

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

3 Wansheng Shi <sup>a,b</sup>, Chunguang Liu <sup>a</sup>, Youju Shu <sup>a</sup>, Chuanping Feng <sup>b</sup>, Zhongfang Lei <sup>a\*</sup>, Zhenya  
4 Zhang <sup>a\*</sup>

5 <sup>a</sup> Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba 305-  
6 8572, Japan

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

9

---

\*Corresponding author:

Zhongfang Lei. Tel/fax: +81 29 853 6703. E-mail: lei.zhongfang.gu@u.tsukuba.ac.jp (Z. Lei);

Zhenya Zhang. Tel/fax.: +81 29 853 4712. E-mail: zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

10

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.

22

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

25

26

## 27 **1. Introduction**

28

29 Hydrothermal treatment (HTT) is very attractive due to its simplicity and effectiveness in  
30 dealing with organic solid waste disposal (Hu *et al.*, 2012; Hwang *et al.*, 2012; Theegala and  
31 Midgett, 2012). Being rich in organic carbon and easily available N, P and K, the solid residues  
32 (or hydrochar) produced from the HTT process can be used as soil amendments to improve the  
33 sorption capacity of soils towards many trace contaminants (PAHs, pesticides, herbicides, and  
34 etc.) as well as carbon sequestration (Gajic *et al.*, 2012; Rillig *et al.*, 2010). Moreover, hydrochar  
35 has also been utilized as a coal-like fuel because its calorific value can be elevated by the  
36 dehydration and decarboxylation occurring in the HTT process (Berge *et al.*, 2011).

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

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

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

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

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

72

## 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 HNO<sub>3</sub>), 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.

87

### 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<sup>-1</sup>, 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.

109

### 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).

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

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.

118 Total HM concentration is a simple and direct index for risk evaluation, which is the main  
119 limiting factor in agriculture, especially for the application of sewage sludge (Zorpas *et al.*,  
120 2008). Furthermore, as Xian (1989) and Angelova *et al.* (2004) pointed out, the risk of HMs in  
121 sludge is strongly controlled by their existing forms.

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

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

141 total) (Huang *et al.*, 2011; Singh *et al.*, 2005), can be applied to the risk evaluation of HMs  
142 before and after the HTT process with or without RH addition. The HMs in sludge can be  
143 classified by using RAC, namely the risk index (RI) as no risk, low risk, medium risk, high risk  
144 and very high risk when the RI value (%) ranges < 1, 1–10, 11–30, 31–50 and > 50, respectively.  
145 In addition, the percentage of HMs in (F1+F2) (% of total) can also reflect the mobility of HMs  
146 in sludge in the environment.

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

149

#### 150 2.4. Analysis

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

156

### 157 3. Results and discussion

#### 158 3.1. HMs binding capacity of rice husk during HTT

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

165 2002; Zorpas *et al.*, 2008). The high HMBC of RH during the HTT process may also be  
166 contributed by the high adsorption affinity of organic functional groups with HMs (Jiang *et al.*,  
167 2012) or their strong binding strength with lignin largely available in RH (Crist *et al.*, 2002;  
168 Yanez *et al.*, 2006).

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

171

## 172 3.2. Risk assessment of HMs in solid residues

### 173 3.2.1. HMs redistribution in liquid and solid phases of sewage sludge after HTT process

174 As for the HMs control in solid waste, both extraction and stabilization effects may occur  
175 simultaneously during the HTT process (Escala *et al.*, 2013; Jin *et al.*, 2013; Shi *et al.*, 2013),  
176 leading to a redistribution of HMs in the liquid (LSs) and solid phases (SRs) (Fig. 2).

177 A small amount of HMs (< 1.3% of total, data not shown) may be extracted into LS0 (no RH  
178 addition) after the sludge being HTT processed at 200 °C for 1 h. As seen from Figs. 2(a) and  
179 2(b), addition of RH changed the redistribution of HMs in the LSs and SRs. The concentrations  
180 of Cr and Ni in LSs were observed to decrease with the increase in RH addition, while those of  
181 Cu and Cd firstly decreased significantly and then showed no significant variation with further  
182 increase in RH addition, partly in accordance with the HMBC of RH used in this study (Figs. 1  
183 and 2(a)).

