMs in SRs collected from the RH-sludge mixtures with different RH/sludge ratios, after being treated at 200 °C. It was found that, RH addition greatly changed the fractionation of HMs in the sludge, resulting in the change of existing forms for all the metals, especially for Cr, Cd and Cu. For these 3 metals, the content in the first 4 fractions all decreased and increased in F5, which implies the positive effect of RH addition on the immobilization of these metals in sludge.

a) HMs in F1 and F2

HMs in F1 and F2 represents the weakly bound fractions and can be easily released into the environment, thus having the highest risk. Seen from Figures 4-4 and 4-5a, the contents of Cr, Ni, Cu and Cd in these two parts decreased after RH addition,

possibly due to the effective HMs binding ability of RH during HTT process. Furthermore, the decrease of HMs in (F1+F2) implies the decreased eco-toxicity of these 4 metals in sludge.

However, Zn and Pb showed a different trend. These 2 metals in (F1+F2) were observed to increase to some extent after RH addition. Especially for Zn, the content of (F1+F2) was increased with the dosage of RH. This means the eco-toxicity of Zn and Pb was increased showing the negative effect of RH addition on the immobilization of Zn and Pb.

A quantitative risk assessment was conducted by RAC based on the percentage of each metal in the first 2 fractions ($RI = (F1+F2)/total \times 100$, Figure 4-5a). For the HMs in the control sludge (SR0, without RH addition during HTT process), Cr and Cu fell into no risk category while the other metals were at the low risk level. After RH addition, the risk of Cr and Cu decreased and showed no risk while the risk of Ni and Cd decreased from low risk to no risk when RH added with a dosage of $RH/sludge=1/1.75$. However, the RI value of Zn and Pb was increased after RH addition showing the increased risk of these 2 metals to some extent, though they still were at the low risk level. Therefore, RH addition played a different role on reducing the direct toxicity and risk of different metals in sludge.

b) HMs in F3 and F4

HMs in F3, F4 and (F3+F4) are relatively stable and pose potential eco-toxicity to the environment and their risk may change with the variation of redox potential of the environment (Fuentes et al., 2008).

From Figures 4-4 and 4-6a, it can be seen that, Cu, Cr, Zn and Cd in these two fractions were decreased with RH addition, while Ni was decreased in F3 and increased in F4 with a resultant content increase in (F3+F4). These two fractions of Pb

were all increased. As metals in (F3+F4) may reflect the potential risk or toxicity of HMs in sludge, the potential toxicity of Cu, Cr, Zn, and Cd all decreased while that for Ni and Pb was increased to some extent after RH addition.

c) HMs in F5

HMs in F5 shows no toxicity because of its stably bound state. Under RH addition, the contents of Cr, Cu, Zn and Cd in F5 increased with the increase of RH/sludge ratio, implying that these metals existed more stably in the RH-sludge matrix. The F5 fraction of Ni and Pb in SRs under RH addition was decreased with RH addition.

The increase of HMs in F5 coupled with the decrease of HMs in (F1+F2) results in a decreased (F1+F2)/F5 ratio, signaling decreased lability of HMs in the sludge residues (Obrador et al., 2001). This observation indicates that the direct toxicity of Cr, Ni, Cu and Cd in the sewage sludge decreased after RH addition during the HTT process, especially at the RH/sludge ratio of 1/1.75.

In addition, it is worth noting that compared with a single HTT, RH addition can bring about a further decrease in the potential toxicity of Cr, Cu, Zn and Cd in sewage sludge after the HTT process.

The above results imply that, during HTT at 200 °C, RH addition enhanced the fractional transformation of HMs in sewage sludge, and the added RH has a synergetic effect on the risk reduction or enhanced immobilization of Cr, Ni, Cu and Cd in sewage sludge through the HTT process while showed some adverse effect on immobilization of Zn and Pb.

(2) Effect of RH addition on fractionation of HMs during HTT process at 280 °C

Figures 4-5b, 4-6b and 4-7 show the fractionation of the tested HMs in sludge after HTT process (280 °C) with and without RH addition.

Figure 4-5b showed that the contents of the tested metals in the weakly bound fractions (F1+F2) were increased to some extent after RH addition, possibly resulting from the redistribution process. During this process, although the newly formed hydrochar exhibited a strong binding capacity of HMs leading to a reduced release of HMs into PW (Figure 4-2), some metals may be weakly bound with the surface of the hydrochar and thus could be released into the extract solution during the first two extraction steps. This phenomenon needs to be investigated further.

Figure 4-6b shows that the other metals except for Ni and Pb in F3+F4 decreased with RH addition after HTT process at 280 °C. After RH addition, Pb in F3+F4 increased to some extent while Ni was firstly increased and then decreased with the dosage of the added RH. This denotes the potential toxicity of Cr, Cu, Zn, Ni and Cd can be decreased by RH addition in HTT process, but the potential toxicity of Pb might be increased.

Furthermore, the metals in F5 is very stable, and the results from Figure 4-7 showed that RH addition resulted in the increased content of Cr, Cu, Zn and Cd in F5 implying these metals became more stable. On the other hand, the content of Pb in F5 was decreased to some extent after RH addition, showing RH addition had adverse effect on the immobilization of Pb. The content of Ni in F5 was firstly decreased and then increased with the increase of RH dosage.

(3) Comparing the effect of RH addition during HTT under 200 °C and 280 °C

From the above analysis, different metals in sludge behaved differently after RH addition during HTT process under different temperatures. Some similarities and differences could be found after comparison.

a) Similarities

After HTT at different temperatures, the RH addition resulted in the following similar trends in fractionation of HMs in sludge. Firstly, the direct toxicity of Zn increased after RH addition. Secondly, the potential toxicity of Cr, Cu, Cd and Zn were decreased while these metals in no toxicity fraction were increased. Thirdly, the direct toxicity and potential toxicity of Pb were increased while the stable bound Pb was decreased.

b) Differences

After HTT at different temperatures, the RH addition also showed different effect on fractionation of metals at different temperatures. Firstly, the direct toxicity of Cr, Cu, Cd and Ni were decreased after RH addition at 200 °C while increased to some extent under the condition of 280 °C. Secondly, the potential toxicity of Ni was increased and the stable bound Ni was decreased after RH addition at 200 °C. Under the condition of 280 °C, however, Ni in potential toxicity fractions was firstly increased and then decreased after RH addition, while for Ni in F5 showed the exactly opposite trend.

Totally, RH addition leads to the fractional transformation of HMs in sludge during HTT process, but its effect was different for different metals under different treatment temperatures. For immobilization of HMs, which based on the fractional transformation of metals from unstable fractions to stable state in sludge, RH addition is more effective during HTT at 200 °C, especially for the immobilization of Cr, Cu, Cd and Ni.

4.3.3. HMs leachability test after RH addition

Leachability and leaching toxicity of HMs in SRs (after HTT) was determined by standard TCLP test. The leaching rate (% of total) depicted in Figure 4-8 reflects the proportion of HMs in the leachable state and their leachability.

It can be seen that the addition of RH exerted an enhancement effect on reducing the leachability of Cr, Ni, Cu, Zn and Cd in SRs from HTT processed RH-sludge matrix.

As for Cr, the leachability was found at a very low level (< 0.4%), and no significant variation was observed on its leachability after RH addition. The leaching rate of Ni decreased gradually with the increase of RH/sludge ratio, while those of Cu and Cd rapidly declined to a very low level (< 0.11%) after RH addition, with no obvious change in their leachability under different RH/sludge ratio conditions. However, the leachability of Pb increased to some extent after RH addition. This phenomenon may be attributable to the binding capacity of RH with these metals and the different vulnerability of the 6 HMs to the environment under the designed experimental conditions.

RH addition exhibited a reduction effect on the leaching toxicity of Cr, Ni, Cu, Zn and Cd during the HTT process, lowering these HM levels in SRs below the limit values. The lowest leaching toxicity of Cr, Ni, Cu, Zn and Cd was achieved at the RH/sludge ratio of 1/1.75, especially at 200 °C, with the leaching toxicity reduced by 41%, 89%, 81% 59% and 71% for Cr, Ni, Cu, Zn and Cd, respectively while increased the leachability of Pb, revealing that the enhancement effect of RH addition at 200 °C on the reduction of Cr, Ni, Cu, Zn and Cd leaching toxicity follows the order of Ni > Cu > Cd > Zn > Cr.

Seen from the results of the leachability test, RH addition also exhibited a synergistic effect on risk reduction and immobilization of Cr, Ni, Cu, Zn and Cd in the sludge during HTT process, which may provide a new method for HMs detoxification in sludge disposal and stabilization processes.

4.3.4. Mechanism analysis

Here, take the behavior of HMs in sludge during HTT process at 200 °C as an example. As mentioned above, a synergistic effect was found for RH addition on some metals immobilization during the HTT process. Based on the present work, the following two points can be arrived at: (1) Under RH addition condition, less HMs was dissolved into the liquid phase because of the excellent HMs binding capacity of newly formed hydrochar from RH. The concentration of HMs in the hydrothermally treated sludge decreased with the increase in RH/sludge ratio applied, mainly owing to some ‘dilution effect’ caused by RH addition. (2) Most importantly, RH addition enhanced fractional transformation of HMs, and the weakly bound (F1+F2) and relatively stable (F3+F4) fractions of some metals in the hydrothermally treated sludge can be transformed into the stable state (F5).

Based on the present results and above discussion, the reduction in HMs toxicity and leachability may be interpreted as a synergistic mechanism of RH addition during the HTT process as Figure 4-9: (1) the unstable or loosely absorbed HMs (F1+F2 and part of F3+F4) are firstly dissolved under HTT conditions, and then can be re-encapsulated or immobilized into the processed sludge matrix. (2) The released HMs can be further entrapped by the enlarged structure of RH or chelated with some functional groups and then fixed in the stable RH-sludge matrix formed during HTT under RH addition, resulting in enhanced HMs immobilization effect. The detailed mechanisms need further investigation, especially for the contribution of organic ingredients (such as lignin and cellulose contained in RH) and inorganic substances (mainly including phosphate, silicate, carbonate, aluminum, and calcium in the sludge) in addition to some functional groups formed during HTT to the immobilization of HMs in the HTT processed RH-sludge matrix.

4.4. Summary

Based on total concentration, bioavailability and leaching toxicity tests, the mobility and leachability of HMs was evaluated after HTT of sludge with RH addition. The present results demonstrate that:

(1) RH addition enhanced the accumulation of HMs in sludge by their strong binding capacity with HMs; however the total concentration of HMs decreased with RH dosage which may be due to the dilution effect.

(2) RH addition enhanced the fractional transformation, which is different for different HMs and different temperatures during HTT process. When treated at 200 °C, RH addition enhanced the transformation of Cr, Cu and Cd from all fractions to the stable state while increased the mobility of Zn and Pb. When treated at 280 °C, all the metals except for Pb were mainly transformed from (F3+F4) to F5 while their concentration in (F1+F2) was slightly increased.

(3) The leachability of all the metals except for Pb was decreased in sludge after being treated both at 200 °C and 280 °C under RH addition, which implies the potential effect of lignocellulosic materials on the immobilization of HMs in sludge. The lowest leaching toxicity of Cr, Ni, Cu, Zn and Cd was achieved at the RH/sludge ratio of 1/1.75, especially at 200 °C, with the leaching toxicity reduced by 41%, 89%, 81% 59% and 71% for Cr, Ni, Cu, Zn and Cd, respectively.

