

# **Study on interaction between phosphorus and cadmium in sewage sludge during hydrothermal treatment by adding hydroxyapatite**

Wansheng Shi <sup>a,b</sup>, Chuanping Feng <sup>a</sup>, Wenli Huang <sup>b</sup>, Zhongfang Lei <sup>b\*</sup>, Zhenya Zhang <sup>b</sup>

<sup>a</sup> School of Water Resources and Environment, China University of Geosciences, Beijing 100083, China

<sup>b</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba 305-8572, Japan

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\*Corresponding author. Tel/fax: +81 29 853 6703. E-mail: lei.zhongfang.gu@u.tsukuba.ac.jp (Z. Lei); zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

## **Abstract**

This study focused on the behavior of phosphorus (P) and its effect on cadmium (Cd) immobilization in sludge during HTT. The results showed after HTT other forms of P in sludge were almost completely converted into apatite P (AP) and the eco-toxicity and leachability of Cd was sharply decreased, signaling the immobilization effect of HTT on Cd in the sludge. Hydroxyapatite (HAP) addition showed a synergetic effect with HTT 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. P content was found to have a strong relationship with the existing forms of Cd during HTT. The present results suggest that HTT with HAP addition could be a promising method for the safe disposal of Cd-contaminated sludge.

*Keywords:* Sewage sludge; Hydrothermal treatment (HTT); Hydroxyapatite (HAP); Cadmium (Cd); Immobilization

## 1. Introduction

A huge amount of sewage sludge is annually produced worldwide, which urgently demands a safe, efficient, and sustainable treatment and disposal method. The best disposal method should not only take full use of the nutrient sources in the sludge but also minimize its potential environmental risk brought by the pollutants contained. Landfill, incineration and land use are known to be the main methods used to cope with sewage sludge at present (Lederer and Rechberger, 2010). Landfill is very simple to treat sewage sludge but it is a kind of waste of nutrient sources and land, which also brings about some secondary pollution. Incineration is not a cost-effective way and causes some air pollution, especially the produced fly ash which is very difficult to deal with because of containing hazardous and high concentration of heavy metals (HMs) (Dewil et al., 2007). Therefore, from a long run, land use may be the best alternative for sewage sludge disposal (Deng et al., 2009; Babel and del Mundo Dacera, 2006).

In order to minimize the environmental risk of pathogens and some other pollutants (especially HMs) in the sewage sludge before land use, appropriate pre-treatment is crucial (Tao et al., 2012; Zhu et al., 2013). Carbonization is now widely recognized as an environmentally friendly way because the produced biochar could provide some easily available nutrient sources, such as N, P and K, which can be used to improve the productivity of soil (Khan et al., 2013a). Moreover, biochar can also provide a kind of additive for the remediation of contaminated soil with its strong binding capacity for some HMs (Méndez et al., 2012) and trace organic pollutants (such as PAH, herbicide, pesticide, etc.) (Khan et al., 2013b).

To date research works are mainly focused on the carbonization of sewage sludge through dry pyrolysis under high temperature conditions (usually  $> 300^{\circ}\text{C}$ ) 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 a 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 of the sludge was greatly improved after HTT process (Shi et al., 2013).

In order to identify the safety of the produced hydrochar before soil application, the risk of HMs should be evaluated and minimized. Previous research indicates that the risk of HMs in the sludge may be changed when the evaluation is made by total concentration and existing forms after HTT process (Hossain et al., 2011). In addition, some metals are found to be mainly accumulated in the produced hydrochar but their existing forms have been transformed from weakly bound forms to more stable state after this process (Shi et al., 2013). Up to now, the fractional transformation is regarded to be the major reason resulting in the immobilization and toxicity reduction of HMs in the sludge. The related mechanism, however, remains unclear.

Furthermore, during HTT the existing forms of other elements in the sludge would also be changed, especially phosphorus (Zhu et al., 2011). Importantly, the existing forms of phosphorus are closely related not only to their bioavailability in soil but also to the environmental risk of some metals bound with phosphorus in the sludge (Chen et al., 2007). Based on its binding capacity with HMs, 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). In addition, some other phosphorus forms (mainly phosphate and phosphate-based minerals) are also found to have immobilization effect on HMs and can be used for the reclamation of contaminated soils by HMs (McGowen et al., 2001; Wu et al., 2013; Chen et al., 2006). Therefore, it is speculated that the behavior of phosphorus may

affect the fractional transformation of HMs during HTT. In order to confirm this speculation, in this study Cd was selected, due to its high toxicity and existed widely in sludge, to investigate the behavior of phosphorus and its interaction with Cd immobilization during HTT process. The effect of phosphorus on the environmental risk and toxicity of Cd in sludge during HTT was also disclosed.

