

**Synergistic effect of rice husk addition on hydrothermal treatment
of sewage sludge: Fate and environmental risk of heavy metals**

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11 **Abstract**

12 Hydrothermal treatment (HTT) at 200°C was applied to immobilize heavy metals (HMs) and
13 the effect of rice husk (RH) addition was investigated based on total HMs concentration,
14 fractionation and leaching tests. The results indicated that a synergistic effect of RH addition and
15 HTT could be achieved on reducing the risk of HMs from medium and low risk to no risk.
16 Metals were redistributed and transformed from weakly bounded state to stable state during the
17 HTT process under RH addition. Notably at a RH/sludge ratio of 1/1.75 (d.w.), all the HMs
18 showed no eco-toxicity and no leaching toxicity, with the concentrations of leachable Cr, Ni, Cu
19 and Cd decreased by 17%, 89%, 95% and 93%, respectively. This synergistic effect of RH
20 addition and HTT on the risk reduction of HMs implies that HTT process with RH addition
21 could be a promising and safe disposal technology for sewage sludge treatment in practice.

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23 Keywords: Sewage sludge; heavy metals (HMs); hydrothermal treatment (HTT); rice husk (RH);
24 environmental risk

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1. Introduction

Hydrothermal treatment (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). Being rich in organic carbon and easily available N, P and K, the solid residues (or hydrochar) produced from the HTT process can be used as soil amendments to improve the sorption capacity of soils towards many trace contaminants (PAHs, pesticides, herbicides, and etc.) as well as carbon sequestration (Gajic *et al.*, 2012; Rillig *et al.*, 2010). Moreover, hydrochar has also been utilized as a coal-like fuel because its calorific value can be elevated by the dehydration and decarboxylation occurring in the HTT process (Berge *et al.*, 2011).

Probably due to its merits in solid waste disposal, researchers began to apply HTT in sewage sludge stabilization and disposal processes with enhanced dehydration capacity and lower moisture content in the processed sludge, which facilitates the volumetric reduction and final disposal of sewage sludge (Escala *et al.*, 2013; He *et al.*, 2013; Meng *et al.*, 2012). Just like other solid wastes treated by this technology, however, the environmental risk of the HTT processed sludge should be evaluated and verified before its final disposal when some trace pollutants, especially heavy metals (HMs) are taken into consideration (Escala *et al.*, 2013).

Previous studies indicate that HMs in sewage sludge can be redistributed in the liquid (process water) and solid (produced hydrochar) phases after the HTT process (Escala *et al.*, 2013; Shi *et al.*, 2013), and this kind of redistribution of HMs is dependent on experimental conditions. Moreover, the fractionation of HMs in the sludge residue (hydrochar) can be greatly altered from weakly bounded forms to a relatively more stable state, resulting in the immobilization of HMs

in the sludge after the HTT process (Li *et al.*, 2012; Shi *et al.*, 2013). It was reported that a single HTT process had an immobilization effect on HMs in the sewage sludge, while the total HMs concentration tended to increase to some extent due to large decrease in sludge volume after the HTT process (Shi *et al.*, 2013). Furthermore, based on the fact that various HMs at different levels co-exist in the sewage sludge (Vogel and Adam, 2011; Zhang *et al.*, 2013), more robust and stable efficiency for HMs immobilization in sludge is a prerequisite for HTT to be applied in practice. To realize this target, some additives can be utilized for the enhancement of HMs immobilization effect during the HTT process.

In this study, rice husk (RH) was selected to act as an additive, due to not only its capability for metallic cations fixation related with specific biomatrix and functional groups (Krishnani *et al.*, 2008; Daifullah *et al.*, 2003), but also the likely formation of hydrochar during HTT (Reza *et al.*, 2013). Besides, RH is an agricultural by-product existed in large quantity, and its disposal also poses a big problem for the environment. During the HTT process, other components contained in the reaction mixture such as phosphate, silicate, carbonate, etc might play roles in the immobilization of HMs. Therefore, it is speculated that the addition of RH into sewage sludge during the HTT process could result in a synergetic enhancement effect on HMs immobilization in sludge and thus a reduced risk to the environment when the processed hydrochar is recycled in agriculture. Up to now, however, little information could be found in the literature.

The objective of the present study was to explore the synergistic effect of RH addition on HMs immobilization when using HTT to treat sewage sludge. The toxicity and bioavailability of HMs in sludge was evaluated before and after the HTT process, and the fractional transformation mechanism is also discussed.

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73 **2. Materials and methods**

74 *2.1. Sewage Sludge and Rice Husk (RH).*

75 Dewatered anaerobically digested sewage sludge was sampled from a wastewater treatment
76 center in Ibaraki prefecture, Japan. Before the HTT process, the concentration of HMs was
77 elevated by adding stock solutions of Cr (VI), Ni (II), Cu (II) and Cd (II) (1000 mg/L in 0.1 M
78 HNO₃), respectively due to low levels of HMs in the original sludge sample. The sludge was
79 homogeneously stirred and then mixed intermittently (5min/day) for one week.