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

187 addition, the concentration of each metal decreased with the increase of RH/sludge ratio (d.w.).  
188 This decrease trend of HMs content in SRs was mostly brought about by a 'dilution effect' due  
189 to RH addition, depending greatly on the RH/sludge ratios applied.

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

195

### 196 3.2.2. HMs fractional transformation and eco-toxicity assessment

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

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

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

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

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

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

233 The increase of HMs in F5 coupled with the decrease of HMs in (F1+F2) results in a decreased  
234 (F1+F2)/F5 ratio, signaling decreased lability of HMs in the sludge residues (Table 2) (Obrador  
235 *et al.*, 2001). This observation indicates that the direct toxicity of HMs in the sewage sludge  
236 decreased after the HTT process, during which the HMs immobilization effect can be largely  
237 enhanced under RH addition, especially for Cr, Cu, and Cd at the RH/sludge ratio of 1/1.75.

238 In addition, it is worth noting that compared with a single HTT, RH addition can bring about a  
239 further decrease in the potential toxicity of Cr, Cu and Cd in sewage sludge after the HTT  
240 process. A decreased potential toxicity of Ni was also found for SRs after RH addition when  
241 compared with the control sludge samples (SRC, before HTT).

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

244

### 245 3.2.3. HMs leachability test

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

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

255 As for Cr, the leachability was found at a very low level (< 0.25%), and no significant  
256 variation was observed on its leachability after RH addition. The leaching rate of Ni decreased  
257 gradually with the increase of RH/sludge ratio, while those of Cu and Cd rapidly declined to a  
258 very low level (< 0.11%) after RH addition, with no obvious change in their leachability under  
259 different RH/sludge ratio conditions. This phenomenon could be attributable to the different  
260 HMBC of RH to these 4 HMs (Fig. 1) and the different vulnerability of the 4 HMs to the  
261 environment under the designed experimental conditions.

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

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

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

277

278 3.3. Mechanism analysis

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

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

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

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

305 Based on the present results and above discussion, the reduction of HMs toxicity and  
306 vulnerability may be interpreted as a synergetic mechanism of RH addition during the HTT  
307 process as Fig. 6: (1) the unstable or loosely absorbed HMs (F1+F2 and part of F3+F4, or HCl-  
308 soluble) are first dissolved under HTT conditions, and then can be re-encapsulated or  
309 immobilized into the processed sludge matrix. (2) The released HMs can also be further  
310 entrapped by the enlarged structure of RH or chelated with some functional groups and then  
311 fixed in the stable RH-sludge matrix formed during HTT under RH addition, resulting in  
312 enhanced HMs immobilization effect. The detailed mechanisms need further investigation,  
313 especially for the contribution of organic ingredients (such as lignin and cellulose contained in  
314 RH) and inorganic substances (mainly including phosphate, silicate, carbonate, aluminum, and  
315 calcium in the sludge) in addition to some functional groups formed during HTT to the  
316 immobilization of HMs in the HTT processed RH-sludge matrix.

317

### 318 *3.4. Environmental implications*

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

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

331

#### 332 **4. Conclusions**

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

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

347

348 **Acknowledgement**

349 The authors want to give thanks to Ms Devena Haggis and the Environmental Diplomatic  
350 Leader (EDL) Writing Center, University of Tsukuba, Japan, for proofreading.

351

352 **References**

- 353 1. Angelova, V., Ivanov, K. & Ivanova, R., 2004. Effect of chemical forms of lead, cadmium,  
354 and zinc in polluted soils on their uptake by tobacco. *J. Plant Nutr.* 27,757-773.
- 355 2. Berge, N. D., Ro, K. S., Mao, J. D., Flora, J. R. V., Chappell, M. A., Bae, S. Y., 2011.  
356 Hydrothermal Carbonization of Municipal Waste Streams. *Environ. Sci. Technol.* 45, 5696-  
357 5703.
- 358 3. Bettinelli, M., Beone, G. M., Spezia, S., Baffi, C., 2000. Determination of heavy metals in  
359 soils and sediments by microwave-assisted digestion and inductively coupled plasma optical  
360 emission spectrometry analysis. *Anal. Chim. Acta.* 424, 289-296.
- 361 4. Crist, R. H., Martin, J. R., Crist, D. R., 2002. Heavy metal uptake by lignin: Comparison of  
362 biotic ligand models with an ion-exchange process. *Environ. Sci. Technol.* 36, 1485-1490.
- 363 5. Daifullah, A. A. M., Girgis, B. S., Gad, H. M. H., 2003. Utilization of agro-residues (rice  
364 husk) in small waste water treatment plans. *Mater. Lett.* 57, 1723-1731.
- 365 6. Escala, M., Zumbuhl, T., Koller, C., Junge, R., Krebs, R., 2013. Hydrothermal  
366 Carbonization as an Energy-Efficient Alternative to Established Drying Technologies for  
367 Sewage Sludge: A Feasibility Study on a Laboratory Scale. *Energ. Fuel.* 27, 454-460.
- 368 7. Fuentes, A., Llorens, M., Saez, J., Aguilar, M. I., Ortuno, J. F., Meseguer, V. F., 2008.  
369 Comparative study of six different sludges by sequential speciation of heavy metals.