## **2. Materials and methods**

### *2.1. Sewage sludge*

The sewage sludge used in this experiment was dewatered anaerobically digested sewage sludge cake obtained from a wastewater treatment plant in Ibaraki prefecture, Japan. The moisture content of the sludge was adjusted by adding deionized water, and then agitated so as to be homogeneously mixed. An appropriate volume of Cd (II) (standard Cd solution, 1000mg/l, pH 6.61) was added into the sludge mixture to elevate the content of Cd because of its low Cd content in the original sludge. Then the mixture was once more agitated to be homogeneously mixed. After that, the mixture was kept in 4 °C, and intermittently agitated once every day in order to make the added Cd be homogeneously distributed in the sludge. Table 1 lists the main characteristics of the sludge used in this study.

### *2.2. Hydrothermal treatment*

HTT experiments were carried out in a stainless steel reactor with a volume of 200 ml. The prepared sludge sample (about 100 g to keep the same volume) was filled into this reactor and heated to 200 °C (HTT200) or 280 °C (HTT280), and then treated at the designated temperature for 1h. After cooling to room temperature, the solid residues (SRs) and process water (PW) were

separated by vacuum filtration. The obtained SRs were dried at 60°C for 2 days, then ground into fine powders and mixed homogeneously, and stored in enclosed plastic bags, which were named SR200 and SR280. The obtained process water were respectively labeled as PW200 and PW280, and then kept in refrigerator at 4°C.

In the control experiment (without HTT process), the prepared sewage sludge was directly dried at 60°C for 2 days. The solid residue collected was labeled as SRC, and no process water was obtained.

### *2.3. Fractionation of phosphorus*

Phosphorus in sludge can be fractionated into different categories by different sequential extraction protocol (Ruban et al., 2001; Ruban et al., 1999). The most widely used method is the Standards, Measurements and Testing (SMT) Programme extraction protocol (Medeiros et al., 2005; Ruban et al., 2001). After sequential extraction based on the SMT method, 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, the P fraction associated with oxides and hydroxides of Al, Fe and Mn), and (5) apatite P (AP, the P fraction associated with Ca). The phosphorus concentration in the supernatant collected after extraction was determined with spectrophotometric method.

### *2.4. Risk assessment of Cd in sludge*

#### *2.4.1. Total concentration*

In order to minimize the environmental risk and toxicity, HMs in sludge should meet stringent standards which are mainly based on their total concentrations. Therefore, total concentration was used in this study as one of the major indices for the assessment of HMs risk in the sludge.

#### *2.4.2. Fractionation of Cd and risk assessment code (RAC)*

On the other hand, it's widely recognized that the risk or eco-toxicity of HMs in sludge is determined not only by the total concentration but also by their existing forms (Xian, 1989), most probably attributable to the fact that HMs in different existing forms possess different binding strength and stability in sludge residue, resulting in the difference in their possible mobility, toxicity and bioavailability (Vela et al., 1993).

Cd in sludge can be fractionated into 5 fractions by using the sequential extraction procedure proposed by Tessier et al. (1979) with 1.0 g sample. The five fractions are exchangeable Cd (F1), carbonate bound Cd (F2), iron and manganese oxides bound Cd (F3), Cd bound to organic and sulfide (F4) and Cd in the residue state (F5). After extraction, the collected samples for Cd in F1-F4 were acidified, filtered and then digested before determination. The samples for the determination of Cd in F5 and total Cd concentration were extracted by acid digestion with a mixture of HCl-HNO<sub>3</sub>-HF (3:1:1, v/v) in PTFE beakers on a heating plate.

Cd in different factions possesses different mobility, eco-toxicity and bioavailability. Based on the binding strength and availability, the fractions of Cd in sludge can be grouped into 3 categories as (F1+F2), (F3+F4) and F5, respectively, reflecting the weakly bound or easily releasable Cd, relatively stable Cd and the Cd remained in the sludge matrix or resultant hydrochar. These 3 parts of Cd are reported to exhibit different eco-toxicity and bioavailability in

the environment as direct toxicity (F1+F2), potential toxicity (F3+F4) and no toxicity (F5), respectively (Li et al., 2012).