80 Rice husk was dried at 105 °C for 2 h and then ground and sieved. The particles between 0.30
81 and 0.45 mm were collected and washed with deionized water, and then dried at 60 °C for 24 h
82 for future use in the experiments. Table 1 lists the characteristics of the sewage sludge and RH
83 used in this study.

84 The tested sample, including single sludge or the mixtures of RH and sludge at different ratios
85 (namely RH/sludge=0, 1/6, 1/3 and 1/1.75 at d.w., respectively based on our preliminary
86 experiments), was mixed manually and homogeneously before the HTT process.

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88 *2.2. Hydrothermal treatment procedure*

89 HTT experiments were conducted in an enclosed stainless steel reactor with a volume of 200
90 ml. The HTT reactor was operated and controlled under the optimum conditions (200 °C, 1.0-1.2
91 MPa for 1 h) determined by our preliminary experiments.

92 In order to assess the HMs binding capacity (HMBC) of RH during the HTT process, 10.0 g
93 RH and 50.0 ml of stock solution containing the designated HMs (Cr, Ni, Cu and Cd) at the same
94 concentration (20.0 mg L⁻¹, pH=6.8) were first mixed and loaded into the reactor, and then

95 treated at 200 °C (1.0 - 1.2 MPa) for 1 h. After the HTT treatment, the RH residue and liquid
96 phase were separated by vacuum filtration. Later the liquid samples were kept in refrigerator at
97 4 °C and the RH residues were dried at 60°C for 48 h before further HMs analysis.

98 As for the synergistic effect of RH addition on the immobilization behavior of HMs in sludge
99 during the HTT process, 100.0 g of sludge or RH-sludge mixture was loaded into the reactor and
100 treated under the same HTT condition mentioned above (at 200 °C for 1 h). After solid-liquid
101 separation by vacuum filtration, the collected solid residue (SR), namely hydrochar was dried,
102 ground and mixed homogeneously, and then stored in an enclosed plastic bag. The SRs obtained
103 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,
104 respectively. The collected liquid samples (LSs, *i.e.* process water) were recorded as LS0, LS1/6,
105 LS1/3 and LS1/1.75, respectively.

106 For the control experiment (no HTT process), the solid residue samples were obtained by
107 directly using the sewage sludge prepared in the Section 2.1, labeled as SRC. No liquid sample
108 was collected because of its high solid content and difficulty in solid-liquid separation.

110 2.3. Evaluation methods and indices

111 In this study, the HMBC of RH was calculated by HMs decrease in the liquid phase after the
112 HTT process as Equation (1).

$$113 \quad \text{HMBC}(\%) = (C_0 - C) / C_0 \times 100 \quad (1)$$

114 where C_0 and C are the concentrations of HMs in the liquid phase before and after the HTT
115 process, respectively.

116 Before and after the HTT process, the risk of HMs in sludge was assessed from 3 aspects: total
117 concentration, fractionation and leaching test.

Total HM concentration is a simple and direct index for risk evaluation, which is the main limiting factor in agriculture, especially for the application of sewage sludge (Zorpas *et al.*, 2008). Furthermore, as Xian (1989) and Angelova *et al.* (2004) pointed out, the risk of HMs in sludge is strongly controlled by their existing forms.

By means of sequential extraction based on the procedure proposed by Tessier *et al.* (1979), the HMs in sludge can be extracted into five fractions (F1-F5): exchangeable metals (F1), metals bound to carbonate (F2), metals bound to iron and manganese oxides (F3), metals bound to organic and sulfide (F4) and metals in residue (F5), respectively. These fractions may be considered to decrease in lability from exchangeable to residual (Obrador *et al.*, 2001) and they can further be grouped into 3 parts based on their bounding strength and availability as (F1+F2), (F3+F4) and F5, respectively, representing the weakly bounded or easily releasable HMs, relatively stable HMs and the entrapped HMs within the crystal structure of the minerals. These three parts of HMs are reported to exhibit different eco-toxicity and bioavailability in the environment as direct toxicity, potential toxicity and no toxicity, respectively (Li *et al.*, 2012; Vela *et al.*, 1993). Thus the immobilization of HMs in sludge can be realized by redistribution and fractional transformation of HMs from weakly bounded or relatively unstable forms to stable state like the entrapped HMs.

In this study, the immobilization efficiency of HMs in sludge was assessed by the change in HMs content (% of total HMs) in fractions of (F1+F2), (F3+F4) and F5. More specifically, the decrease of HMs in the first two fractions are of great importance for HMs immobilization due to their vulnerability to ionic strength and pH changes in circumstance, and thus become more rapidly bioavailable (Sundaray *et al.*, 2011). Taking this into consideration, a risk assessment code (RAC), the proportion of HMs in (F1+F2) to the total concentration in the sludge (% of

total) (Huang *et al.*, 2011; Singh *et al.*, 2005), can be applied to the risk evaluation of HMs before and after the HTT process with or without RH addition. The HMs in sludge can be classified by using RAC, namely the risk index (RI) 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. In addition, the percentage of HMs in (F1+F2) (% of total) can also reflect the mobility of HMs in sludge in the environment.