370 Bioresour. Technol. 99, 517-525.

371 8. Gajic, A., Ramke, H. G., Hendricks, A., Koch, H. J., 2012. Microcosm study on the  
372 decomposability of hydrochars in a Cambisol. Biomass Bioenerg. 47, 250-259.

373 9. Ginter, M. O., Grobicki, A. M., 1995. Analysis of anaerobic sludge containing heavy metals:  
374 A novel technique. Water Res. 29(12), 2780-2784.

375 10. He, C., Giannis, A., Wang, J.-Y., 2013. Conversion of sewage sludge to clean solid fuel  
376 using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior.  
377 Appl. Energ. 111, 257-266.

378 11. Hu, Y. Y., Zhang, P. F., Chen, D. Z., Zhou, B., Li, J. Y., Li, X. W., 2012. Hydrothermal  
379 treatment of municipal solid waste incineration fly ash for dioxin decomposition. J. Hazard.  
380 Mater. 207, 79-85.

381 12. Huang, H. J., Yuan, X. Z., Zeng, G. M., Zhu, H. N., Li, H., Liu, Z. F., Jiang, H. W., Leng, L.  
382 J., Bi, W. K., 2011. Quantitative evaluation of heavy metals' pollution hazards in  
383 liquefaction residues of sewage sludge. Bioresour. Technol. 102, 10346-10351.

384 13. Hwang, I. H., Aoyama, H., Matsuto, T., Nakagishi, T., Matsuo, T., 2012. Recovery of solid  
385 fuel from municipal solid waste by hydrothermal treatment using subcritical water. Waste  
386 Manage. 32, 410-416.

387 14. Jiang, J., Xu, R.-k., Jiang, T.-y., Li, Z., 2012. Immobilization of Cu(II), Pb(II) and Cd(II) by  
388 the addition of rice straw derived biochar to a simulated polluted Ultisol. J. Hazard. Mater.  
389 229-230, 145-150.

390 15. Jin, Y. Q., Ma, X. J., Jiang, X. G., Liu, H. M., Li, X. D., Yan, J. H., Cen, K. F., 2013. Effects  
391 of Hydrothermal Treatment on the Major Heavy Metals in Fly Ash from Municipal Solid  
392 Waste Incineration. Energ. Fuel. 27, 394-400.

- 393 16. Khan, S., Chao, C., Waqas, M., Arp, H. P. H., Zhu, Y.-G., 2013. Sewage Sludge Biochar  
394 Influence upon Rice (*Oryza sativa* L) Yield, Metal Bioaccumulation and Greenhouse Gas  
395 Emissions from Acidic Paddy Soil. *Environ. Sci. Technol.*47, 8624-8632.
- 396 17. Krishnani, K. K., Meng, X. G., Christodoulatos, C., Boddu, V. M., 2008. Biosorption  
397 mechanism of nine different heavy metals onto biomatrix from rice husk. *J. Hazard. Mater.*  
398 153,1222-1234.
- 399 18. Li, L., Xu, Z. R., Zhang, C. L., Bao, J. P., Dai, X. X., 2012. Quantitative evaluation of heavy  
400 metals in solid residues from sub- and super-critical water gasification of sewage sludge.  
401 *Bioresour. Technol.* 121, 169-175.
- 402 19. Meng, D., Jiang, Z., Kunio, Y., Mu, H., 2012. The effect of operation parameters on the  
403 hydrothermal drying treatment. *Renew. Energ.* 42, 90-94.
- 404 20. Obrador, A., Rico, M. I., Alvarez, J. M., Novillo, J., 2001. Influence of thermal treatment on  
405 sequential extraction and leaching behaviour of trace metals in a contaminated sewage  
406 sludge. *Bioresour. Technol.* 76, 259-264.
- 407 21. Reza, M. T., Lynam, J. G., Uddin, M. H., Coronella, C. J., 2013. Hydrothermal  
408 carbonization: Fate of inorganics. *Biomass Bioenerg.* 49, 86-94.
- 409 22. Rillig, M. C., Wagner, M., Salem, M., Antunes, P. M., George, C., Ramke, H. G., Titirici, M.  
410 M., Antonietti, M., 2010. Material derived from hydrothermal carbonization: Effects on  
411 plant growth and arbuscular mycorrhiza. *Appl. Soil Ecol.* 45, 238-242.
- 412 23. Shi, W., Liu, C., Ding, D., Lei, Z., Yang, Y., Feng, C., Zhang, Z., 2013. Immobilization of  
413 heavy metals in sewage sludge by using subcritical water technology. *Bioresour. Technol.*  
414 137,18-24.
- 415 24. Singh, K. P., Mohan, D., Singh, V. K., Malik, A., 2005. Studies on distribution and