Furthermore, the risk of Cd in sludge can also be evaluated by the weakly bound fractions (F1+F2), because Cd in these fractions are easily affected by ionic strength and vulnerable to pH changes in soil environment resulting in a very high mobility (Lasheen and Ammar, 2009). Based on this consideration, the specific quantity evaluation of Cd in sludge can be realized by using a risk assessment code (RAC) according to the proportion of these two fractions (F1+F2) to the total amount of Cd extracted from the sludge, namely the risk index (RI) (Singh et al., 2005). Then Cd 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.

#### *2.4.3. Toxicity characteristic leaching procedure (TCLP)*

Leachability is another important parameter for assessing the mobility and bioavailability of Cd in sludge. In this study, the U.S. EPA TCLP leaching procedure (USEPA, 1997) was applied. The leaching tests of Cd were carried out by extraction with acetic acid solution at pH 2.88, liquid/solid ratio of 20:1, and extraction for 18 h. After extraction, the supernatant collected by centrifugation was filtered, acidified and digested for Cd determination.

#### *2.5. Effect of phosphorus on behavior of Cd during HTT*

In order to investigate the effect of phosphorus in sludge on the behavior of Cd during HTT, hydroxyapatite (HAP) was added into the HTT system based on our preliminary results that phosphorus was mainly existed in the tested sludge in the form of AP (Table 2). The differences of Cd in redistribution, fractionation and leachability before and after HAP addition were examined and used to indicate the effect of phosphorus on Cd behavior during HTT. HAP was



added into the HTT reactor with the dosage of 0%, 10% and 40% (P basis) according to the total phosphorus content in the sludge (i.e.  $\text{HAP-P}/\text{TP}_{\text{sludge}} = 0\%, 10\% \text{ and } 40\%, \text{ w/w, respectively}$ ).

After HTT at 200°C or 280°C, Cd in the obtained process water and solid residue were analyzed.

## 2.6. Analysis

The concentration of each metal was determined by using ICP-MS (ELAN DRC-e, PerkinElmer). Phosphorus was determined by ammonium molybdate spectrophotometric method. Each test was conducted in triplicate and the results were expressed as mean values  $\pm$  SD.

## 3. Results and discussions

### 3.1. Redistribution of phosphorus and major metals in sludge after HTT process

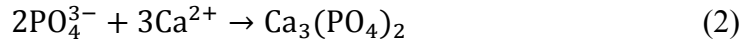
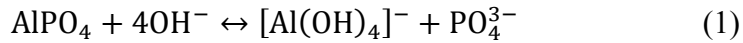
HTT usually has both extraction and stabilization effects for some inorganics and therefore leads to redistribution of these elements (Escala et al., 2012; Jin et al., 2012).

Fig. 1 shows the redistribution of phosphorus and the major metals closely related to the existing forms of phosphorus in PW and SR 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, and the extent of this kind of accumulation increased with the increase of treatment temperature. Ca was existed 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.

Table 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 ascribing to a higher content of Ca and relatively lower contents of Fe, Al and Mn (Fig. 1).

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 be converted into inorganic P. 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 NAIP to AP. This 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 favored the dissolution of NAIP (Eq. 1) and the released  $\text{PO}_4^{3-}$  could combine with Ca to form the relatively stable Ca bound P (Eq. 2) (Petzet et al., 2012).



### 3.2. Effect of phosphorus on redistribution of Cd

After HTT process, the treated sludge was separated into PW and SR, in which the content of Cd was analyzed with the results shown in Fig. 2. A very small part of Cd was observed to release into PW after HTT process (< 0.2%) with the majority left in the SRs, meaning that HTT brought about the redistribution of Cd in these two phases. The accumulated amount of Cd indicated that the potential environmental risk of Cd in sludge was increased after HTT when assessing the risk of Cd by the total concentration in SRs.

Fig. 2 also shows the effect of HAP addition on the redistribution of Cd in PW and SRs. From Fig. 2b it can be seen that when HAP was added into the tested sludge, the concentration of Cd decreased slightly in the sludge before HTT process, most probably due to a dilution effect because of HAP addition. During HTT process, HAP addition caused an obvious reduction in the content of Cd released into PW (Fig. 2(a)) while a slight increase in the content of Cd in SRs (Fig. 2(b)), probably contributed by the strong binding capacity of HAP with Cd.