The leachability and leaching toxicity test of HMs in SRC and SRs was conducted according to the standard Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1997).

2.4. Analysis

The concentration of each metal was determined by using ICP-MS (ELAN DRC-e, PerkinElmer). The HMs in fraction F5 and the total concentration of HMs in SRC and SRs were determined after digestion on a hot plate with an acid mixture (HCl:HNO₃:HF=3:1:1, v/v) in PTFE beakers (Bettinelli *et al.*, 2000). Each test was conducted in triplicate and the results were expressed as mean values ± SD.

3. Results and discussion

3.1. HMs binding capacity of rice husk during HTT

Figure 1 shows the HMs distribution in the solid (RH) and liquid phases after the HTT process designed for testing the HMBC of RH. After the HTT process, it was found that the pH of liquid phase decreased to about 3, still, the HMBC of RH was very high, *i.e.* about 99%, 98%, 74%, and 27% respectively for Cu, Cr, Cd, and Ni under the designed hydrothermal condition. Restated, RH exhibits excellent HMBC with Cu and Cr, and the highest HMBC with Cu is probably attributable to the high affinity of Cu to organic matter contained in RH (Crist *et al.*,

2002; Zorpas *et al.*, 2008). The high HMBC of RH during the HTT process may also be contributed by the high adsorption affinity of organic functional groups with HMs (Jiang *et al.*, 2012) or their strong binding strength with lignin largely available in RH (Crist *et al.*, 2002; Yanez *et al.*, 2006).

The excellent HMBC of RH provides a basis for application of RH in HMs immobilization in sewage sludge.

3.2. Risk assessment of HMs in solid residues

3.2.1. HMs redistribution in liquid and solid phases of sewage sludge after HTT process

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; Shi *et al.*, 2013), leading to a redistribution of HMs in the liquid (LSs) and solid phases (SRs) (Fig. 2).

A small amount of HMs (< 1.3% of total, data not shown) may be extracted into LS0 (no RH addition) after the sludge being HTT processed at 200 °C for 1 h. As seen from Figs. 2(a) and 2(b), addition of RH changed the redistribution of HMs in the LSs and SRs. The concentrations of Cr and Ni in LSs were observed to decrease with the increase in RH addition, while those of Cu and Cd firstly decreased significantly and then showed no significant variation with further increase in RH addition, partly in accordance with the HMBC of RH used in this study (Figs. 1 and 2(a)).

Obviously, the vast majority of HMs were accumulated in the SRs (solid phase) after the HTT process (Fig. 2(b)). The total concentration of each metal in SR0 reflected an increase in the solid samples after HTT (Fig. 2(b)), signaling higher potential environmental risk. 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.

In addition, after the HTT process, the pH values were found to decrease slightly from 8.52 (LS0, single sludge) to 7.64(LS1/6), 7.35(LS1/3) and 7.21(LS1/1.75) under RH addition conditions, likely due to the decomposition of the cellulose and lignin contained in RH during HTT (Yáñez *et al.*, 2006) and subsequent production of some acidic substances. The latter needs further confirmation.

3.2.2. HMs fractional transformation and eco-toxicity assessment

By sequential extraction, the percentages of HMs in (F1+F2), (F3+F4) and F5 (Fig. 3) were used in this study to evaluate environmental risk according to their eco-toxicity posed to the environment as direct toxicity, potential toxicity and no toxicity, respectively.

HMs in (F1+F2) represents the weakly bounded fractions and can be easily released into the environment, thus having the highest risk. Seen from Fig. 3(a), the contents of all the four HMs in this part decreased after the HTT process, and further large decrease was observed after RH addition for Ni, possibly due to the effective HMs binding ability of RH (Fig. 1) and relatively higher level of Ni contained in the sewage sludge used in this study (Table 1). No significant change in the percentages of (F1+F2) was observed for Cr, Cu and Cd after further increase in RH addition (when RH/sludge ratio varied from 1/3 to 1/1.75), which could be attributed to the rapid and excellent HMBC of RH to these three HMs (Fig. 1).

A quantitative risk assessment was conducted by RAC based on the percentage of each metal in the first 2 fractions ((F1+F2)/total, Table 2). For the HMs in the initial control sludge (SRC,

before HTT), Cd posed medium risk, and Cr, Ni and Cu were all at low risk. The risk of the tested HMs, however, was reduced to a lower rank after the HTT process, *i.e.*, no risk for Cr, no risk for Cu and low risk for Cd, respectively, and Ni still remained at low risk level. This observation is in agreement with the results obtained in Section 3.1, in which RH possessed a lower HMBC with Ni, and a relatively high level of Ni contained in both sewage sludge and RH used in this study (Table 1) may cause some difficulty for its immobilization during the HTT process. Definitely, all the risk of the tested four HMs could be reduced to no risk level if RH addition was further increased, such as RH/sludge ratio=1/1.75 in this study (Table 2).