(4) The positive effect of RH addition during HTT may be resulted from the speculations that the released HMs could be further entrapped by the enlarged structure of RH or chelated with some functional groups and then fixed in the stable RH-sludge matrix formed during HTT under RH addition.

Generally, the present results suggest that HTT supplemented with RH addition is a new method for sludge treatment, especially for the immobilization of Cr, Cu and Cd in the contaminated sewage sludge.

Table 4-1 Physicochemical characteristics of rice husk (RH) used in the experiments.

Parameters	Rice husk
Solid content (%)	94.47 ± 0.58
Loss of ignition (%)	69.32 ± 1.41
HMs (mg/kg, dry weight)	
Cr	13.50 ± 1.53
Ni	41.74 ± 2.59
Cu	8.08 ± 1.92
Cd	0.17 ± 0.01
Zn	34.87 ± 5.55
Pb	5.28 ± 0.18

Table 4-2 Content of lignocellulosic composition in sewage sludge and rice husk

	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Sludge	13.91	2.82	17.38
Rice husk	25.15	19.53	26.58

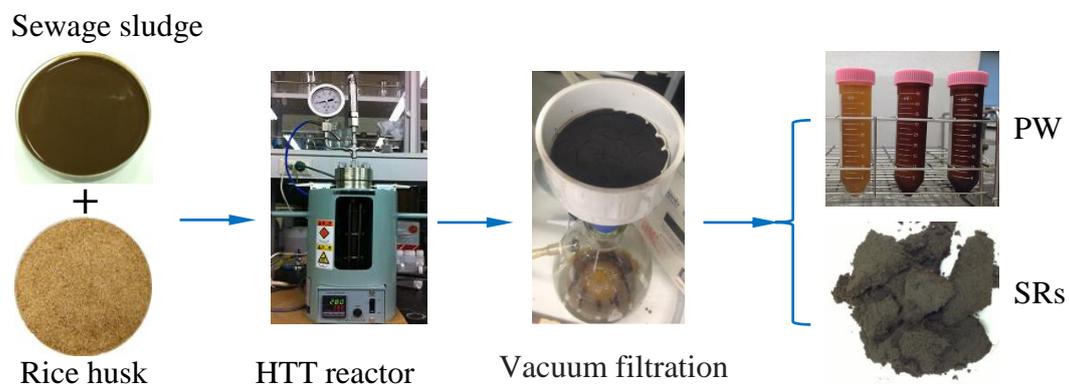


Figure 4-1 HTT process for sludge treatment with RH addition. HTT, hydrothermal treatment; PW, process water separated after HTT; SRs, solid residues of sludge after HTT.

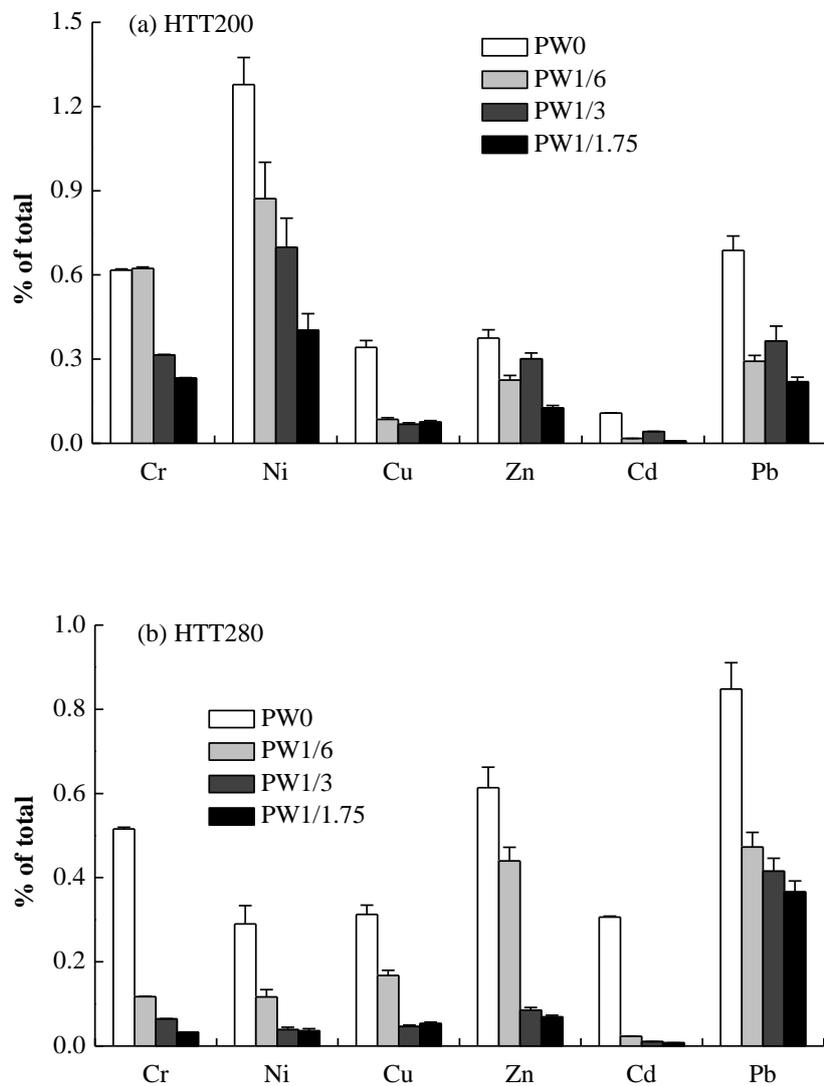


Figure 4-2 HMs in process water after HTT process at 200 °C (a) and 280 °C (b) with different dosage of rice husk. PW0, PW1/6, PW1/3 and PW1/1.75 denote the process water obtained after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

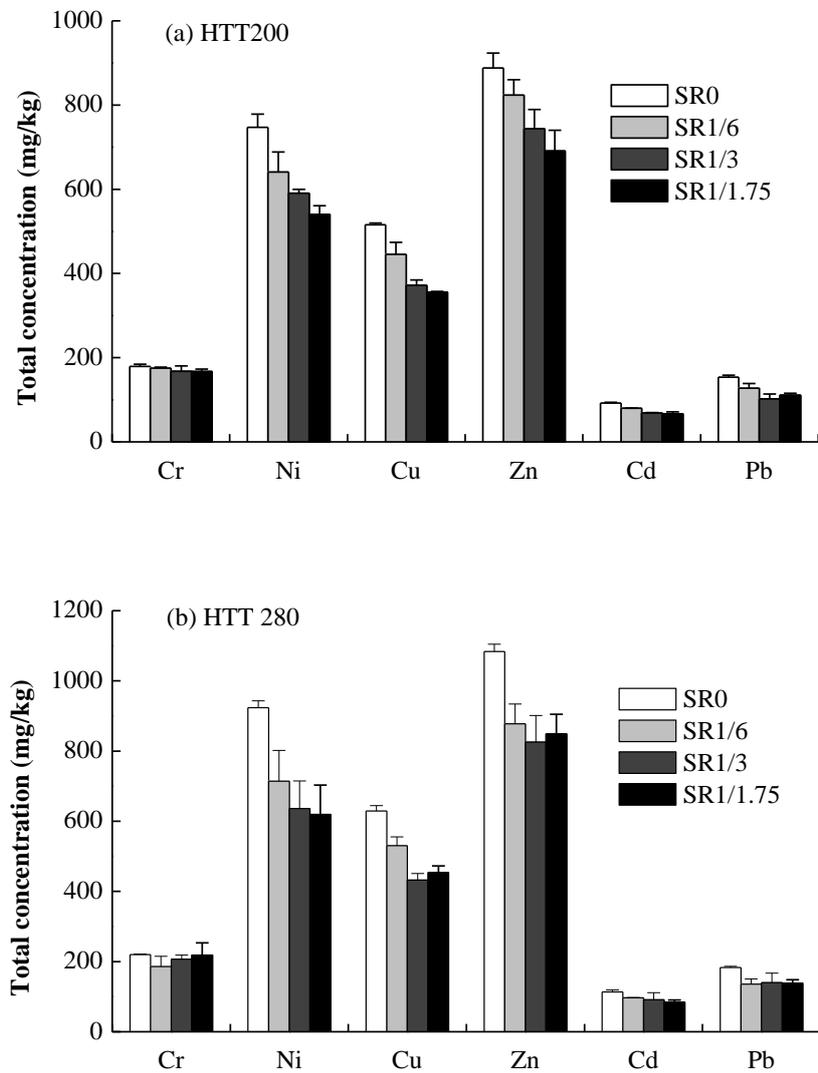


Figure 4-3 Total concentration of HMs in sludge after HTT process at 200 °C and 280 °C with different rice husk dosage. SR0, SR1/6, SR1/3 and SR1/1.75 denote the solid residues collected after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

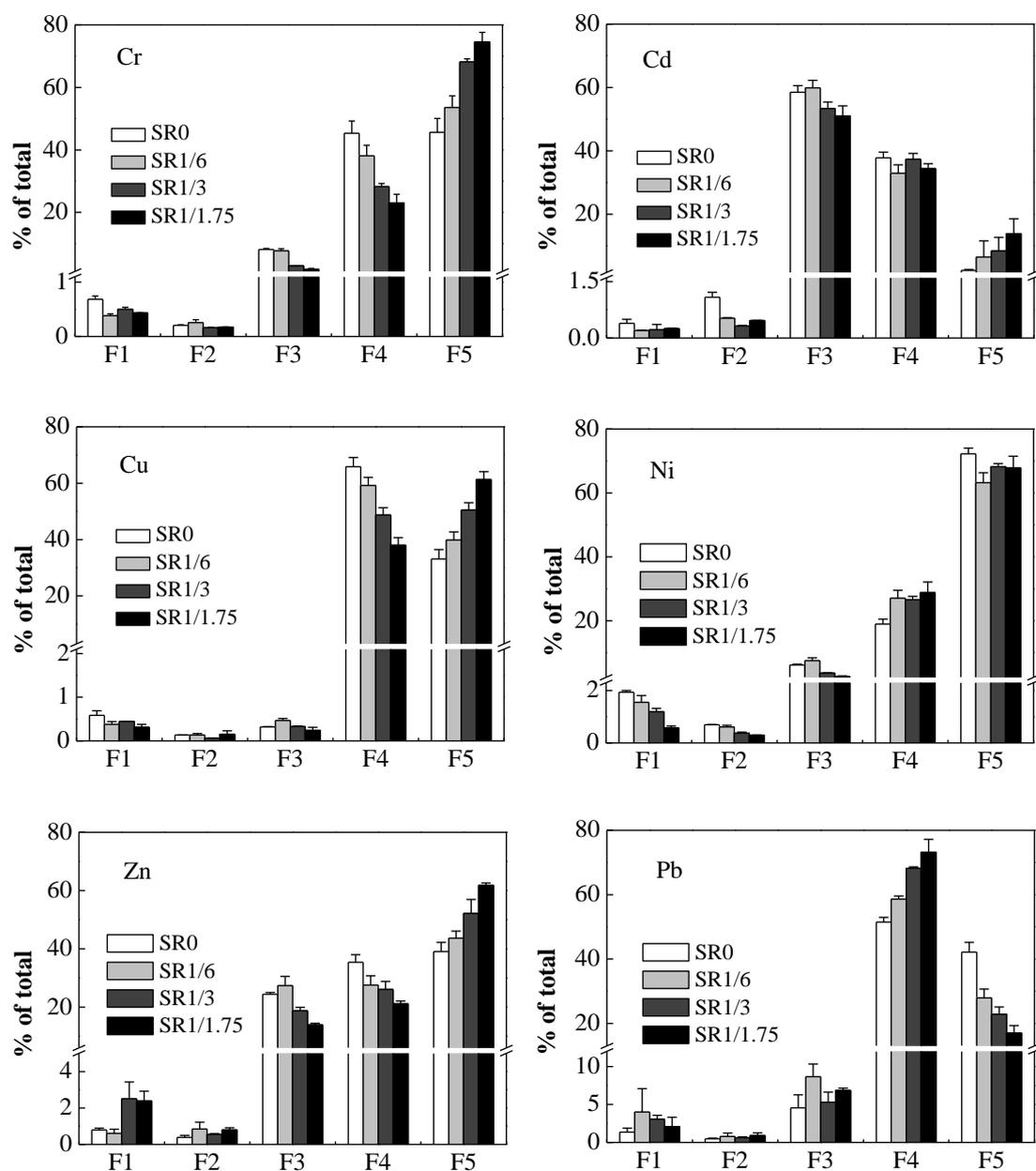


Figure 4-4 Fractionation of HMs in sludge after HTT at 200 °C under different dosage of rice husk. SR0, SR1/6, SR1/3 and SR1/1.75 denote the solid residues collected after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