The above results indicated that the potential risk of Cd was increased to some extent after HTT process with or without HAP addition when evaluated by total Cd concentration in the treated sludge (sludge residue).

### *3.3. Effect of phosphorus on fractionation of Cd*

After HTT process, the fractionation of Cd in sludge was determined by sequential extraction, and the result is shown in Fig. 3. The content of Cd in different fractions can be used to reflect its eco-toxicity due to these existing forms are closely related to its mobility and bioavailability in sludge during soil application. The result indicated that more than half of Cd was bound to iron and manganese oxides (F3, 53.76%), followed by organic and sulfide bound fraction (F4, 24.24%), indicating that Cd was mainly existed in the potential toxicity forms (F3+F4) with very small part in exchangeable (F1) and residue state (F5).

Hydrothermal treatment can induce the decomposition of organics in sludge and redistribution of Cd, and then alter the fractionation of Cd in the treated sludge. This fractional transformation of Cd can be discerned from Fig. 3. After HTT, Cd in the first 2 fractions was sharply decreased while Cd in the last 2 fractions (F4 and F5) was increased with the increase of treatment temperature. Cd in F3 was first slightly increased (200°C) and then largely decreased (280 °C),

likely attributable to the thermostability of Cd binding with Fe and Mn oxides. The fractional transformation of Cd from weakly bound forms (F1 and F2) to a relatively stable form (F4) and stable state (F5) implies the immobilization and risk reduction effect of HTT on Cd in the sludge.

Furthermore, HAP addition can enhance this immobilization effect of 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 (Fig. 3). 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 have 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 in Fig. 3 show 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) to low risk (in SR200) and no risk (in SR280). When HAP was added, Cd in fraction (F1+F2) decreased with the increase in HAP dosage both in the drying and HTT processes, showing HAP addition had a synergetic effect with HTT process on reduction in the direct toxicity of Cd. Fig. 3 also shows that this synergetic effect was more significantly when HTT was conducted under 200°C.

Table 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 a strongly negative relationship with P content in the sludge, while a strongly positive relationship existed between

F4 and P content in the sludge. Specifically, under HTT of 200°C condition all Cd fractions were found to have strong relationship with P concentration, 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 investigation.

The result clearly indicates that phosphorus plays a very important role on the fractional transformation of Cd in sludge during HTT process. The strong relationship between Cd fractions (especially F1, F3, and F4) and phosphorus content in sludge implies that the effect of HTT on Cd immobilization is partly contributed by the strong binding capacity of phosphorus in the sludge matrix.

#### *3.4. Effect of phosphorus on leachability of Cd*

The risk of Cd in sludge can also be reflected directly by its leachability which is closely related to its mobility. The leaching toxicity of Cd in sludge was determined with the standard TCLP test. The leaching concentration of Cd from the sludge residue is shown in Fig. 4.

Lower than 1.0 mg kg<sup>-1</sup> of Cd was detected to be released into the solution, and the leached content of Cd was sharply decreased from 2.0% (in SRC) to 0.13% (in SR200) and 0.08% (in SR280) after HTT process, respectively. Therefore, Cd in sludge was definitely immobilized after HTT process from the leachability test results, and the toxicity of Cd was decreased with the increase of treatment temperature, showing the positive effect of HTT on reducing the leaching toxicity and leachability of Cd in sludge.

Besides, HAP addition further reduced the leaching content of Cd from the SRs collected from both drying and HTT processes. More reduction in leaching toxicity was observed after HAP addition, also signaling the synergetic effect of phosphorus and HTT on reducing the toxicity of Cd in sludge.

### *3.5. Implication of this study to practice*

In this study, the behavior of Cd during HTT under 200°C and 280°C was investigated along with its interaction with phosphorus in sludge by HAP addition. The experimental results showed that although the total Cd concentration increased to some extent in the solid residues after HTT process, the risk of Cd was found to decrease largely when evaluated by its existing forms and leachability, indicating the feasibility of using HTT for the disposal of sewage sludge in practice. Furthermore, HAP addition can add this Cd immobilization effect by further reducing the risk and toxicity of Cd in sludge. Restated, the observed synergetic effect implies that the phosphorus existed in the sludge to a certain degree should have some contribution to Cd immobilization in the sludge during HTT. Furthermore, HAP addition may provide a new applicable method for enhancing the HMs immobilization in sludge by HTT process, providing a safe and sustainable treatment method for HMs-contaminated sludge before land use.