HMs in (F3+F4) poses potential eco-toxicity to the environment and their risk may change with the variation of redox potential (Fuentes *et al.*, 2008). Figure 3(b) shows that the potential eco-toxicity of Cr, Cu and Cd increased to some extent in SR0 (no RH addition), but all of them decreased with the increase of RH/ sludge ratio after HTT under RH addition, especially for Cr and Cu with much lower (F3+F4) contents in SRs compared with the control samples (SCR, before HTT process). For Ni, the potential toxicity decreased after HTT, while a slight increase in (F3+F4) was detected after RH addition. Still, the potential toxicity of Ni in SRs after HTT with RH addition was lower than that of the control sludge samples (SRC, before HTT).

HMs in F5 shows no toxicity because of its stably bounded state. After the HTT process, F5 fractions of Ni and Cu increased (*i.e.*, became more stable), while those of Cr and Cd decreased under no RH addition (Fig. 3(c)). Under RH addition, the F5 contents of Cr, Cu and Cd increased with the increase of RH/sludge ratio, implying that these metals existed more stably in the RH-sludge matrix. Probably due to a lower HMBC to RH (Figs. 1 and 3(b)), the F5 fraction of Ni in SRs under RH addition was a little lower than that in SR0 (no RH addition), but still higher than that in the control sludge samples (SRC, before HTT).

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 (Table 2) (Obrador *et al.*, 2001). This observation indicates that the direct toxicity of HMs in the sewage sludge decreased after the HTT process, during which the HMs immobilization effect can be largely enhanced under RH addition, especially for Cr, Cu, and Cd 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 and Cd in sewage sludge after the HTT process. A decreased potential toxicity of Ni was also found for SRs after RH addition when compared with the control sludge samples (SRC, before HTT).

The above results imply that RH addition has a synergetic effect on the risk reduction or enhanced immobilization of HMs in sewage sludge through the HTT process.

3.2.3. HMs leachability test

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

All the leaching rates of the 4 metals were very low (< 2%). The leachability of the metals in the control sludge sample (SRC, before HTT) was determined in the order of Ni > Cu > Cd > Cr. After the HTT process, all the leaching rates of the tested HMs sharply decreased except for a slight increase in that of Cr, showing an excellent HMs immobilization role on the HTT process of sewage sludge. The addition of RH exerted an enhancement effect on reducing the leachability of HMs in SRs from HTT processed RH-sludge matrix.

As for Cr, the leachability was found at a very low level ($< 0.25\%$), 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. This phenomenon could be attributable to the different HMBC of RH to these 4 HMs (Fig. 1) and the different vulnerability of the 4 HMs to the environment under the designed experimental conditions.

In this study, the leaching toxicity of the metals was quantitatively evaluated by the HMs concentrations in the leachate (Table 3). The leached concentrations of the metals in the control sludge sample (SRC) were lower than the USEPA permissible limits (SW-846) except for Ni, which was about twice the limit value. After the single HTT the leaching toxicity of Cr and Ni in SR0 slightly increased, while that of Cu and Cd significantly decreased, showing the different immobilization effects of the HTT process on HMs leaching.

RH addition, however, exhibited reduction effects on the leaching toxicity of HMs during the HTT process, lowering all the HM levels in SRs below the limit values. The lowest leaching toxicity of metals was achieved at the RH/sludge ratio of 1/1.75, with the leaching toxicity reduction of about 17%, 89%, 95% and 93% for Cr, Ni, Cu and Cd, respectively, revealing that the enhancement effect of RH addition on the reduction of HMs leaching toxicity follows the order of $\text{Cu} \geq \text{Cd} > \text{Ni} > \text{Cr}$.

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

3.3. Mechanism analysis

As mentioned above, a synergetic effect was found for RH addition on HMs immobilization during the HTT process. Based on the present work, the following three points can be arrived at: (1) HTT may bring about a slight dissolution of HMs in sludge into the liquid phase (process water), leaving the majority of HMs in the solid residue (Fig. 2). The dissolved HMs can be easily removed from the sludge by solid-liquid separation after HTT. (2) Under RH addition condition, less HMs were dissolved into the liquid phase because of the excellent HMBC of RH. The concentration of HMs in the HTT processed sludge decreased with the increase in RH/sludge ratio applied, mainly owing to some 'dilution effect' caused by RH addition (Fig. 2). (3) Most importantly, the weakly bounded (F1+F2) and relatively stable (F3+F4) fractions of HMs in the processed sludge can be transformed into a stable state (F5), especially under RH addition conditions (Fig. 3).

In order to illustrate the immobilization mechanism of HMs in the RH-sludge matrix during the HTT process, an additional experiment was carried out in this study to clarify the distribution change of HMs, namely outside the matrix or inside the matrix by using a rapid extraction method proposed by [Ginter and Grobicki \(1995\)](#). In the experiment, 10% HCl was adopted to separate the HCl-soluble HMs (outside) and HCl-insoluble HMs (inside), which can be used to distinguish the HMs precipitated or accumulated outside of the RH-sludge matrix from those fixed inside the matrix. Thus HMs in F5 fraction obtained from the sequential extraction method ([Tessier *et al.*, 1979](#)) should have a close relationship with the latter part, HCl-insoluble HMs.