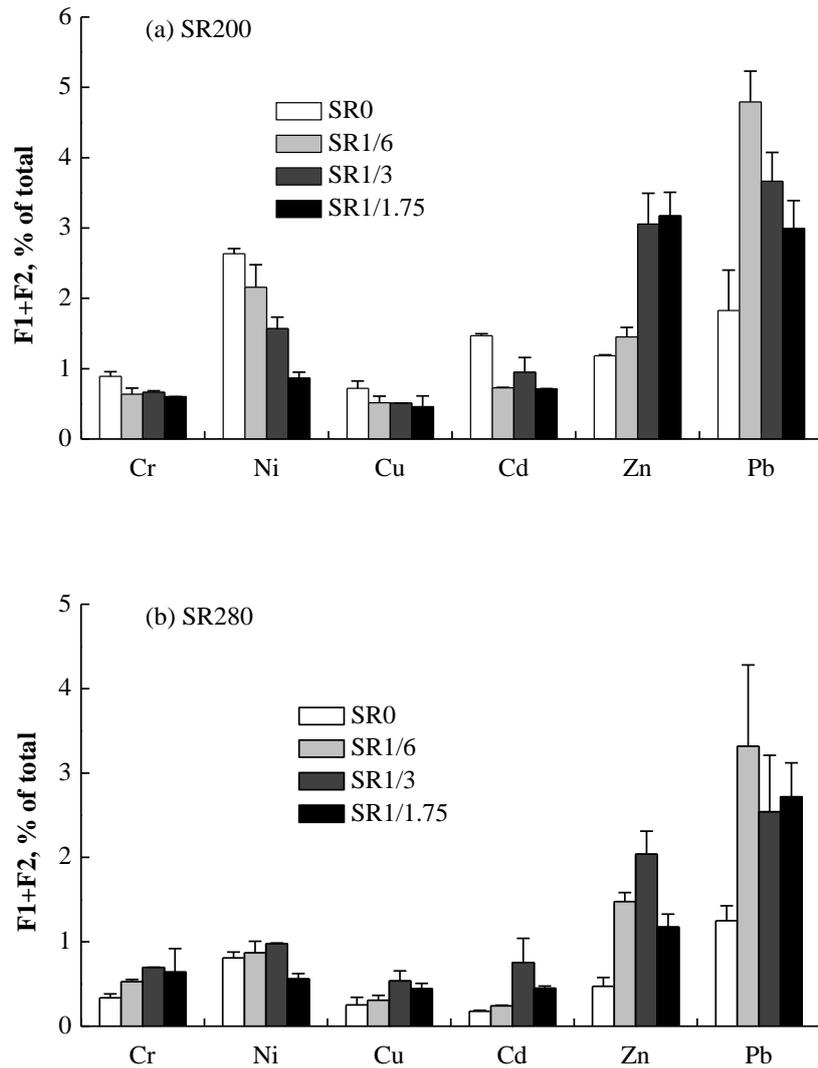


Figure 4-5 Content of HMs in weakly bound fractions (F1+F2) in sludge after HTT at 200 °C (a) and 280 °C (b) with different dosage of rice husk. SR0, SR1/6, SR1/3 and SR1/1.75 denote the solid residues collected after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

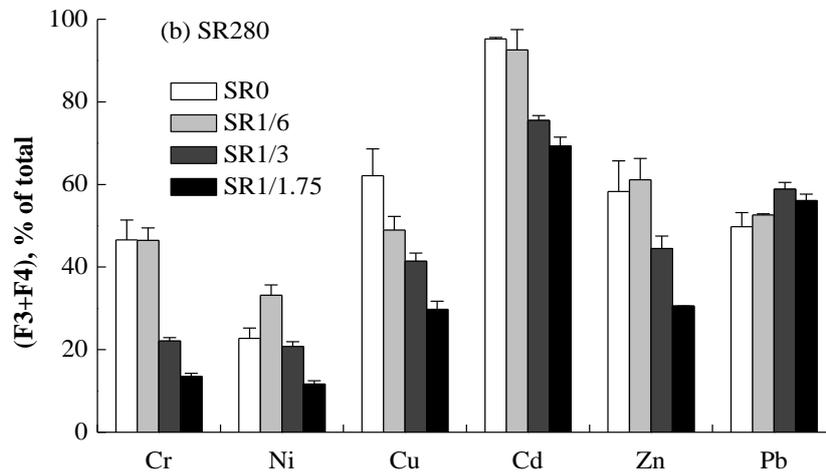
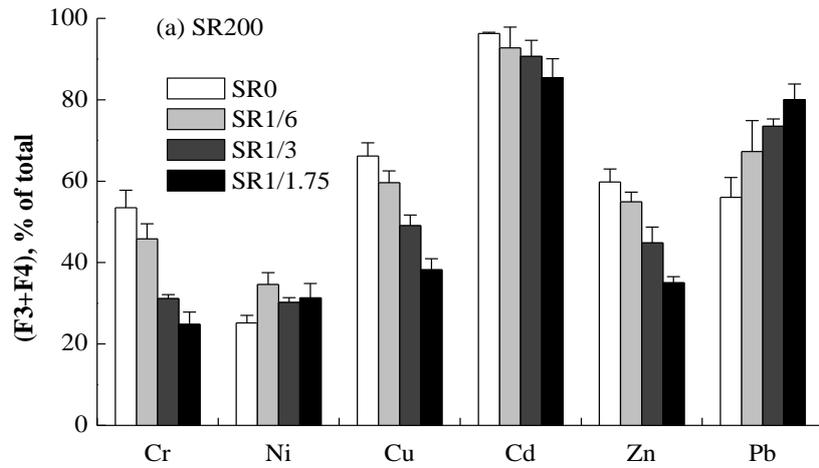


Figure 4-6 The percentages (% of total) of HMs in (F3+F4) in the sludge residues after HTT process at 200 °C (a) and 280 °C (b) with different dosage of rice husk. SR0, SR1/6, SR1/3 and SR1/1.75 denote the solid residues collected after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

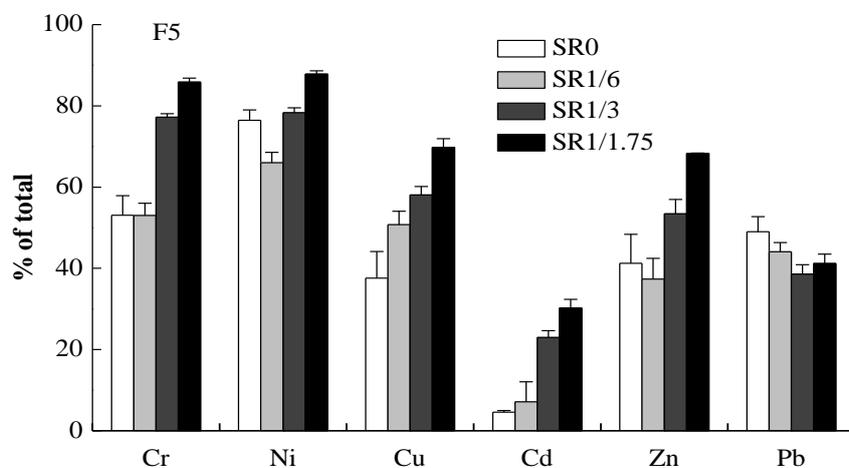


Figure 4-7 The percentages (% of total) of HMs in F5 in the sludge residues after HTT process at 280 °C with different dosage of rice husk. SR0, SR1/6, SR1/3 and SR1/1.75 denote the solid residues collected after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

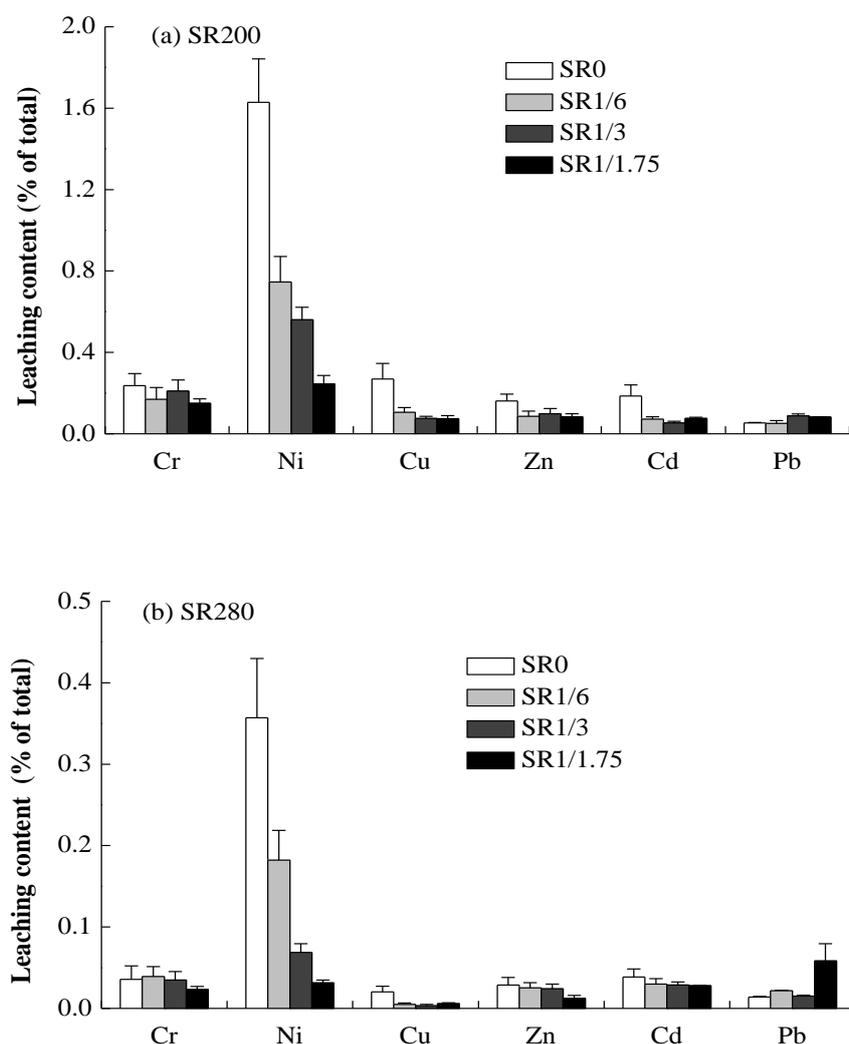


Figure 4-8 Content of HMs in the leachate from sludge after HTT process at 200 °C (a) and 280 °C (b) with different dosage of rice husk. SR0, SR1/6, SR1/3 and SR1/1.75 denote the solid residues collected after hydrothermally treating the RH-sludge mixtures in which the RH/sludge ratios were 0, 1/6, 1/3 and 1/1.75, respectively.