## **4. Conclusion**

This study presented a promising method for the enhancement of Cd immobilization in sludge through HTT process. During HTT, phosphorus was clearly found to be converted into apatite P from other fractions, and Cd was immobilized in the treated sludge with its toxicity and risk being greatly reduced. The present results also indicate that HAP addition has a synergetic

immobilization effect on the redistribution, fractionation and leachability of Cd, implying that the immobilization of Cd during HTT process can be partly ascribed to the phosphorus in the sludge due to its strong binding affinity with Cd.

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Table 1 Physicochemical characteristics of the sludge used in the experiment

Parameters	Value(Mean $\pm$ SD <sup>a</sup> )
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
TN <sup>b</sup> (g kg <sup>-1</sup> dry weight)	21.06 $\pm$ 0.03
TP <sup>c</sup> (g kg <sup>-1</sup> dry weight)	26.18 $\pm$ 0.35
Cd (mg kg <sup>-1</sup> dry weight)	48.31 $\pm$ 3.25
Major metals in the sludge (g kg <sup>-1</sup> 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

<sup>a</sup> SD, standard deviation; <sup>b</sup> TN, total nitrogen; <sup>c</sup> TP, total phosphorus.

Table 2 Changes in the existing forms of phosphorus in the solid residues (unit: mg g<sup>-1</sup>)

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

<sup>a</sup> SRC, solid residue as control (sludge before HTT), <sup>b</sup> SR200 and SR280 represent solid residues obtained after HTT at 200°C and 280°C, respectively.

Table 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 <sup>a</sup>		-0.981	-0.251	-0.498	-0.883	0.945	-0.998
SR200 <sup>b</sup>	Phosphorus content	-0.871	-1.000	-0.990	-0.973	0.974	0.966
SR280 <sup>b</sup>		-0.886	0.660	-0.783	-0.835	0.903	-0.175

<sup>a</sup> SRC, solid residue control (before HTT), <sup>b</sup> SR200 and SR280 represent solid residues obtained after HTT at 200°C and 280°C, respectively.

## Figure captions

Fig.1. Distribution of total phosphorus and major metals of sludge in process water (PW) (a) and solid residue (SR) (b) before and after HTT process. 200 and 280 indicate the treatment temperature is 200°C and 280°C, respectively; SRC, the solid residue control (i.e., the sludge sample before HTT).

Fig. 2. Redistribution of Cd in process water (PW) (a) and solid residue (SR) (b) after HTT process with or without HAP addition. 200 and 280 indicate the treatment temperature is 200°C and 280°C, respectively; SRC, the solid residue control (the sludge sample before HTT); HAP-0%, -10% and -40% denote the hydroxyapatite addition dosage is 0%, 10% and 40% (P basis,  $\text{HAP-P}/\text{TP}_{\text{sludge}}$ , w/w), respectively.

Fig. 3. Changes of Cd fractionation in sludge after HTT with or without HAP addition. 200 and 280 indicate the treatment temperature is 200°C and 280°C, respectively; SRC, solid residue control (sludge before HTT); HAP-0%, -10% and -40% denote the hydroxyapatite addition dosage is 0%, 10% and 40% (P basis,  $\text{HAP-P}/\text{TP}_{\text{sludge}}$ , w/w), respectively.

Fig. 4. Leaching concentration of Cd from sludge residues. 200 and 280 indicate the treatment temperature is 200°C and 280°C, respectively; SRC, the solid residue control (the sludge sample before HTT); HAP-0%, -10% and -40% denote the hydroxyapatite addition dosage is 0%, 10% and 40% (P basis,  $\text{HAP-P}/\text{TP}_{\text{sludge}}$ , w/w), respectively.