Figure 5 shows the results of HCl-soluble HMs from sludge residues obtained in this study. A similar decrease in HCl-soluble part was found for all tested HMs in the sludge samples after the HTT process. The HCl-soluble Cr, Cu and Cd were further decreased after RH addition. As for

Ni, the HCl-soluble part first increased to some extent and then decreased when RH/sludge ratio increased. Moreover, the decrease in HCl-soluble HMs coincided with the increase of HMs in F5 (Fig. 3(c)), especially for Cr in the SRs after HTT, exhibiting a strong negative correlation with HMs in F5 ($R^2=0.9726$, Figs. 5 and 3(c)).

Based on the present results and above discussion, the reduction of HMs toxicity and vulnerability may be interpreted as a synergetic mechanism of RH addition during the HTT process as Fig. 6: (1) the unstable or loosely absorbed HMs (F1+F2 and part of F3+F4, or HCl-soluble) are first dissolved under HTT conditions, and then can be re-encapsulated or immobilized into the processed sludge matrix. (2) The released HMs can also 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.

3.4. Environmental implications

It has been recently reported that the sludge residue (*i.e.* hydrochar or biochar) collected from sewage sludge after HTT process possess a good potential for resource recovery and carbon sink (Escala *et al.*, 2013; Khan *et al.*, 2013). The most important and problematic is the stability and accumulation of HMs in soil after utilization of the processed sludge residue. The present study demonstrates that, based on total concentration, potential lability and leaching toxicity tests, the

HMs toxicity in sewage sludge can be greatly decreased after HTT process with RH addition. HMs can be stably immobilized into the RH-sludge matrix according to the results of HMs fractionation before and after HTT process. The RAC analysis indicates that all the tested HMs have no eco-toxicity to the environment after processed by HTT under RH addition, especially at RH/sludge ratio of 1/1.75. Therefore, HTT process with RH addition is a promising technology for sewage sludge disposal, and the HTT processed RH-sludge can be regarded as a kind of safe resources with respect to HMs problem.

4. Conclusions

The present study shows that RH addition has a synergetic effect on HMs immobilization in sewage sludge during HTT process. No eco-toxicity and no leaching toxicity was detected under appropriate RH/sludge ratios ($\geq 1/1.75$ (d.w.) in this study). This synergetic effect is mostly brought about by the excellent HMs binding capacity of RH. Under the designed experimental conditions, the enhancement effect of RH addition on the reduction of HMs leaching toxicity follows the order of $\text{Cu} \geq \text{Cd} > \text{Ni} > \text{Cr}$. Detailed investigation into the HMs immobilization mechanisms during this HTT process is in progress.

In this study, RH showed high binding capacity with HMs in HTT process and RH addition further enhanced the transformation and immobilization effect of metals in sewage sludge during hydrothermal treatment. In HTT process, the risk of all the tested metals in the collected hydrochar was significantly decreased as referred to the total concentrations, RAC evaluation and TCLP test after RH addition. Therefore, a synergetic effect on HMs risk reduction can be achieved when RH added into sewage sludge in HTT process demonstrating the practical feasibility of this treatment method.

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445

446 **Tables**

447 Table 1. Physicochemical characteristics of the sewage sludge and rice husk used in the
448 experiments.

Parameters	Sewage sludge	Rice husk
Solid content (%)	14.53 \pm 0.39	94.47 \pm 0.58
Loss of ignition (%)	46.09 \pm 0.16	69.32 \pm 1.41
Total phosphorus (g kg ⁻¹ , d.w.)	17.15 \pm 1.84	N.D.
pH	6.43 \pm 0.21	N.D.
HMs (mg kg ⁻¹ , d.w.)		
Cr	150.18 \pm 1.22	13.50 \pm 1.53
Ni	638.56 \pm 96.15	41.74 \pm 2.59
Cu	415.00 \pm 29.46	8.08 \pm 1.92
Cd	73.02 \pm 0.63	0.17 \pm 0.01

449 Mean \pm standard deviation. N.D., no determination.

450

Table 2. Average RAC values and potential lability of HMs in SRs after the HTT process with and without RH addition.

Sludge	RAC ^a : (F1+F2)/Total × 100				Potential lability: (F1+F2)/F5 (×10 ⁻²)			
residue	Cr	Ni	Cu	Cd	Cr	Ni	Cu	Cd
SRC ^b	1.07 (L)	3.82 (L)	2.84 (L)	16.66 (M)	2.25	6.34	8.95	265.44
SR0 ^c	0.89 (N)	2.63 (L)	0.72 (N)	1.47 (L)	1.95	3.64	2.18	66.19
SR1/6	0.64 (N)	2.16 (L)	0.52 (N)	0.72 (N)	1.19	3.41	1.30	11.17
SR1/3	0.66 (N)	1.57 (L)	0.51 (N)	0.95 (N)	0.97	2.30	1.02	11.33
SR1/1.75	0.60 (N)	0.86 (N)	0.46 (N)	0.71 (N)	0.81	1.28	0.75	5.15

^a RAC, risk assessment code. RAC (%) <1, 1-10, 11-30, 31-50 and > 50 indicate no risk (N), low risk (L), medium risk (M), high risk and very high risk, respectively.