- 416 fractionation of heavy metals in Gomti river sediments - a tributary of the Ganges, India. *J.*  
417 *Hydrol.* 312,14-27.
- 418 25. Sundaray, S. K., Nayak, B. B., Lin, S., Bhatta, D., 2011. Geochemical speciation and risk  
419 assessment of heavy metals in the river estuarine sediments-A case study: Mahanadi basin,  
420 India. *J. Hazard. Mater.* 186, 1837-1846.
- 421 26. Tessier, A., Campbell, P. G. C., Bisson, M., 1979. Sequential Extraction Procedure for The  
422 Speciation of Particulate Trace-Metals. *Anal. Chem.* 51, 844-851.
- 423 27. Theegala, C. S., Midgett, J. S., 2012. Hydrothermal liquefaction of separated dairy manure  
424 for production of bio-oils with simultaneous waste treatment. *Bioresour. Technol.* 107,456-  
425 463.
- 426 28. USEPA, 1997. Test methods for evaluating solid waste—physical chemical methods. SW-  
427 846. Washington, DC: U.S. Environmental Protection Agency.
- 428 29. Vela, L. D., Jarvis, R. E., Krishnan, S. S., 1993. The leachability of elements in solid- wastes.  
429 *J. Radioanal. Nucl. Chem. Art.* 169, 39-45.
- 430 30. Vogel, C., Adam, C., 2011. Heavy Metal Removal from Sewage Sludge Ash by  
431 Thermochemical Treatment with Gaseous Hydrochloric acid. *Environ. Sci. Technol.* 45,  
432 7445-7450.
- 433 31. Xian, X., 1989. Effect of Chemical Forms of Cadmium, Zinc, and Lead in Polluted Soils on  
434 Their Uptake by Cabbage Plants. *Plant Soil* 113, 257-264.
- 435 32. Yáñez, R., Alonso J. L., Parajó J. C., 2006. Enzymatic saccharification of hydrogen  
436 peroxide-treated solids from hydrothermal processing of rice husks. *Process Biochem.*  
437 41,1244-1252.
- 438 33. Zhang, G., Hai, J., Ren, M. Z., Zhang, S. K., Cheng, J., Yang, Z. R., 2013. Emission, Mass

439 Balance, and Distribution Characteristics of PCDD/Fs and Heavy Metals during  
440 Cocombustion of Sewage Sludge and Coal in Power Plants. *Environ. Sci. Technol.* 47,  
441 2123-2130.

442 34. Zorpas, A. A., Inglezakis, V. J., Loizidou, M., 2008. Heavy metals fractionation before,  
443 during and after composting of sewage sludge with natural zeolite. *Waste Manage.* 28, 2054-  
444 2060.