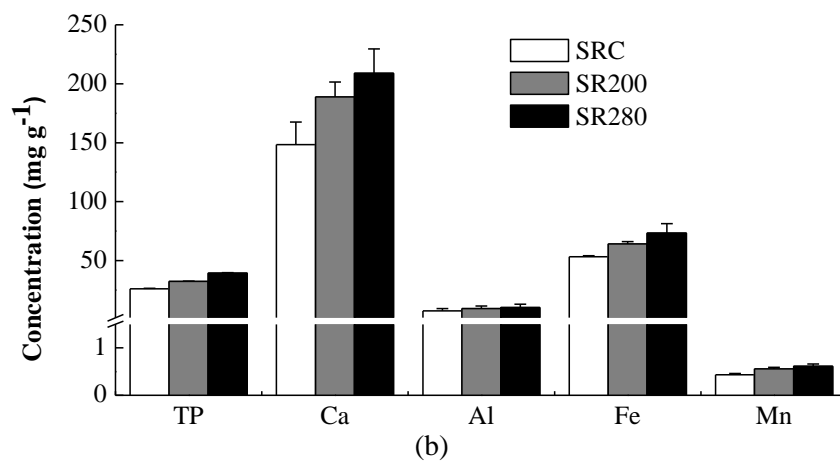
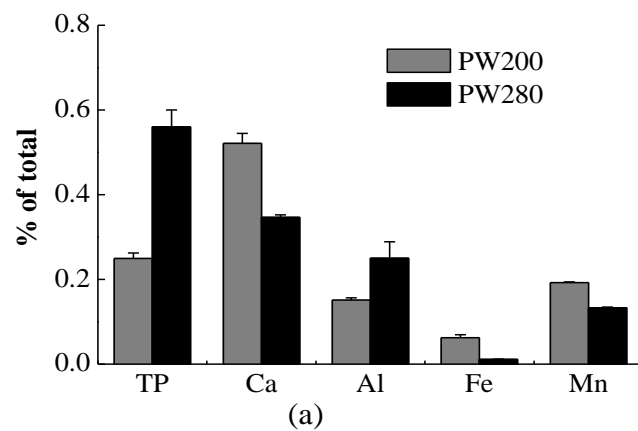


Fig.1. Shi et al.



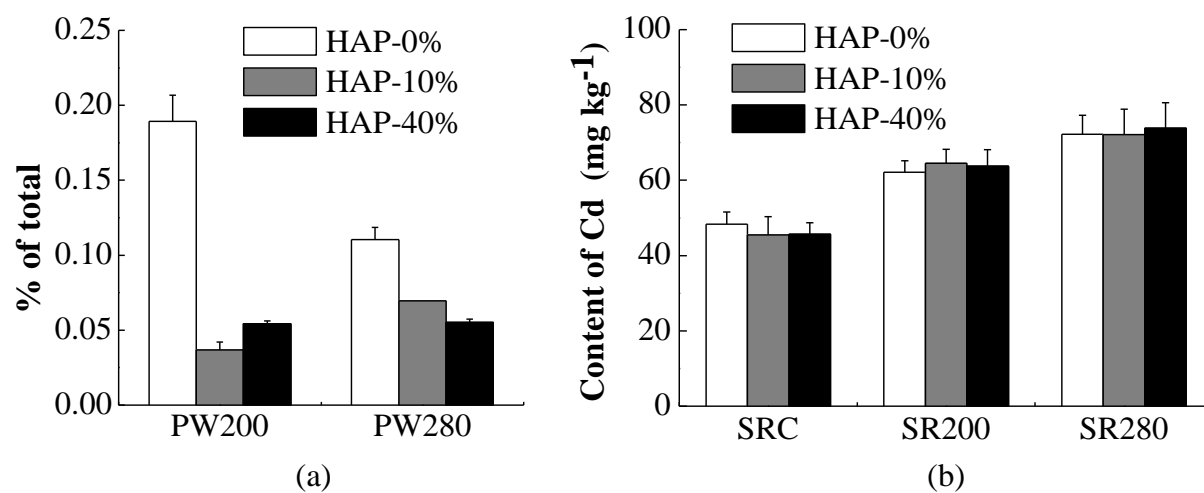


Fig. 2. Shi et al.