^b SRC, solid residue in the control experiment (before HTT).

^c SR0, SR1/6, SR1/3 and SR1/1.75 denotes the sludge residue (SR) after the HTT process at RH/sludge ratios (d.w.) of 0, 1/6, 1/3 and 1/1.75, respectively.

460

461 Table 3. Concentrations of heavy metals leached in TCLP tests (unit: mg kg⁻¹).

HMs	SRC ^a	SR0 ^b	SR1/6	SR1/3	SR1/1.75	Permissible limits ^c
Cr	0.300±0.061	0.424±0.053	0.298±0.100	0.351±0.092	0.249±0.038	5
Ni	11.751±1.62	12.165±1.596	4.783±0.802	3.311±0.362	1.322±0.228	5
Cu	5.047±0.709	1.387±0.393	0.470±0.101	0.281±0.040	0.266±0.053	Not enlisted
Cd	0.722±0.092	0.171±0.050	0.058±0.009	0.036±0.006	0.050±0.004	1

462 ^a SRC, sludge residue in control experiment (before the HTT process)

463 ^b SR0, SR1/6, SR1/3 and SR1/1.75 denotes the sludge residue (SR) after the HTT process at RH/sludge ratios
 464 (d.w.) of 0, 1/6, 1/3 and 1/1.75, respectively.

465 ^c USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

466

Figure captions

Fig. 1. HMs distribution in solid and liquid phases of RH after the HTT process. 10.0 g RH was dosed into 50.0 ml of 20.0 mg L⁻¹ tested HMs solution.

Fig. 2. Distribution of HMs in liquid (a) and solid (b) phases after the HTT process with or without RH addition. LS-liquid sample after HTT, SR-solid residue after HTT, SRC-solid residue in control experiment. The ratios right after LS and SR, namely 0, 1/6, 1/3, and 1/1.75 denote the RH/sludge ratios at dry basis.

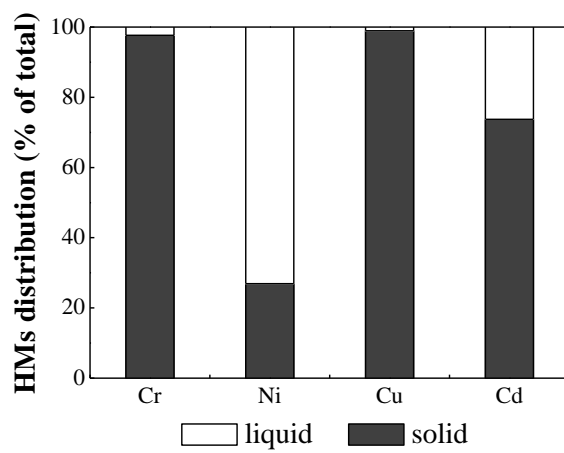
Fig. 3. The percentages (% of total) of HMs existing in the fractions (F1+F2) (a), (F3+F4) (b) and F5 (c) in the sludge residues (SRs) after the HTT process and the control sludge samples (SRC, before HTT). The ratios right after SR, namely 0, 1/6, 1/3, and 1/1.75 denote the RH/sludge ratios at dry basis.

Fig. 4. Leaching rates of heavy metals in sludge residues before HTT (SRC) and after HTT (SR0, SR1/6, SR1/3, and SR1/1.75) in the TCLP tests. The ratios right after SR, namely 0, 1/6, 1/3, and 1/1.75 denote the RH/sludge ratios at dry basis.

Fig. 5. Changes of HCl-soluble HMs proportion in sludge residues by using a rapid extraction method proposed by Ginter and Grobicki (1995). SRC, sludge residue in control experiment (before HTT, SRC), SR0, SR1/6, SR1/3, and SR1/1.75 denote the sludge residue after HTT under RH addition at RH/sludge ratio (d.w.) of 0, 1/6, 1/3 and 1/1.75, respectively.

Fig. 6. Schematic and image of HMs immobilization into the HTT processed sludge under RH addition. SS, sewage sludge; SS-M, HMs entrapped in the sludge matrix; RH, rice husk; M, heavy metals existed in unstable state.

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Fig. 1. Shi et al.