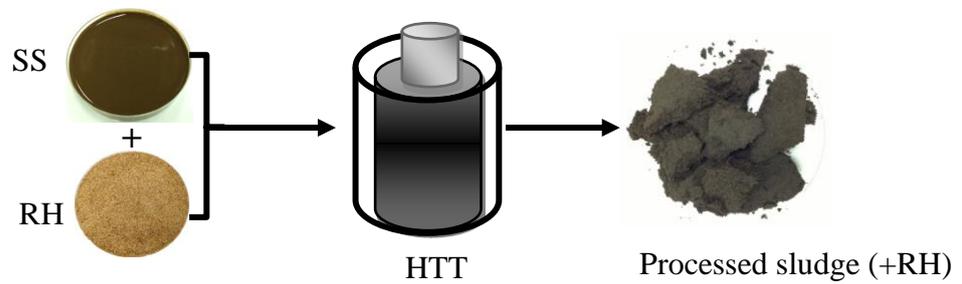
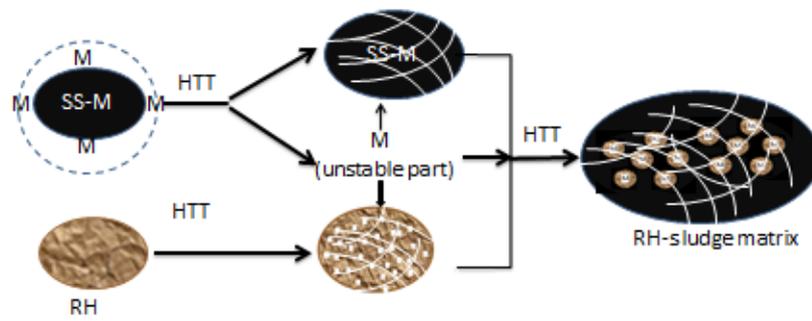


Figure 4-9 Schematic and image of HMs immobilization into the HTT processed sludge under RH addition. HTT, hydrothermal treatment; SS, sewage sludge; RH, rice husk; M, heavy metal.

Chapter 5 Effect of phosphate on behavior of HMs in sludge during HTT

5.1. Introduction

Phosphate and phosphate- based minerals are now widely used for stabilization of HMs in soil (Abbaspour and Golchin, 2011; Wu et al., 2013; McGowen et al., 2001; Chen et al., 2006) because of its strong binding capacity with some metals and therefore suppress the mobility and bioavailability of HMs. Also, some trial has been carried out on the effectiveness of phosphorus (by using phosphoric acid and monobasic calcium phosphate) on HMs immobilization in tannery sludge after incineration (Tang et al., 2013). Therefore, phosphate- based materials are very important for combining HMs and suppressing their mobility.

In the previous experiments (Chapters 3 and 4), HTT was used for immobilization of HMs in sewage sludge, and the results showed the metals in sludge could be stabilized after HTT process resulting in the reduction of their mobility, bioavailability and eco-toxicity. Because of the high phosphorus content (2.62% in the sewage sludge used in this study) and strong binding capacity, the effect of phosphorus on the behavior of HMs in sludge during HTT process should be investigated.

Furthermore, it has been reported that during HTT, the existing forms of phosphorus in the sludge would be changed (Zhu et al., 2011). Importantly, the existing forms of phosphorus are closely related to their bioavailability in soil, and also may affect the environmental risk of some metals bound with phosphorus in the sludge (Chen et al., 2007). Therefore, it's speculated that the behavior of phosphorus

may affect the fractional transformation of HMs during HTT. In order to confirm this speculation, some trials were carried out in this study to investigate the behavior of phosphorus and its interaction with HMs immobilization during HTT process, and then the effect of phosphorus on the environmental risk and toxicity of HMs in sludge during HTT was also disclosed.

In this chapter, the effect of phosphorus on immobilization of HMs in sludge was analyzed from two aspects: (1) the behavior of phosphorus in sludge during HTT process; (2) the effect of phosphorus on immobilization of HMs was explored by changing the content of phosphorus in sludge. This study adopted the method of increasing the phosphorus content by adding some P- based materials. Finally the relationship between phosphorus content and HMs immobilization effect during HTT process was expected to reveal.

5.2. Materials and methods

5.2.1. Sewage sludge

The sewage sludge used in this experiment was dewatered anaerobically digested sludge cake obtained from a wastewater treatment plant in Ibaraki prefecture, Japan. After collection, the sludge was kept at 4 °C, and then the sludge sample was prepared with the same procedure presented in Chapter 2 (Section 2.2.1.). Table 5-1 lists the main characteristics of the sludge used in this study.

5.2.2. Experimental design

In order to know the behavior of phosphorus in sludge during HTT process and the effect of phosphorus contained in sludge on the immobilization of HMs during HTT, the experiment study was carried out with the following scheme (Figure 5-1) which included three steps.

The fractionation and existing forms of phosphorus in sludge was firstly identified in Step 1. After this identification, a P- based material that containing the similar main form of phosphorus with sludge was selected and added into the HTT system to change the content of phosphorus in sludge. After adding the P- based material, HTT was carried out at temperatures of 200 °C and 280 °C, and then the behavior of phosphorus in sludge during HTT process was investigated in Step 2. After HTT process, the behavior of HMs in sludge was analyzed based on the redistribution, fractionation and leaching test in Step 3. Finally, the effect of phosphorus on behavior of HMs and their interaction in sludge during HTT process was speculated based on the behavior variation of HMs caused by the change of P content in sludge during HTT.

The HTT procedure for sewage sludge treatment was the same with that presented in Chapter 3 (Section 3.2.2.), and the treatment was carried out at 200 °C and 280 °C, respectively. After reaching the expected temperature, the HTT process lasted for 1.0 h, and then the sludge mixtures (with or without P addition) were cooled to room temperature. The process water (PW) and solid residues (SRs) were separated and collected after vacuum filtration.

By doing these experiments, analysis was done on the contribution of phosphorus contained in sludge to the immobilization of HMs during HTT.

5.2.3. Phosphorus and its fractionation

Phosphorus in sludge can be fractionated into different categories by different sequential extraction protocol (Ruban et al., 1999; Ruban et al., 2001). The most widely used method is the Standards, Measurements and Testing (SMT) Programme extraction protocol (Medeiros et al., 2005; Ruban et al., 2001). The extraction procedure for phosphorus in sludge is shown in Figure 5-2. After sequential extraction,

phosphorus in sludge can be fractionated into the following 5 categories: (1) concentrated HCl-extractable P, namely total P (TP), (2) organic P (OP), (3) inorganic P (IP), (4) non-apatite inorganic P (NAIP, P fraction associated with oxides and hydroxides of Al, Fe and Mn), and (5) apatite P (AP, P fraction associated with Ca).

Furthermore, during HMs sequential extraction process illustrated in Chapter 2 (Section 2.2.2.), phosphorus in sludge was also extracted along with HMs into different fractions, here being defined as P1, P2, P3, P4 and P5 according to the sequential extraction procedure. Although no data show this kind of speciation of phosphorus is reasonable or not, the extraction of phosphorus into the 5 parts at least can reflect the bound state or strength of phosphorus in sludge, and also the stability of metals that bound with it.

5.2.4. Analytical methods

Analytical methods for determining HMs and other parameters are the same with those presented in Chapter 2 (Section 2.2.3.). All the metals were determined by ICP-MS (ELAN DRC-e, PerkinElmer).

The phosphorus concentration was determined with molybdate ascorbic acid method by using a Shimadzu UV1800 spectrophotometer.

For data analysis, the correlation coefficients (r) between phosphorus content and different fractions of HMs were calculated by using Microsoft Excel 2010.

5.3. Results and discussion

5.3.1. Redistribution of phosphorus in PW and SR after HTT

HTT usually has both extraction and stabilization effects for some inorganics, which therefore leads to the redistribution of these elements in PW and SRs (Escala et al., 2013; Jin et al., 2012).

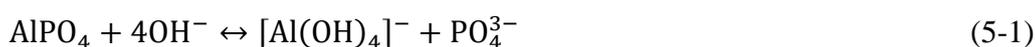
Figure 5-3 shows the redistribution of phosphorus and the major metals (which were closely related to the existing forms of phosphorus) in PW and SRs after HTT. A very small part of phosphorus, Ca, Al, Fe and Mn were detected to release into PW (< 0.6 %) while the majority of them were accumulated in the collected SRs. The extent of this kind of accumulation increased with the increase of treatment temperature. This kind of accumulation resulted in the preservation of phosphorus in the sludge. Ca was found to exist at a very high level (14.84 %) in the sludge, followed by Fe (5.34%), Al (0.73%) and Mn (0.04%). These four metals may influence the behavior of phosphorus in the sludge during HTT process because of their high possibility of precipitation with phosphorus.

5.3.2. Fractionation of phosphorus in sludge after HTT

Table 5-2 shows the changes in fractionation of phosphorus in sludge before and after HTT. The phosphorus was mainly existed in the form of inorganic P (IP) in the tested sludge and its organic P (OP) was very low. In addition, apatite P (AP) was the main form of inorganic P (IP), possibly being ascribed to a higher content of Ca and the relatively lower contents of Fe, Al and Mn (Figure 5-3b).

After HTT, significant increase was found in the content of inorganic P with the treatment temperature increased from 200 °C to 280 °C, while sharp decrease occurred correspondingly to the organic P fraction in the sludge residue, signaling the organic P could almost completely be converted into inorganic P. This phenomenon may be resulted from the destruction of organics during HTT process. Furthermore, non-apatite inorganic P was detected to decrease after HTT process in spite of the increase in inorganic P fraction, indicating phosphorus was mainly transformed from OP and NAIP to AP. This kind of conversion of phosphorus into AP could be resulted not only from the high content of Ca in the tested sludge to form apatite, but also from

the large increase in pH value of the sludge mixture in the reactor from 6.4 (original tested sludge) to 8.7 (PW200) and 9.4 (PW280) after HTT process. The resultant alkaline condition may favor the dissolution of NAIP (Eq. 5-1) and the released PO_4^{3-} could combine with Ca to form the relatively stable Ca bound P (Eq. 5-2) (Petzet et al., 2012). Also, the phosphorus converted from OP can then be recombined to AP with Ca (Eq. 5-2).