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 ± 0.39	94.47 ± 0.58
Loss of ignition (%)	46.09 ± 0.16	69.32 ± 1.41
Total phosphorus (g kg <sup>-1</sup> , d.w.)	17.15 ± 1.84	N.D.
pH	6.43 ± 0.21	N.D.
HMs (mg kg <sup>-1</sup> , d.w.)		
Cr	150.18 ± 1.22	13.50 ± 1.53
Ni	638.56 ± 96.15	41.74 ± 2.59
Cu	415.00 ± 29.46	8.08 ± 1.92
Cd	73.02 ± 0.63	0.17 ± 0.01

449 Mean ± standard deviation. N.D., no determination.

450

451

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

Sludge residue	RAC <sup>a</sup> : (F1+F2)/Total × 100				Potential lability: (F1+F2)/F5 (×10 <sup>-2</sup> )			
	Cr	Ni	Cu	Cd	Cr	Ni	Cu	Cd
SRC <sup>b</sup>	1.07 (L)	3.82 (L)	2.84 (L)	16.66 (M)	2.25	6.34	8.95	265.44
SR0 <sup>c</sup>	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

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

456 <sup>b</sup> SRC, solid residue in the control experiment (before HTT).

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

459

460

461 Table 3. Concentrations of heavy metals leached in TCLP tests (unit: mg kg<sup>-1</sup>).

HMs	SRC <sup>a</sup>	SR0 <sup>b</sup>	SR1/6	SR1/3	SR1/1.75	Permissible limits <sup>c</sup>
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 <sup>a</sup> SRC, sludge residue in control experiment (before the HTT process)

463 <sup>b</sup> 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 <sup>c</sup> USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846).

466

467 **Figure captions**

468 Fig. 1. HMs distribution in solid and liquid phases of RH after the HTT process. 10.0 g RH was  
469 dosed into 50.0 ml of 20.0 mg L<sup>-1</sup> tested HMs solution.

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

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

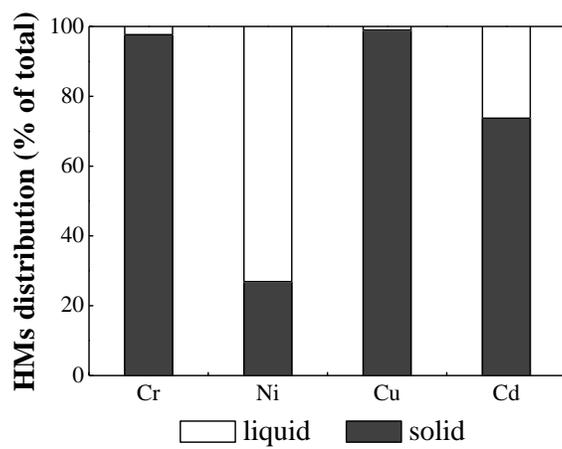
478 Fig. 4. Leaching rates of heavy metals in sludge residues before HTT (SRC) and after HTT (SR0,  
479 SR1/6, SR1/3, and SR1/1.75) in the TCLP tests. The ratios right after SR, namely 0, 1/6, 1/3, and  
480 1/1.75 denote the RH/sludge ratios at dry basis.

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

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

488

489



490

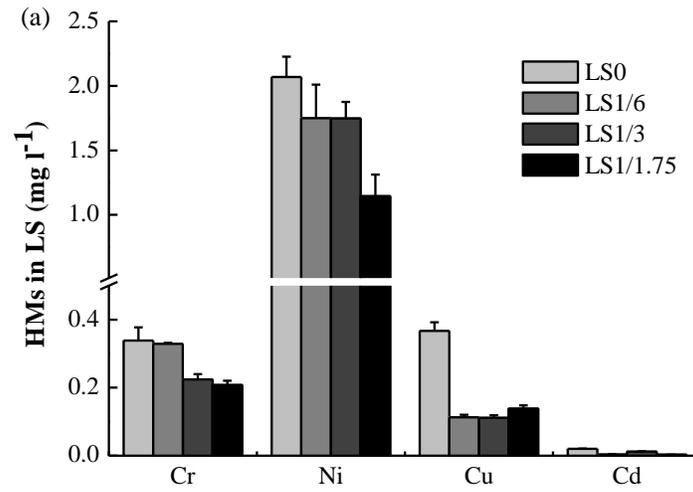
491

492

Fig. 1. Shi et al.