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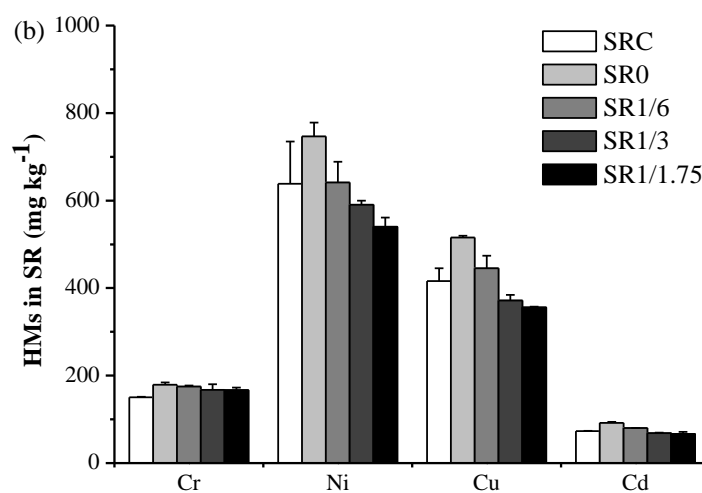
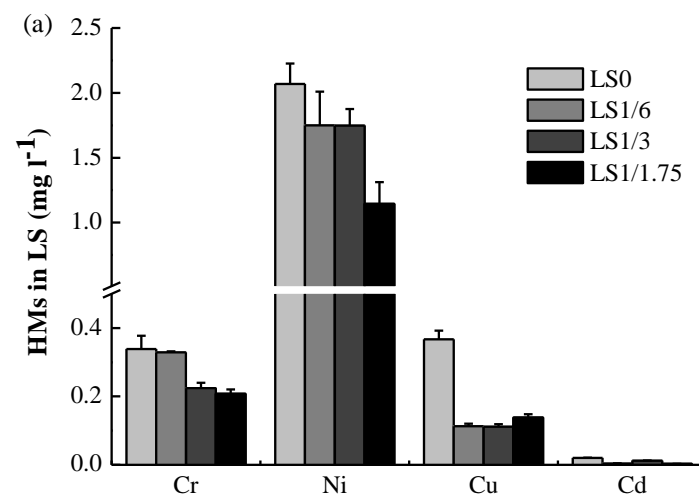


Fig. 2. Shi et al.

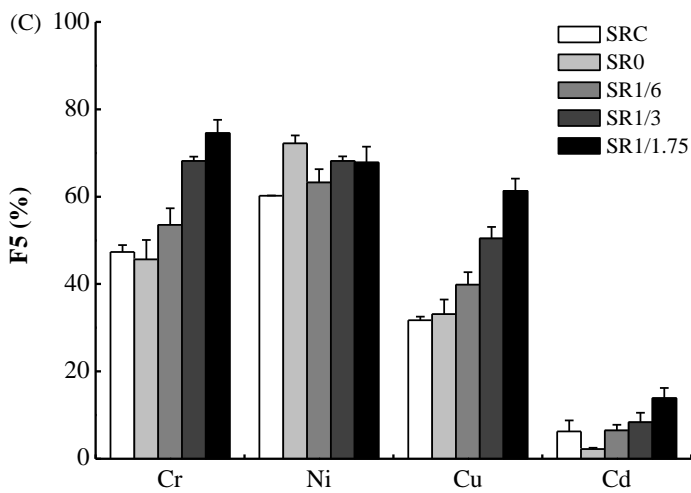
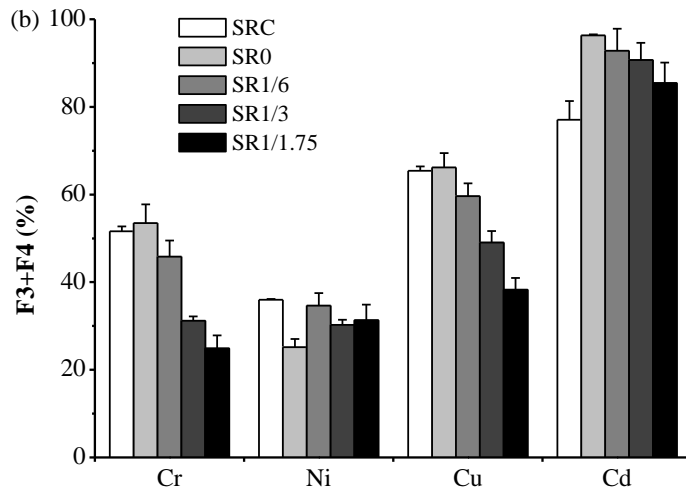
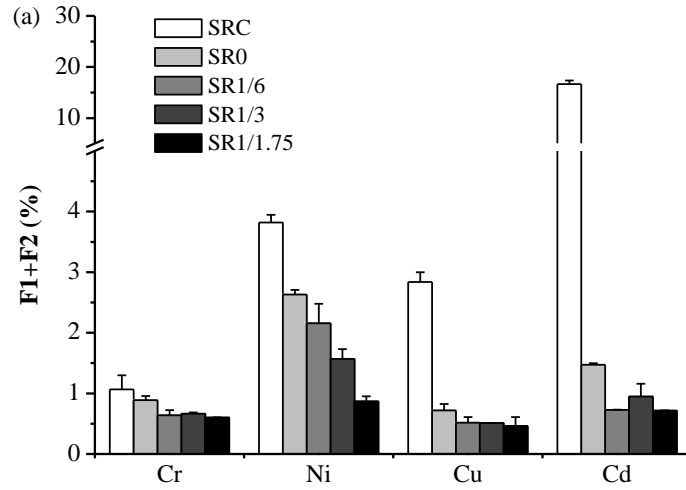


Fig. 3. Shi et al.