5.3.3. Fractionation of phosphorus in sludge when extracting HMs with Tessier's method

As illustrated in Chapter 2, the fractionation of HMs can be analyzed by using the sequential extraction method proposed by Tessier et al. (1979) (Figure 2-1). This extraction procedure can be probably used to reflect the state of phosphorus in sludge, especially the phosphorus which bound with the HMs at different existing forms. Figure 5-4 shows the fractionation of phosphorus along with the speciation of HMs in sludge by using Tessier's method. After sequential extraction, phosphorus in different parts was defined as P1 to P5, and it was found the phosphorus in the raw sludge was mainly existed in P4 (93.8%) which may relate to the apatite phosphorus in sludge, and phosphorus in all the other fractions were very low. After HTT process, phosphorus in fractions P1 to P4 were all decreased and the content of phosphorus in P5 increased, showing HTT process significantly changed the fractionation of phosphorus in sludge, and the fractional transformation may provide some chance for HMs recombination with phosphorus in sludge. Furthermore, the phosphorus transformation from weakly bound fractions to stable state suggests the stability of HMs might be improved after HTT process.

5.3.4. Effect of HAP addition on HMs redistribution during HTT

The result showed that AP was the main existing form of phosphorus in the raw sludge, and other forms of phosphorus were almost converted to AP during HTT process. In order to investigate the effect of phosphorus on the behavior of HMs in sludge during HTT process, hydroxyapatite (HAP) was added into the HTT system with dosage of 0%, 10% and 40% (P basis) according to the total phosphorus content in the sludge ($\text{HAP-P}/\text{TP}_{\text{sludge}} = 0\%, 10\% \text{ and } 40\%$, w/w). After HTT at 200 °C or 280 °C for 1 h, HMs in the obtained PW (PW200 and PW280) and SRs (SR200 and SR280) were analyzed. The differences of HMs in redistribution, fractionation and leachability before and after HAP addition were examined and used to indicate the effect of phosphorus on HMs behavior during HTT.

Furthermore, the control samples (SRC) were prepared by directly drying the sludge at 60 °C for 48h after adding HAP with dosage of 0%, 10% and 40% (P basis).

After HTT process, the treated sludge was separated into PW and SR. The content of HMs was analyzed with the results shown in Figures 5-5 and 5-6. For all the metals, a very small part of them were observed to release into PW after HTT process with the majority left in the SRs, meaning that HTT brought about the redistribution of HMs in these two phases.

Figures 5-5 and 5-6 also show the effect of HAP addition on the redistribution of HMs in PW and SRs. It can be seen that when HAP was added into the tested sludge, no obvious change was observed in the concentration of HMs (Figure 5-6). During HTT process, HAP addition caused an obvious reduction in the content of HMs released into PW (Figure 5-5), which is likely attributable to the strong binding capacity of HAP with these metals. This reduction of HMs in PW after HAP addition

can also be used to partly explain the proposed “dissolution - precipitation” mechanism of HMs redistribution during HTT process.

5.3.5. Effect of HAP addition on fractionation of HMs during HTT

After HTT process, the fractionation of HMs in sludge was determined by sequential extraction, and the fractional variation of HMs in sludge with or without HAP addition can be used to reflect the effect of phosphorus on the behavior of HMs during HTT. Because of so much data obtained, Cd was selected as an example in this study to give more detailed analysis and explanation on the behavior of HMs after HAP addition. Some additional discussion on the other metals was also provided.

(1) For Cd

Figure 5-7 shows the fractionation of Cd in the raw sludge and hydrothermally treated sludge before and after HAP addition.

The result indicated that, in the raw sludge used in this study, more than half of Cd was bound to iron and manganese oxides (F3, 53.76%), which was mainly existed in the potential toxicity forms (F3+F4). After HTT, the fractionation of Cd was transformed from weakly bound forms (F1 and F2) to a relatively stable form (F4) and stable state (F5), implying the immobilization and risk reduction effect of HTT on Cd in the sludge.

Furthermore, HAP addition can enhance this immobilization effect of HTT on Cd thus achieving its risk reduction in sludge after HTT process. The risk reduction of Cd in the sludge can be clearly observed after directly drying the sludge (SRC) and HTT process (SR200 and SR280) with HAP addition. The content of Cd in the first 3 fractions decreased while Cd in F4 increased with HAP addition almost in a dose-dependent manner. Cd in F5 decreased slightly in SRC and SR280 while significantly increased in SR200 with HAP addition. Anyhow, HAP addition showed a

positive effect on immobilization and risk reduction of Cd by transforming Cd into more stable state which may be ascribed to the strong binding affinity of phosphate.

For the quantitative risk evaluation of Cd, RAC method based on Cd in fractions (F1+F2) can be used to reflect its direct eco-toxicity, mobility and bioavailability. The results showed that Cd in the tested sludge exhibited medium risk to the environment. After HTT at 200 °C and 280 °C, Cd in (F1+F2) decreased by 95% and 98%, respectively, thus the risk of Cd in SRs was sharply decreased from medium risk (in the original tested sludge, SRC) to low risk (in SR200) and no risk (in SR280). When HAP was added, Cd in fraction (F1+F2) decreased with the increase of HAP dosage both in the drying and HTT processes, showing HAP addition had a synergistic effect on reducing the direct toxicity of Cd with HTT process. Figure 5-7 also shows that this synergistic effect was more significant when HTT was conducted at 200 °C.

Table 5-3 lists the correlation coefficient (r) between fractions of Cd and phosphorus content in the sludge after HTT process. Cd in F1 and F3 were found to have strongly negative relationship with P content in the sludge, while a strongly positive relationship existed between F4 and phosphorus content in sludge. Specifically, under HTT of 200 °C condition, all the Cd fractions were found to have strong relationship with the phosphorus content, indicating 200 °C might be the crucial temperature when taking the stability of formed Cd-sludge matrix, especially the binding stability of Cd with Fe and Mn oxides into consideration.

In contrast, no clear relationship could be concluded with respect to phosphorus content and the fractions of Cd in F2 and F5 in the sludge, which needs further detailed investigation.

The result clearly indicated that phosphorus played a very important role on the fractional transformation of Cd in sludge during HTT process. The strong

correlationship between Cd fractions (especially F1, F3, and F4) and phosphorus content in sludge implies that the effect of HTT on Cd immobilization was partly contributed by the strong binding capacity of phosphorus in the sludge matrix.

(2) For Cr, Ni, Cu, Zn and Pb

The fractional transformation of Cr, Ni, Cu, Zn and Pb after HAP addition is shown in Table 5-4.

① **Without HTT**

From Table 5-4 it can be seen, the metals except for Cr in (F1+F2) were all decreased to some extent after HAP addition during the drying process. The contents of Cr and Ni in (F3+F4) decreased while those of the other metals showed no change. As For F5, except for Cr and Pb, the other metals were all increased after HAP addition. Therefore, in general, during the drying process HAP addition had some positive effect on immobilization of Ni, Cu and Zn.

② **After HTT**

a) Metals in fractions (F1+F2)

From Table 5-4, the contents of Cr and Ni in (F1+F2) decreased after HAP addition while the contents of Cu, Zn and Pb in (F1+F2) increased to some extent. This implies the direct toxicity of Cr and Ni was decreased while that of the other 3 metals was increased.

b) Metals in fractions (F3+F4)

From Table 5-4, when treated at 200 °C the content of Cr and Cu showed no obvious change after HAP addition, while the contents of Ni, Zn and Pb decreased indicating the potential toxicity of these 3 metals could be further decreased because of HAP addition.

When the sludge was treated at 280 °C, the content of Ni and Zn in (F3+F4) were firstly increased and then decreased with the increase in HAP dosage, while the contents of Cr and Cu were increased showing the increased potential toxicity. Furthermore, the content of Pb in these fractions was decreased with HAP dosage implying the potential toxicity of Pb could be further reduced.

Generally, the effect of HAP addition on reducing the potential toxicity of HMs during HTT was different for different treatment temperatures and HMs types. When the sludge was treated at 200 °C, the reduction effect on the potential toxicity of HMs was more obvious.

c) Metals in F5

Metals in F5 is very stable, and therefore the HMs will be more stable with a higher content of HMs in this fraction while lower in (F1+F2) when the total concentration is fixed. From Table 5-4, it can be seen that:

Firstly, when the sludge was treated at 200 °C, the metals except for Cu were all increased with HAP dosage.

Secondly, when the sludge was treated at 280 °C, the content of Pb in F5 was increased with HAP addition. The content of Cr in F5 was firstly increased and then decreased, while Ni and Zn changed in an opposite trend. Besides, the content of Cu in F5 decreased with HAP addition.

From the above analysis, the addition of HAP during HTT greatly changed the fractional transformation of HMs in sludge. After this process, the risk of Cr and Ni was decreased while that of Zn, Cu and Pb increased. When HTT was conducted at 200 °C, the effect of HAP addition on immobilization of HMs was relatively more obvious. Under this condition, only Cr and Ni transformed from weakly bound fractions to relatively stable and stable state.

5.3.6. Effect of HAP addition on leachability of HMs in sludge

The risk of HMs in sludge can be directly reflected by its leachability which is closely related to its mobility. The leaching toxicity of HMs in sludge was determined with the standard TCLP test, and the leaching concentration of HMs in sludge residues is shown in Figure 5-8.

After HAP addition, the leachability of Cu, Zn and Cd was decreased in SRC while that of Cr and Ni was increased to some extent. After HTT at 200 °C, the contents of Cr, Cu, Zn and Cd in the leachate were decreased while those of Ni and Pb showed no obvious change. After HTT at 280 °C, the leachability of Cr, Cu, Zn, Cd and Pb were all decreased to some extent while that of Ni was increased to a certain extent and then decreased with the increase of phosphorus content.

Generally, HAP addition further reduced the leaching content of Cr, Cu, Zn and Cd from the SRs collected from HTT processes, which signals the synergistic effect of phosphorus and HTT on reducing the leaching toxicity of Cr, Cu, Zn and Cd in sludge.

5.4. Summary

HTT process changed not only the fractionation of HMs but also the state of phosphorus in sludge. The interaction between phosphorus and HMs in sludge during HTT process was investigated, and the main results were as follows:

(1) Phosphorus was mainly existed in the form of apatite P (AP) in the tested sludge. After HTT, other forms of phosphorus were almost completely converted into AP. Moreover, phosphorus was mainly extracted in the F4 fraction and HTT caused the transformation of phosphorus in sludge into more stable state.

(2) HAP addition significantly changed the fractionation of HMs, especially for

Cr, Ni and Cd. After HTT process, HAP showed further immobilization effect on these metals while no obvious effect on Cu immobilization was observed.

(3) HAP addition could reduce the leaching toxicity of Cr, Cu, Zn and Cd in sludge.

(4) Phosphorus content in sludge partly contributes to the immobilization of some metals, especially for Cr, Ni and Cd.

Generally, the synergistic effect of HAP addition and HTT implies that the HAP can be used for immobilization of some metals (especially for Cd) during HTT process.

