Bioresource Technology 102 (2011) 10346–10351

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Quantitative evaluation of heavy metals' pollution hazards in liquefaction residues of sewage sludge

Huajun Huang [a,b], Xingzhong Yuan [a,b,*], Guangming Zeng [a,b], Huina Zhu [a,b], Hui Li [a,b], Zhifeng Liu [a,b], Hongwei Jiang [a,b], Lijian Leng [a,b], Wenkai Bi [a,b]

[a] *College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China*
[b] *Key Laboratory of Environment Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, PR China*

ARTICLE INFO

Article history:
Received 17 June 2011
Received in revised form 26 August 2011
Accepted 29 August 2011
Available online 5 September 2011

Keywords:
Sewage sludge
Liquefaction residues
Heavy metals
Pollution level
Ecological risk

ABSTRACT

Liquefaction residues (LR) are the main by-products of sewage sludge (SS) liquefaction. This study quantitatively evaluates the potential ecological risk and pollution degrees of heavy metals (Pb, Zn, Cu, Cd, Cr and Ni) in LR versus SS. The leaching rates (R_1) of heavy metals in LR were much lower than those in SS, revealing that the mobility/leachability of heavy metals was well suppressed after liquefaction. Geo-accumulation index (I_{geo}) indicated that the liquefaction process significantly weakened the contamination degrees of heavy metals. Potential ecological risk index (RI) demonstrated that overall risks caused by heavy metals were obviously lowered from 1093.56 (very high risk) in SS to 4.72 and 1.51 (low risk) in LR1 and LR2, respectively. According to the risk assessment code (RAC), each tested heavy metal had no or low risk to the environments after liquefaction. In a word, the pollution hazards of heavy metals in LR were markedly mitigated.

1. Introduction

The broader application of activated sludge process in domestic and industrial wastewater treatment plants leads to a rapid increase of sewage sludge (SS) production (Tian et al., 2011). Generally speaking, the SS is viewed as a kind of typical pollution sources, such as odor, water pollution, veterinary hazards and contamination by heavy metals. On the other hand, it is also a species of potential bioresource for its high content of organic matters and substantial N and P concentrations. Therefore, it is very important to develop a proper technology which can combine material recycling and sludge disposal at the same time (Yuan et al., 2011). The common disposal processes for SS currently used are agricultural application, landfill and incineration. Such processes become more and more unacceptable due to land limitations and more restrictive legislation (Kim and Parker, 2008; Cao et al., 2010). Sludge incineration results in emissions that contain dioxins and heavy metals, while land application and landfill disposal raise similar concerns with the accumulation of heavy metals and toxic organic pollutants in soils and plants (Mondala et al., 2009).

Energy recovery from SS is recognized as the renewable strategy and technology with high potential towards sustainable development in the near future (Zuo et al., 2011). The liquefaction of SS is a thermal process which involves decomposing the sludge in the present of various solvents, leading to the production of gas, bio-oil and liquefaction residues (LR). This technology has generated significant interest in recent years due to its characteristics of both SS treatments and energy recovery (Xu and Lancaster, 2008; Huang et al., 2010; Li et al., 2010; Zhang et al., 2010; Vardon et al., 2011). The influences of diverse liquefaction parameters on the yields of products from the liquefaction of SS have been systematically investigated, such as the reaction temperature, the solid–liquid ratio (solid: SS, liquid: solvent), the type and dosage of catalyst, and the solvent filling ratio and so on. Meanwhile, some physical and chemical properties of gas and bio-oil have been studied in detail, too.

Bio-oils, which are refined to high quality hydrocarbon fuels, might have some advantages, such as the facilities of transport, storage, combustion and flexibility in marketing. Additionally, bio-oils are potential sources of light aromatics, such as benzene, toluene, and xylene, which command a higher market value than the raw oils (Tian et al., 2011). Xu and Lancaster (2008) reported that the dominant species in gas products is CO_2, followed by C_3 (propane + propylene), CO, CH_4, H_2 and C_2 (ethylene + ethane) species. In other words, the environmental quality of LR can be seen as the key point of whether the technology of SS liquefaction can bring secondary pollution problems. Specifically, whether the potential ecological risk and pollution level of heavy metals in SS can be mitigated after liquefaction are probably the main factors

---

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 731 88821413; fax: +86 731 88823701.

E-mail address: yxz@hnu.cn (X. Yuan).

0960-8524/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2011.08.117

to bear in mind. However, to the best of our knowledge, there have been very few studies focusing on this absolutely new problem/topic. Yuan et al. (2011) have determined the total concentrations and chemical speciation of heavy metals in LR of SS and qualitatively analyzed their risk to the environments. To obtain more comprehensive understanding of this new topic, it is necessary to systematically conduct quantitative evaluation of heavy metals' pollution hazards in LR, which is just the issue discussed in depth in the present paper.