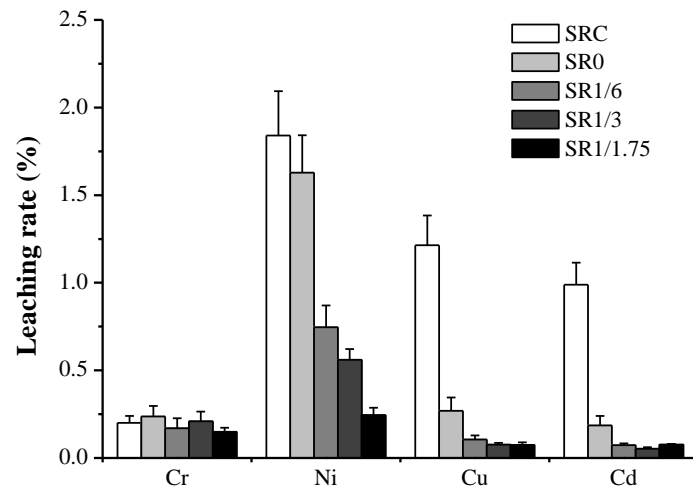


Fig. 4. Shi et al.

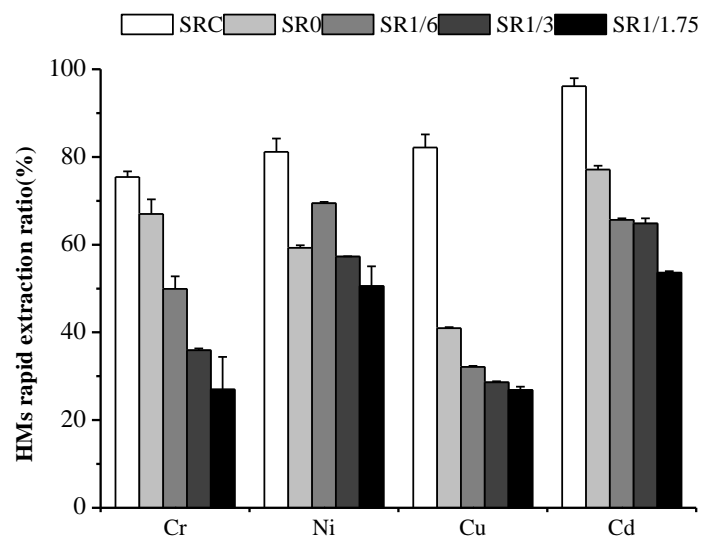


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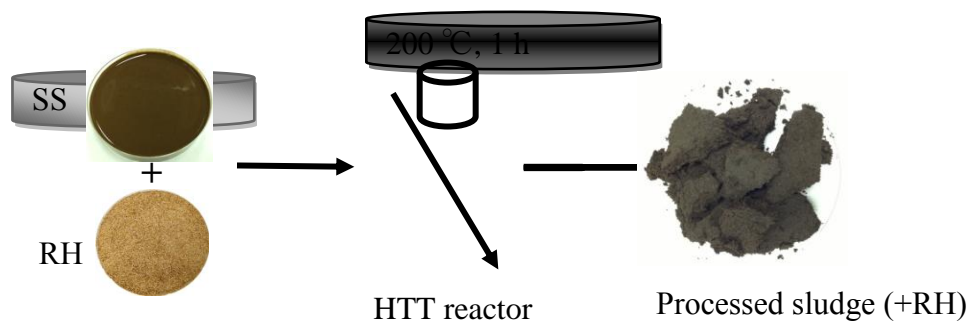
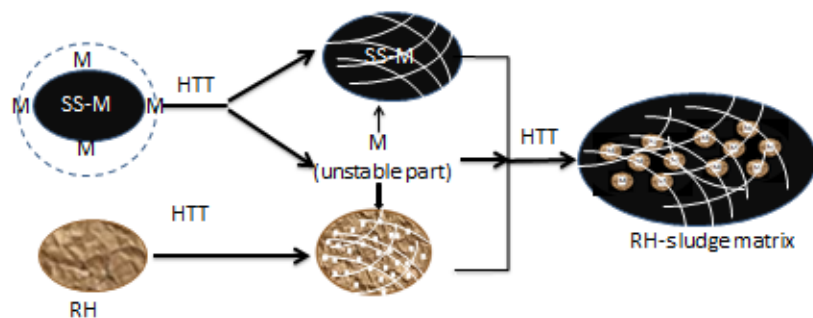


Fig. 6. Shi et al.