Table 5-1 Physicochemical characteristics of the sludge used in the experiment

Parameters	Value(Mean \pm SD [*])
Moisture content (%)	84.98 \pm 0.47
Organic matter (%)	46.25 \pm 0.31
Ash (%)	53.75 \pm 0.31
pH	6.43 \pm 0.21
TP ^b (g/kg, dry weight)	26.18 \pm 0.35
HMs in the sludge (mg/kg, dry weight)	
Cr	152.81 \pm 41.35
Ni	545.58 \pm 111.73
Cu	402.09 \pm 37.28
Zn	484.68 \pm 41.15
Cd	48.31 \pm 3.25
Pb	50.83 \pm 13.40
Other main metals in the sludge (g/kg, dry weight)	
Na	2.85 \pm 0.72
K	2.99 \pm 0.50
Mg	10.22 \pm 1.45
Al	7.33 \pm 2.03
Ca	148.42 \pm 19.13
Mn	0.43 \pm 0.03
Fe	53.35 \pm 0.83

* SD, standard deviation; ^b TP, total phosphorus.

Table 5-2 Changes in the existing forms of phosphorus in the solid residues (Unit: mg/g)

Sludge residue	NAIP	AP	IP	OP	TP
SRC	0.28±0.01	23.24±0.26	24.13±0.28	2.10±0.02	26.18±0.35
SR200	0.15±0.02	32.25±0.11	32.33±0.22	0.003±0.00	32.37±0.34
SR280	0.06±0.02	38.16±0.18	38.33±0.54	0.001±0.00	38.43±0.26

TP, OP, IP, NAIP and AP represent total phosphorus, organic phosphorus, inorganic phosphorus, non-apatite inorganic phosphorus, and apatite phosphorus, respectively. SRC represents the solid residue in the control experiment (without HTT); SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C, respectively.

Table 5-3 Correlation coefficients (r) between fractions of Cd and phosphorus content in the sludge

Samples	Parameter correlated	Fractions of Cd					
		F1	F2	F1+F2	F3	F4	F5
SRC		-0.98	-0.25	-0.50	-0.88	0.94	-1.00
SR200	Phosphorus content	-0.87	-1.00	-0.99	-0.97	0.97	0.97
SR280		-0.89	0.66	-0.78	-0.84	0.90	-0.18

SRC represents the solid residue in the control experiment (without HTT); SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C, respectively.

Table 5-4 Fractionation of Cr, Ni, Cu, Zn and Pb in sludge before and after HTT

	F1+F2 (%)			F3+F4 (%)			F5 (%)		
	P-0%	P-10%	P-40%	P-0%	P-10%	P-40%	P-0%	P-10%	P-40%
Chromium (Cr)									
SRC	<u>1.79</u>	<u>3.66</u>	<u>6.06</u>	<u>89.44</u>	<u>88.68</u>	<u>84.31</u>	8.77	7.67	9.62
SR200	<u>2.00</u>	<u>1.12</u>	<u>1.24</u>	80.20	79.09	80.40	<u>17.8</u>	<u>19.8</u>	<u>18.36</u>
SR280	<u>1.47</u>	<u>0.97</u>	<u>1.00</u>	<u>71.19</u>	<u>71.06</u>	<u>75.72</u>	27.34	27.97	23.27
Nickel (Ni)									
SRC	<u>5.01</u>	<u>4.03</u>	<u>4.57</u>	<u>87.81</u>	<u>86.38</u>	<u>85.62</u>	<u>7.18</u>	<u>9.59</u>	<u>9.81</u>
SR200	<u>0.76</u>	<u>0.66</u>	<u>0.67</u>	<u>42.78</u>	<u>36.79</u>	<u>38.88</u>	<u>56.46</u>	<u>62.55</u>	<u>60.45</u>
SR280	0.19	0.21	0.16	28.10	29.74	26.25	71.70	70.05	73.6
Copper (Cu)									
SRC	<u>4.92</u>	<u>4.42</u>	<u>4.56</u>	90.20	90.52	89.61	<u>4.87</u>	<u>5.06</u>	<u>5.84</u>
SR200	<u>1.57</u>	<u>1.61</u>	<u>1.73</u>	90.23	90.41	89.90	8.20	7.98	8.37
SR280	<u>0.89</u>	<u>1.22</u>	<u>1.04</u>	<u>86.75</u>	<u>87.95</u>	<u>88.52</u>	<u>12.36</u>	<u>10.83</u>	<u>10.44</u>
Zinc (Zn)									
SRC	<u>3.04</u>	<u>2.76</u>	<u>1.66</u>	90.04	90.07	90.43	<u>6.92</u>	<u>7.16</u>	<u>7.90</u>
SR200	<u>0.74</u>	<u>0.96</u>	<u>1.48</u>	<u>77.49</u>	<u>73.42</u>	<u>73.07</u>	<u>21.76</u>	<u>25.63</u>	<u>25.45</u>
SR280	<u>0.33</u>	<u>0.36</u>	<u>2.70</u>	69.78	71.35	67.20	29.89	28.29	30.09
Lead (Pb)									
SRC	3.94	5.72	2.58	89.72	88.07	90.63	6.34	6.21	6.79
SR200	<u>1.79</u>	<u>2.31</u>	<u>3.76</u>	<u>70.91</u>	<u>63.21</u>	<u>64.12</u>	<u>27.30</u>	<u>34.49</u>	<u>32.12</u>
SR280	<u>3.25</u>	<u>3.01</u>	<u>4.33</u>	<u>50.03</u>	<u>46.62</u>	<u>37.00</u>	<u>46.73</u>	<u>50.37</u>	<u>58.66</u>

Note: the single line represents the decrease trend; the double line denotes the increase trend.

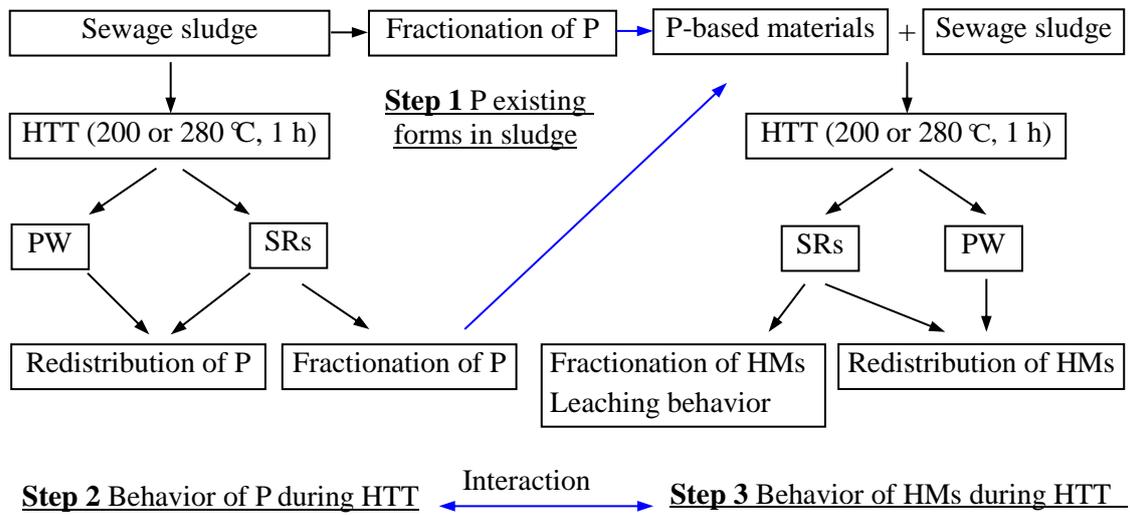


Figure 5-1 Experimental procedure in this study. HTT denotes hydrothermal treatment; PW represents the process water collected after HTT process; SRs denotes the solid residues obtained after HTT of sludge; P means phosphorus; HMs denotes heavy metals.

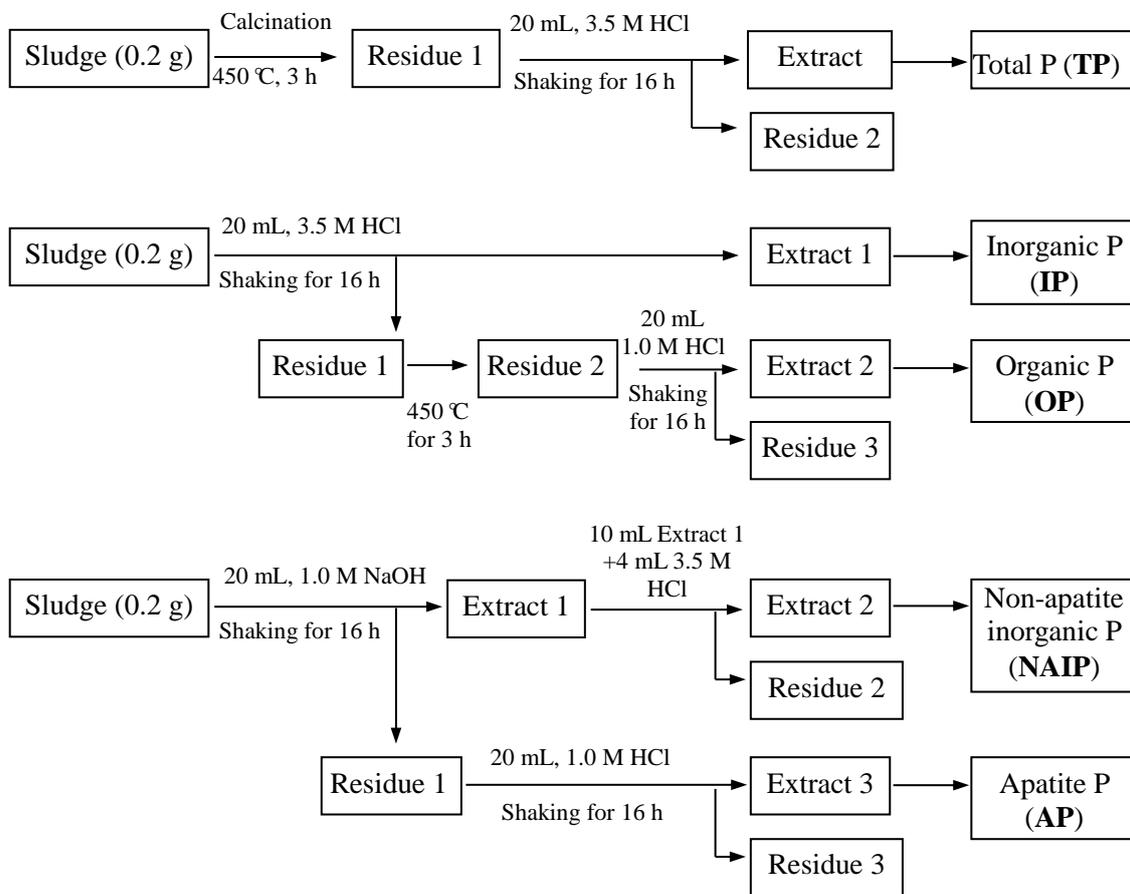


Figure 5-2 The Standards, Measurements and Testing (SMT) Programme extraction protocol for fractionation of phosphorus in sludge (Medeiros et al., 2005; Ruban et al., 2001)