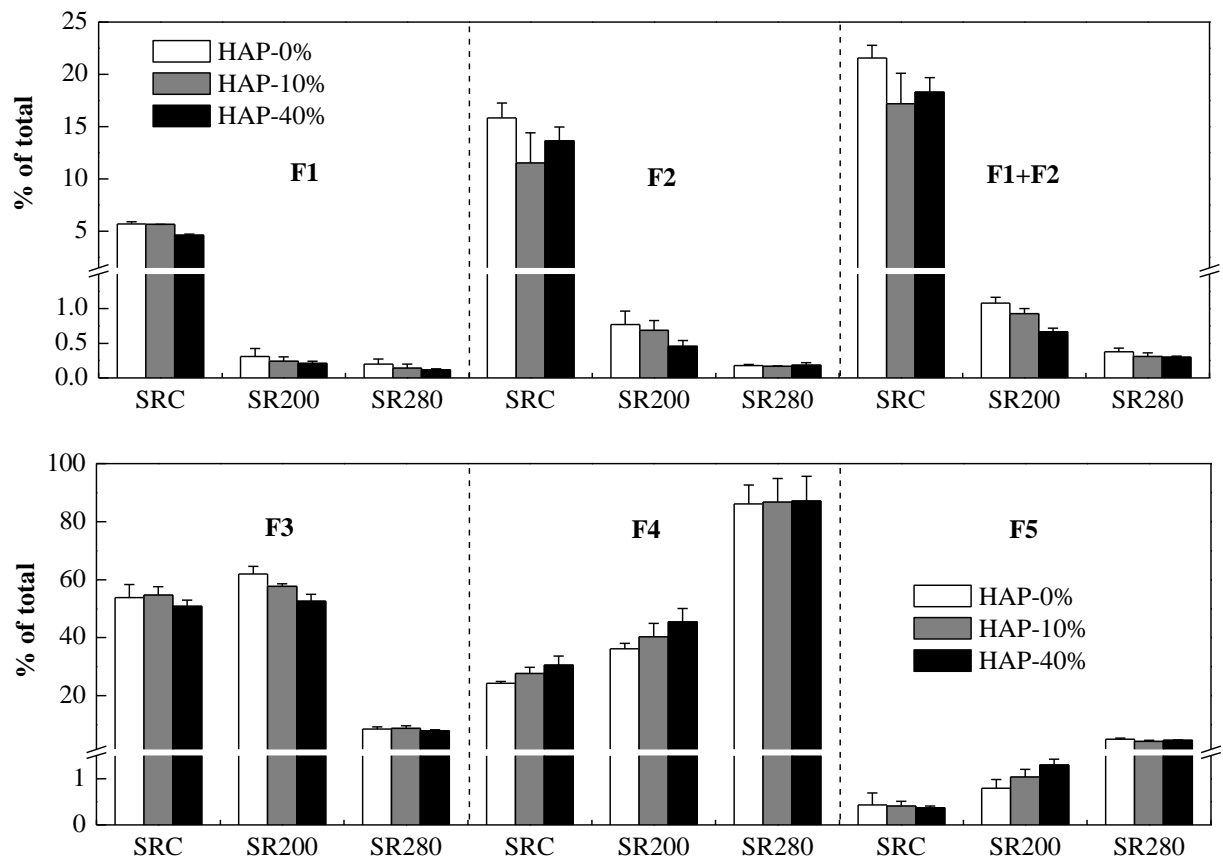


Fig. 3. Shi et al.

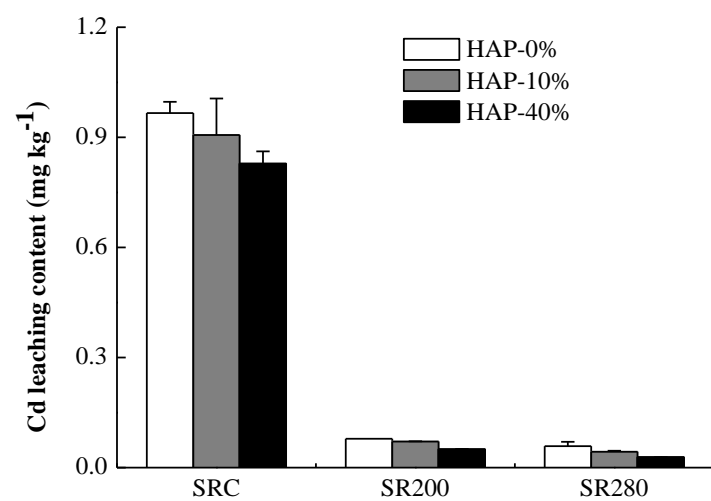


Fig. 4. Shi et al.