Therefore, the driving force of this paper is to quantitatively evaluate the potential ecological risk and pollution degrees of heavy metals in LR of SS on the basis of their chemical speciation distribution (Yuan et al., 2011). This study was focused on: (1) determining the leachable metal concentrations according to the toxicity characteristic leaching procedure (TCLP); (2) evaluating the metal contamination degrees by geo-accumulation index (I_{geo}); (3) assessing the potential ecological risk caused by metals with the aid of risk assessment code (RAC) and potential ecological risk index method (RI). For a comparative purpose, the same analyses were carried out on SS.

2. Methods

2.1. Sample preparation

Sewage sludge sample and two kinds of liquefaction residue samples were prepared according to the methods mentioned by Yuan et al. (2011). Dewatered sewage sludge sample was obtained from a sewage plant in Changsha City, Hunan Province. Two kinds of liquefaction residue samples were collected from the study on conversion of SS to bio-oil products by thermochemical liquefaction (Huang et al., 2010). The first kind of liquefaction residue sample (LR1) was obtained when SS was liquefied at 593 K in a 1000 mL GSHA-1 type autoclave with solid–liquid ratio 1/20 (acetone as the solvent), solvent filling ratio 20% and without catalyst. The second kind of liquefaction residue sample (LR2) was obtained when SS was liquefied at 593 K with solid–liquid ratio 1/20 (acetone as the solvent), solvent filling ratio 20% and 0.5 g of NaOH as the catalyst.

Meanwhile, some physicochemical analyses of the LR and SS samples were also conducted, including the content of organic matters and ash (proximate analysis), the elemental compositions (ultimate analysis), electronic conductivity (EC) and pH. Specific analysis methods and results can be found in Yuan' paper (Yuan et al., 2011).

All chemicals used were of analytical reagent grade. Freshly prepared daily-diluted solutions were prepared using deionized water. All glassware and plastic containers were washed with 15% nitric acid solution and rinsed thoroughly with deionized water.

2.2. Experiments

The toxicity characteristic leaching procedure (TCLP) (Nair et al., 2008; Wang et al., 2008) was designed to simulate the leaching of heavy metals from the SS and LR samples. The dried SS or LR samples were mixed thoroughly with the requisite amount of deionized water using a mixer. TCLP leaching of SS and LR was carried out by extracting (liquid-to-solid ratio, 20:1) using glacial acetic-acid solution (pH = 2.8) as medium. The SS and LR samples along with leaching fluid were placed in a rotatory shaker and shaken at 120 revs (per min) for 20 h. Then the samples were filtered and analyzed for heavy metals.

The concentrations of Cu, Zn, Pb, Cd, Cr and Ni in all extracts were determined by atomic absorption spectrophotometer (ASS, Hitachi Z-2000). Each experiment was conducted in triplicate. The results reported in this study were the average values with standard deviation.

2.3. Contamination assessment methodology

2.3.1. Geo-accumulation index (I_{geo})

Pollution levels of heavy metals in SS and LR could be characterized by the geo-accumulation index (I_{geo}) put forward by Müller (1969). This contamination assessment index was commonly cited by researchers in environmental studies (Abrahim and Parker, 2008; Lu et al., 2009; Shi et al., 2010), and can be defined as the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \tag{1}$$

where C_n: the measured content of individual heavy metal in SS and LR; B_n: the background or pristine value of individual heavy metal (Table 1); 1.5: the constant factor introduced to analyze natural fluctuations in the contents of a given substance in the environment and very small anthropogenic influences. Seven classes of the geo-accumulation index are shown in Table 2 (Müller, 1981).

2.3.2. Potential ecological risk index (RI)

The assessment of ecological risks of heavy metals in SS and LR was carried out using the potential ecological risk index (RI) proposed by Hakanson (1980). RI method covers a variety of researching domains, i.e. biological toxicology, environmental chemistry as well as ecology, and can evaluate ecological risks caused by heavy metals comprehensively (Shi et al., 2010; Sun et al., 2010). The calculating methods of RI are listed below.

$$C_f^i = \frac{C_D^i}{C_R^i} \tag{2}$$

$$E_r^i = T_r^i \times C_f^i \tag{3}$$

$$\mathrm{RI} = \sum_{i=1}^{n} E_r^i \tag{4}$$

where C_f^i: the single heavy metal pollution index; C_D^i: concentration of individual heavy metal in samples; C_R^i: the reference value for heavy metals defined as B_n; E_r^i: the monomial potential ecological risk factor; T_r^i: the heavy metal toxic response factor. The values for each element are in the order of Zn = 1 < Cr = 2 < Cu = Ni = Pb = 5 < Cd = 30 (Hakanson, 1980); RI: the potential ecological risk caused by the overall contamination. Five categories of E_r^i and four classes of RI were defined, as shown in Table 3 (Ren et al., 2007).