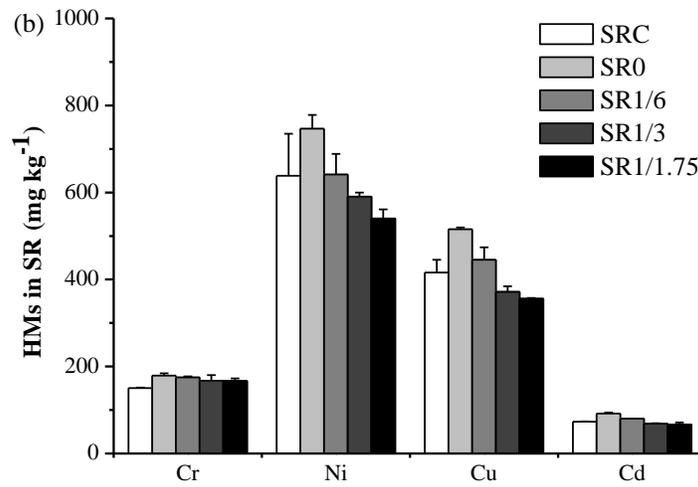
493

494



495

496



497

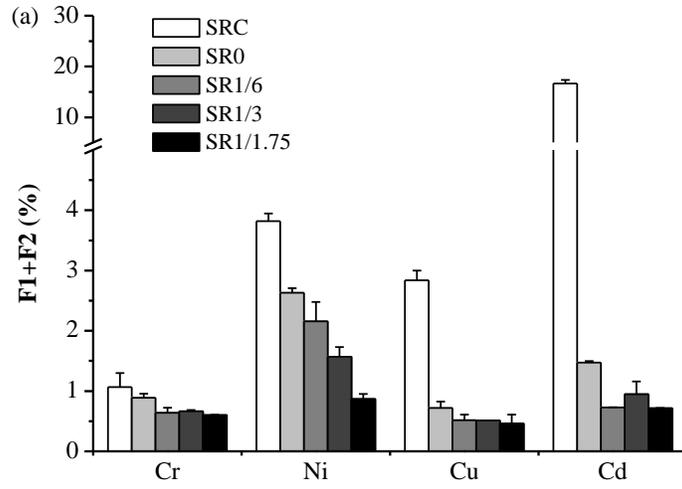
498

499

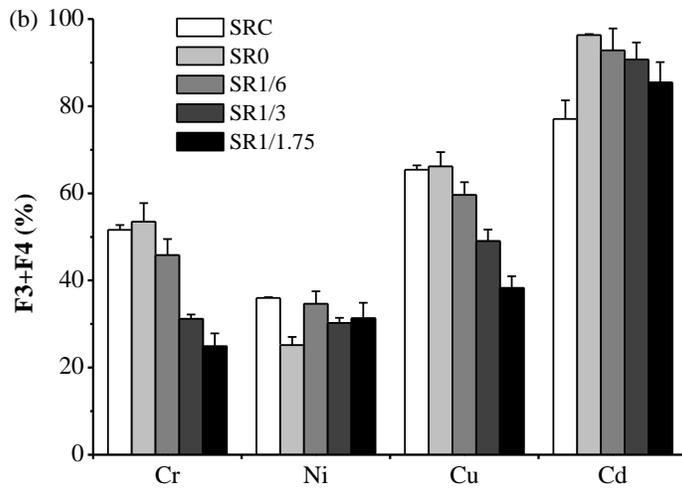
Fig. 2. Shi et al.