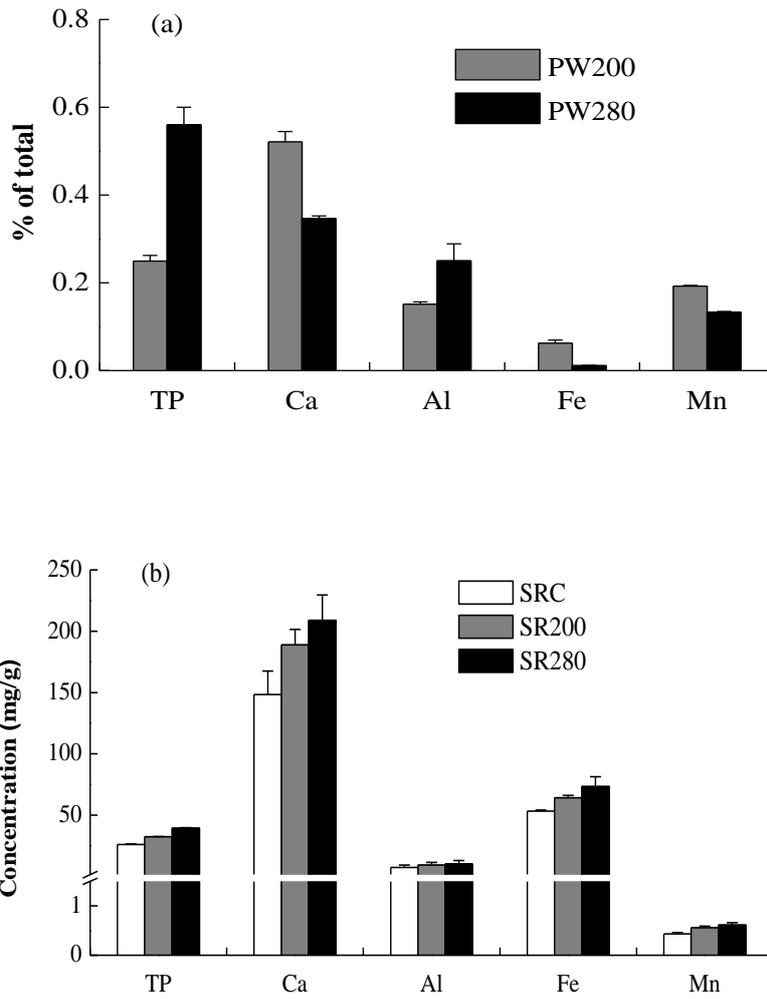


Figure 5-3 Redistribution of phosphorus and other main metals of sludge in process water (PW) (a) and solid residue (SR) (b) before and after HTT process. PW200 and PW280 denote the process water collected after hydrothermal treatment at 200 °C and 280 °C; SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C; SRC represents the solid residue in the control experiment (without HTT).

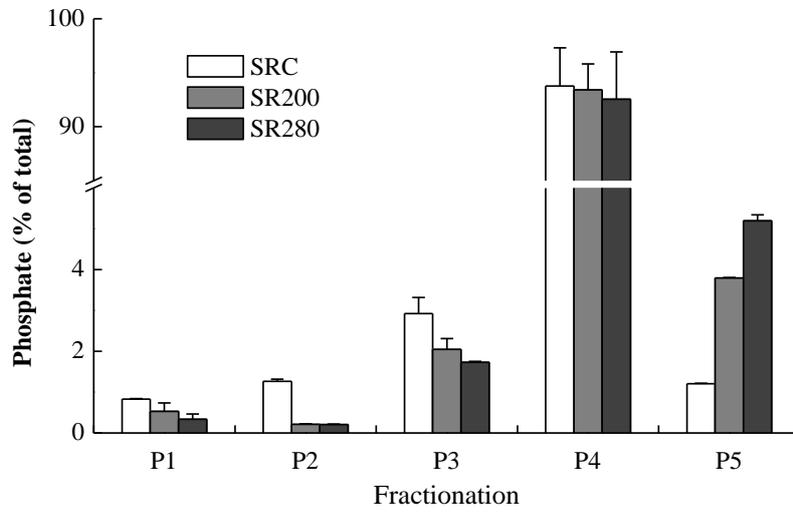


Figure 5-4 Fractionation of phosphate in sludge before and after HTT process. SRC represents the solid residue in the control experiment (without HTT); SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C; P1 to P5 denotes the corresponding phosphorus part along with HMs extraction into 5 fractions by using Tessier's method.

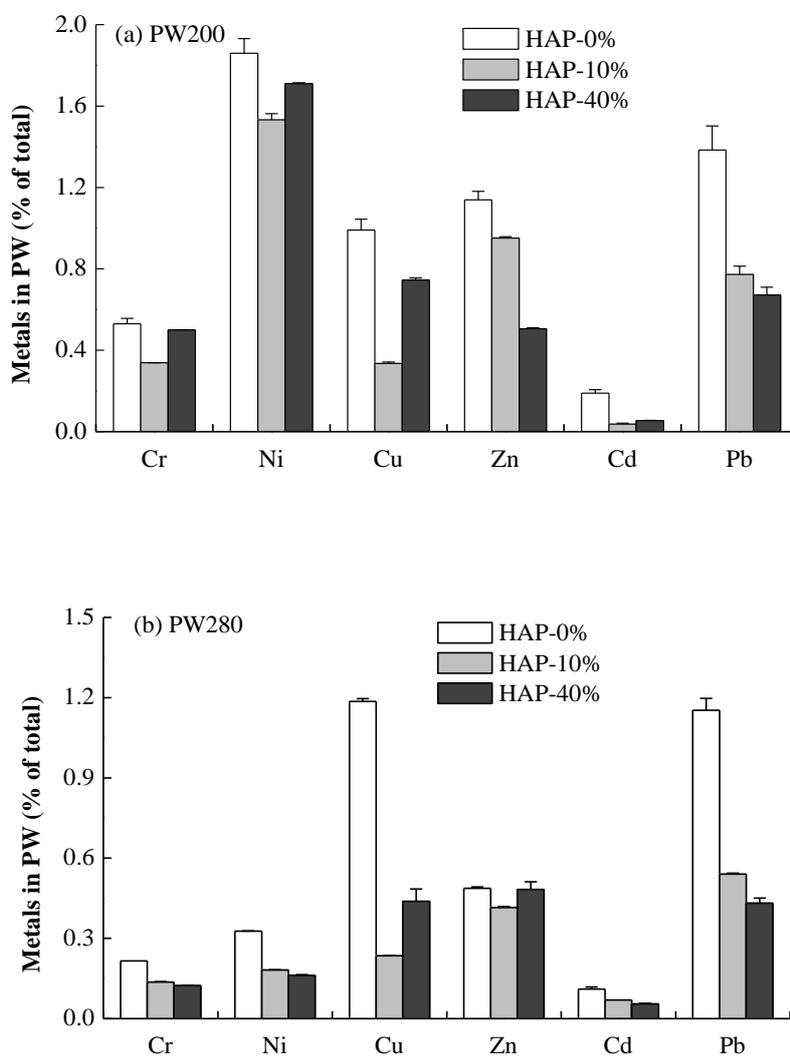


Figure 5-5 HMs in process water (PW), PW200 (a) and PW280 (b), after hydrothermal treatment. HAP-0%, HAP-10%, HAP-40% denote the hydroxyapatite addition dosage was 0%, 10% and 40% (P basis, $\text{HAP-P}/\text{TP}_{\text{sludge}}$, w/w), respectively.

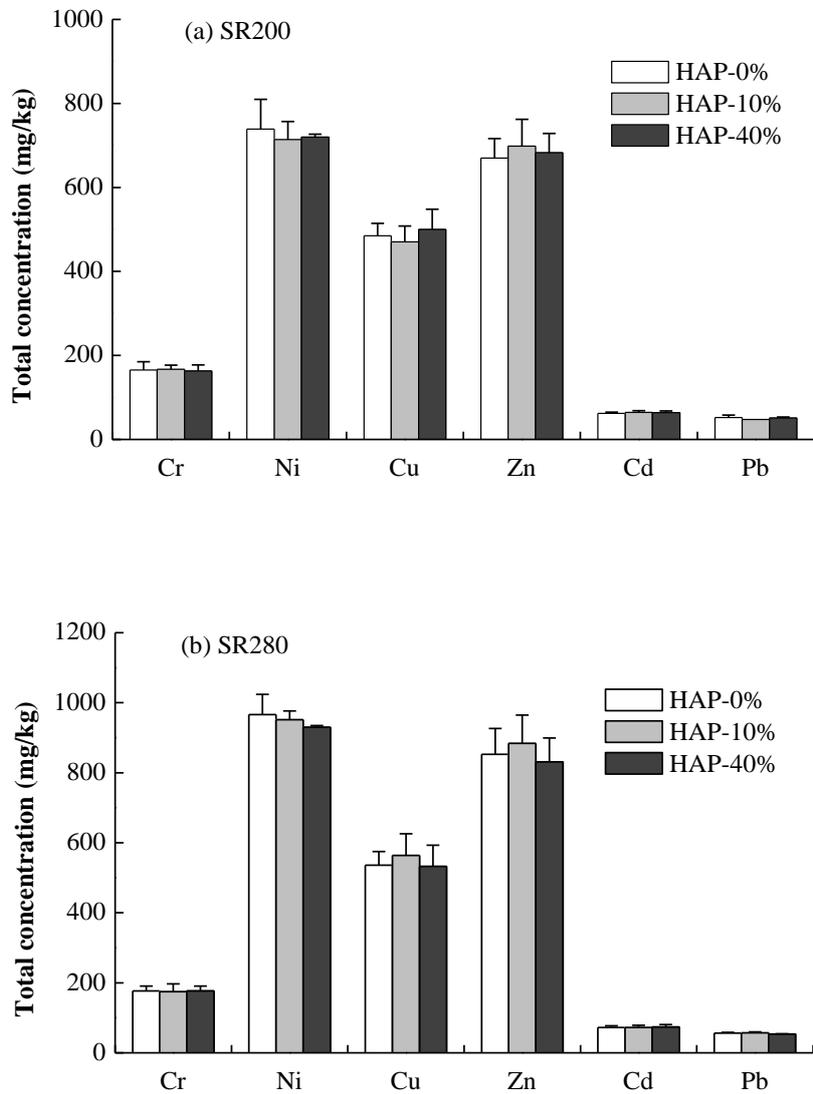


Figure 5-6 Total concentration of HMs in sludge after HTT process. SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C; HAP-0%, HAP-10%, HAP-40% denote the hydroxyapatite addition dosage was 0%, 10% and 40% (P basis, $\text{HAP-P}/\text{TP}_{\text{sludge}}$, w/w), respectively.