500

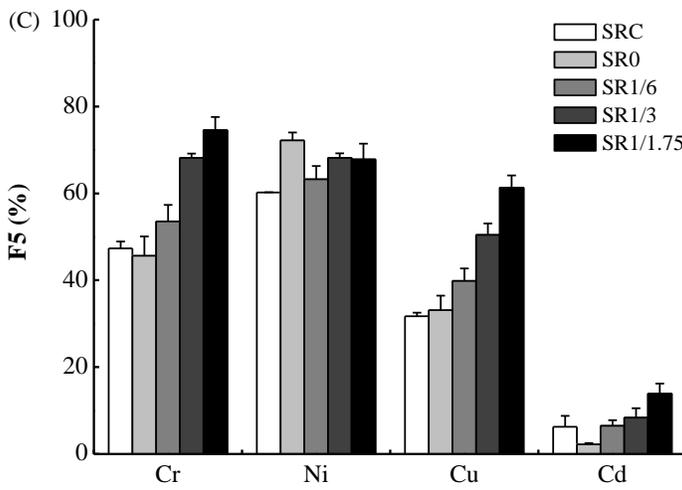
501



502

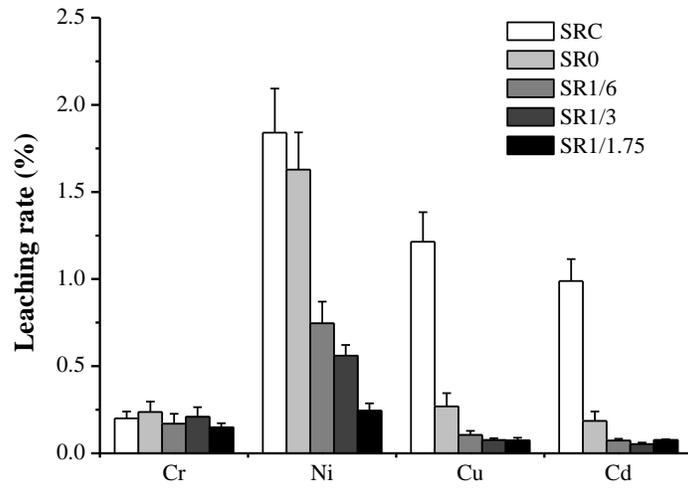


503



504

Fig. 3. Shi et al.



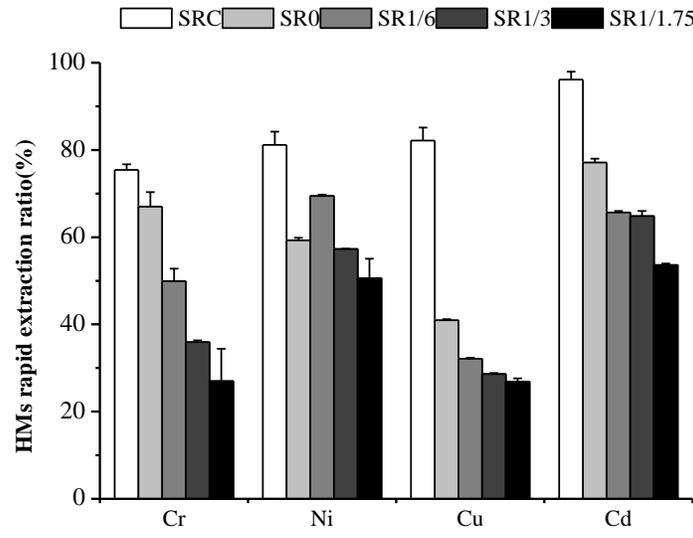
505

506

507

Fig. 4. Shi et al.

508



509

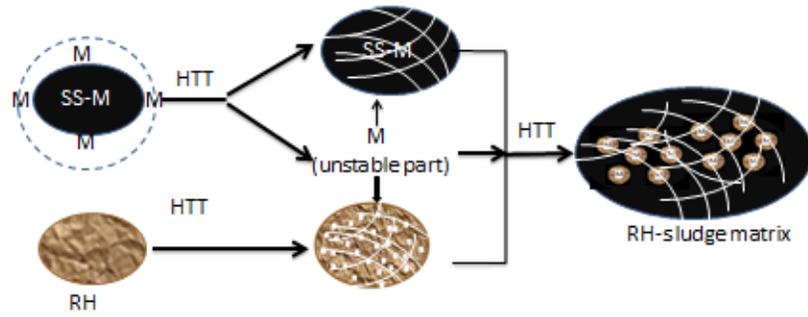
510

511

Fig. 5. Shi et al.

512

513



514

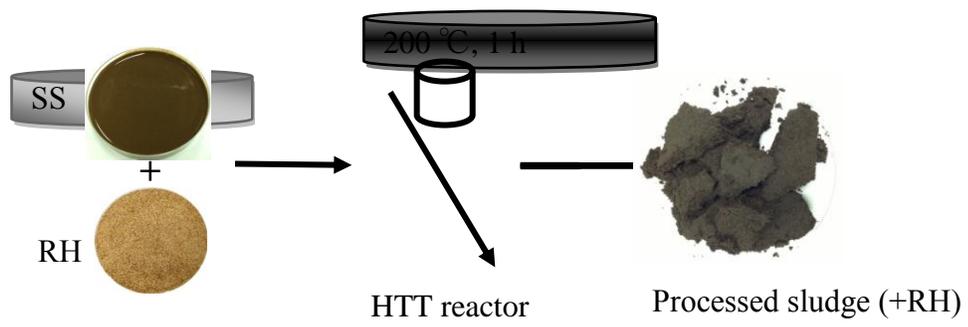
515

516

517

518

519



520

521

Fig. 6. Shi et al.

522