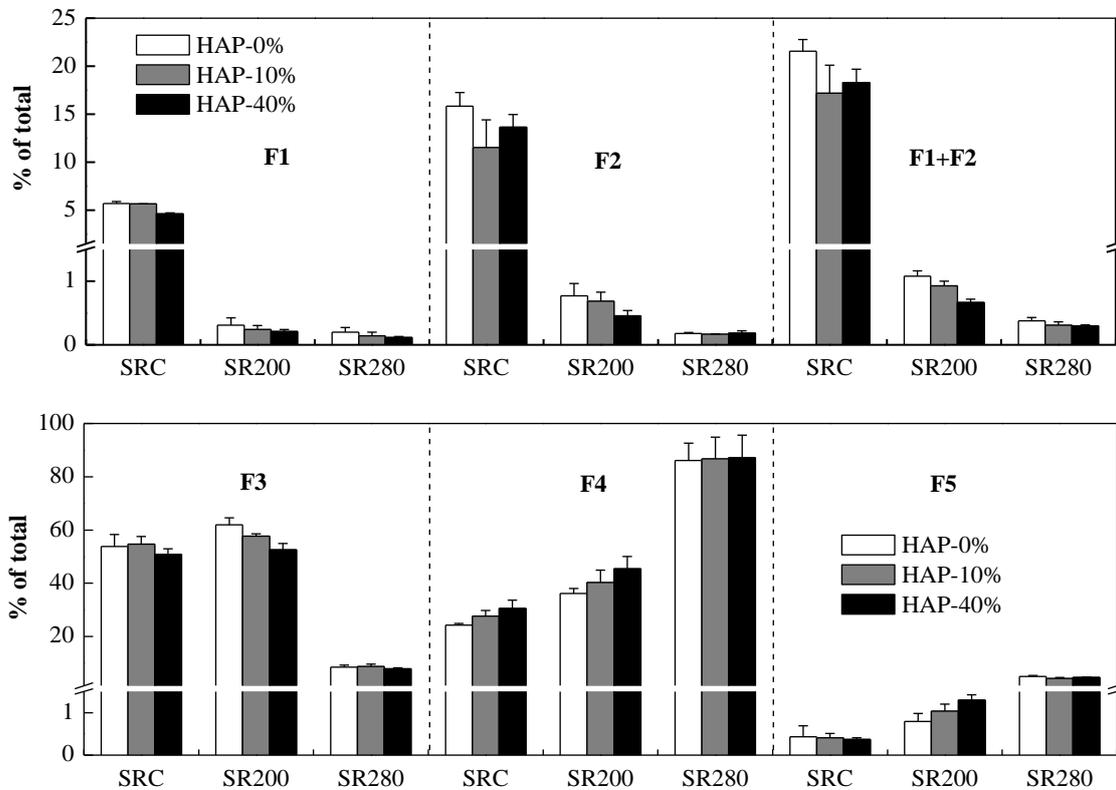


Figure 5-7 Changes of Cd fractionation in sludge with or without HAP addition. SRC represents the solid residue in the control experiment (without HTT); SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C; HAP-0%, HAP-10%, HAP-40% denote the hydroxyapatite addition dosage was 0%, 10% and 40% (P basis, $\text{HAP-P}/\text{TP}_{\text{sludge}}$, w/w), respectively.

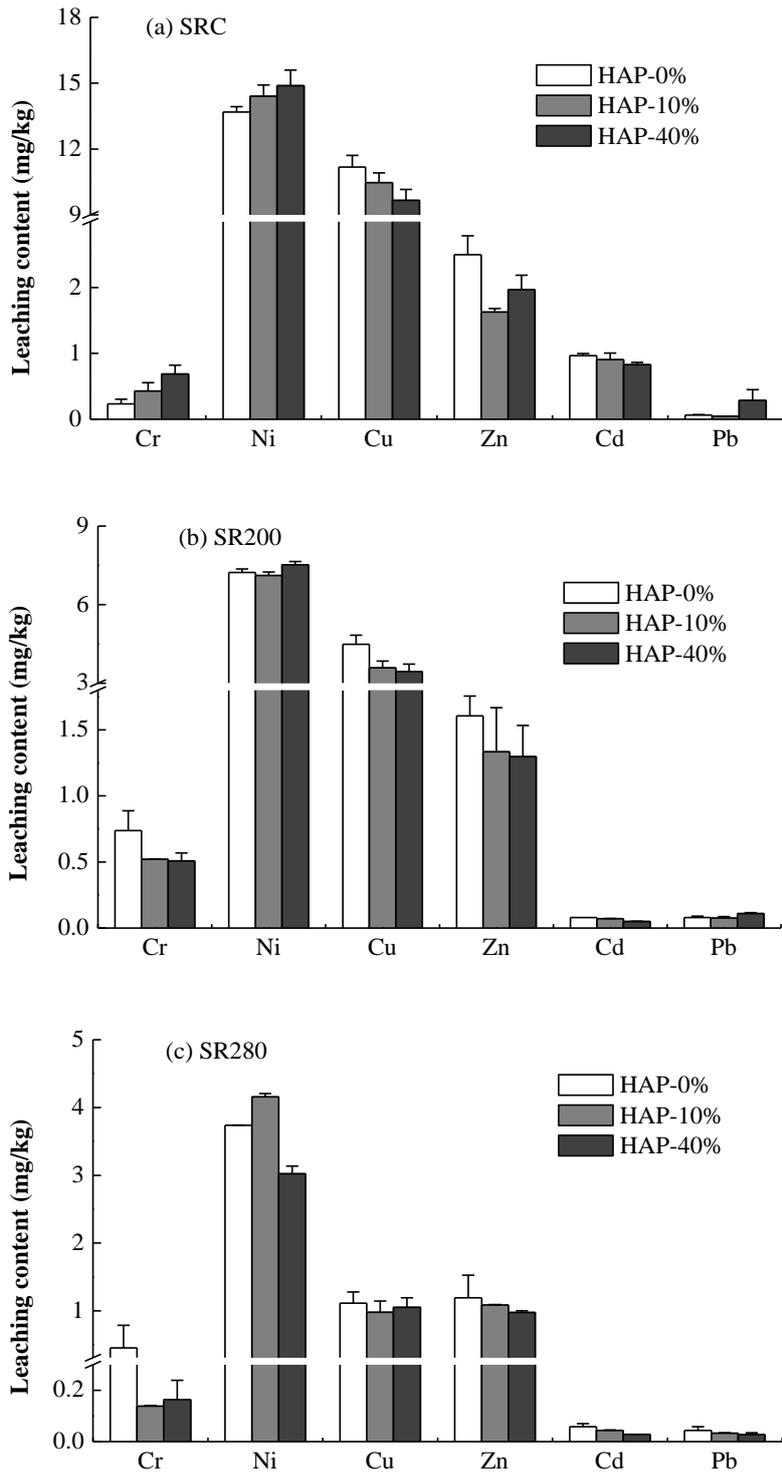


Figure 5-8 Leaching content of HMs in sludge before and after HTT process. SRC represents the solid residue in the control experiment (without HTT); SR200 and SR280 denote the solid residue of hydrothermally treated sludge at 200 °C and 280 °C; HAP-0%, HAP-10% and HAP-40% denote the hydroxyapatite addition dosage was 0%, 10% and 40% (P basis, HAP-P/TP_{sludge}, w/w), respectively.

Chapter 6 Conclusions and future research

6.1. Conclusions

In this thesis, HTT was adopted for sewage sludge stabilization before discharge into the environment. This method is widely regarded as environmentally friendly. After using this method for sewage sludge treatment, the risk of HMs was evaluated to make clear its contribution to secondary pollution based on total concentration, fractionation, and leaching test.

(1) The sewage sludge used in the study was not safe for land application because the risks of metals in sludge where Cd may exhibit medium risk to environment while the other 5 metals may pose low risk.

(2) By using HTT, the dewaterability of sewage sludge was greatly improved, and the volume of sludge was sharply decreased by 42%, 61% and 74% when the sludge was treated at 170 °C, 200 °C and 280 °C, respectively. The decomposition of organic matters resulted in the stabilization of sludge. Moreover, the sludge-derived hydrochar exhibited excellent adsorption capacity for HMs which can be used for soil remediation.

(3) After HTT, the metals in sludge transformed from weakly bound fractions into relatively more stable or stable state. The risk of all the metals decreased after HTT, especially when the sludge treated at 280 °C, the content of metals related to direct toxicity were decreased by 68.48%, 78.78%, 91.10%, 75.62%, 98.93% and 74.29% for Cr, Ni, Cu, Zn, Cd and Pb, respectively. Cr, Ni, Cu, Zn, Cd showed no toxicity while Pb showed low toxicity. The leachability of all the metals decreased in sludge after HTT process. After HTT at 280 °C, the leachable content was decreased

by 97.46%, 93.91%, 86.14%, 73.67%, 71.93% and 10.71% for Cu, Cd, Zn, Cr, Ni and Pb, respectively.

(4) Lignocellulosic materials showed significant effect on immobilization of HMs by RH addition. For instance, when treated at 200 °C, the RH addition enhanced the transformation of Cr, Cu and Cd from all fractions to stable state while increased the mobility of Ni and Pb. The leachability of all the metals except for Pb was decreased in sludge during HTT combined with RH addition. The positive effect of RH addition during HTT may be interpreted as that the released HMs could be further entrapped by the enlarged structure of RH or chelated with some functional groups and then fixed in the stable RH-sludge matrix formed during this treatment process.

(5) Phosphate was mainly existed in the form of apatite P (AP) in the tested sludge, and other forms of phosphorus were almost completely converted into AP after HTT. HAP addition significantly changed the fractionation of HMs, especially for Cr, Ni and Cd, after HTT process, HAP addition showed enhanced effect on the immobilization of all the tested metals except Cu, which also resulted in the reduction in leaching toxicity of Cr, Cu, Zn and Cd in the treated sludge.

From the above results, it's clear that HTT process can not only stabilize the organics in sludge but also immobilize HMs in sludge. Lignocellulosic materials and phosphorus in sludge were found to have enhancement effect on the immobilization of some HMs. This study can also provide some fundamental mechanisms for improving the immobilization of HMs in the hydrothermally treated sludge.

6.2. Future research and suggestions

In present study, HTT showed positive effect on immobilization of HMs. By investigating the influence factors, such as treatment temperature, the contained lignocellulosic materials and phosphate, the immobilization mechanism of HMs in

sludge during HTT process can be partly elucidated and discovered. However, because of the complexity of components of sludge, there is still a long way before clearly understanding the behavior of HMs in sludge during the HTT process. In the future, more research work should be done with respect to following points.

(1) To investigate the effect of treatment temperature and pressure in more detail by narrowing the temperature span to find the optimal treatment condition.

(2) Due to the complexity of sewage sludge composition, the behavior of HMs during sludge HTT process will be affected by other components of sludge, such as silicate, Ca, Al, Fe, and so on. Therefore, to investigate the effect of these components on the behavior of HMs will be of great importance.

(3) Different types of sewage sludge (such as activated sludge, anaerobically digested sludge, and so on) have different characteristics and compositions, and therefore the behavior of HMs in sludge during HTT process may be different. Based on this consideration, the behavior of HMs in different types of sewage sludge during HTT process will be valuable for practical application of HTT method in sewage sludge pretreatment.

(4) For assessing the risk of the sludge-derived hydrochar, phytoavailability is another important aspect, and it can be determined by plant pot experiments. The experiments can be done by mixing hydrochar with different types of soil with different ratios (hydrochar/soil), and then plant some designated plant. The effect of hydrochar application on the phytoavailability of HMs in both hydrochar and soil can be analyzed based on the plant growth and the accumulation and distribution of HMs in different parts of the plant. The result from this kind of experiment will be more direct and clear for evaluating the risk of HMs in sludge-derived hydrochar.

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Publications

(1) Journal papers

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- [2] Huang F., Shi W., Feng C.. Column Study for Aerobic Biodegradation of BTEX in Groundwater. The 4th China-Japan Graduate Student Forum. 24-27 September, 2011, Beijing, China. (page 429-432)