Soil background values in Hunan Province (China) were selected as the reference in assessment of toxic metal pollution. To accurately describe the pollution degree and potential ecological risk of heavy metals in SS and LR, the content of individual heavy metal distributed in mobile fractions, instead of each heavy metal's total concentration, was adopted as the measured value during the calculation of I_{geo} and RI (Ren et al., 2007). The concentrations of heavy metals bound to mobile fractions, including acid soluble/exchangeable fraction (F1) and reducible fraction (F2), were determined using the BCR three-step procedure proposed by Standards, Measurements and Testing (SM&T) Programme of European Commission (Yuan et al., 2011). And the analysis results of mobile heavy metals content are listed in Table 1. The bioavailable fraction was defined as the sum of F1 and F2. In addition, the non-bioavailable fraction consisting of oxidizable fraction (F3) and residual fraction (F4) was analyzed through the BCR three-step procedure, too (Yuan et al., 2011).

Table 1
Concentrations of heavy metals in bioavailable and non-bioavailable fractions (mg/kg).

Sample	Cu		Zn		Pb		Cd		Cr		Ni	
	Bio[a]	Nbio[b]	Bio	Nbio	Bio	Nbio	Bio	Nbio	Bio	Nbio	Bio	Nbio
SS	54.7 ± 2.5[c]	505.8 ± 21.9	1006.0 ± 9.6	420.8 ± 12.5	–	119.1 ± 5.9	2.8 ± 0.1	2.4 ± 0.3	–	74.8 ± 3.8	48.0 ± 2.4	33.0 ± 1.1
LR1	–[d]	992.9 ± 26.1	418.0 ± 14.0	1696.5 ± 33.2	–	214.7 ± 12.5	–	9.6 ± 0.6	–	147.2 ± 13.0	–	123.3 ± 9.5
LR2	–	988.7 ± 20.8	134 ± 6.4	1875.8 ± 38.2	–	199.9 ± 6.0	–	9.2 ± 1.4	–	148.8 ± 15.8	–	112.0 ± 6.4
BV[e]	25.4		88.6		27.3		0.079		64.9		29.4	

[a] Bioavailable fraction.
[b] Non-bioavailable fraction.
[c] Results are expressed as the mean ± standard deviations.
[d] Below the detection limits.
[e] Background values of Hunan Province.

Table 2
Pollution grades of geo-accumulation index (I_{geo}) of heavy metals.

I_{geo} class[a]	I_{geo} value	Quality
0	$I_{geo} \leqslant 0$	Uncontaminated (UC)
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated (UMC)
2	$1 < I_{geo} < 2$	Moderately contaminated (MC)
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated (MHC)
4	$3 < I_{geo} < 4$	Heavily contaminated (HC)
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated (HEC)
6	$5 < I_{geo}$	Extremely contaminated (EC)

[a] Müller (1981).

Table 4
Risk assessment code (RAC)[a].

Category	Risk	Metal in carbonate and exchangeable fractions (%)
I	No risk (NR)	<1
II	Low risk (LR)	1–10
III	Medium risk (MR)	11–30
IV	High risk (HR)	31–50
V	Very high risk (VHR)	>50

[a] Sundaray et al. (2011).

Table 5
Leachable metal concentrations based on TCLP test.

Sample	TCLP (mg/kg)					
	Cu	Zn	Pb	Cd	Cr	Ni
SS	12.17 ± 0.10[a]	87.38 ± 0.80	–[b]	0.28 ± 0.08	–	1.68 ± 0.08
LR1	1.95 ± 0.08	17.93 ± 0.81	–	0.23 ± 0.03	–	1.07 ± 0.18
LR2	1.27 ± 0.15	6.83 ± 0.58	–	–	–	1.42 ± 0.08
Threshold values[c]	–[d]	5.0	5.0	1.0	5.0	5.0

[a] Results are expressed as the mean ± standard deviations.
[b] Below the detection limits.
[c] Nair et al. (2008).
[d] Not enlisted.

2.3.3. Risk assessment code (RAC)

A risk assessment code (RAC) was also applied to estimating the environmental risk associated with heavy metal pollution in SS and LR. This method was widely used by several authors for evaluation of heavy metal pollution in sediments or soils (Liu et al., 2008; Rodríguez et al., 2009; Sundaray et al., 2011). RAC assesses the availability of metals by applying a scale to the percentage of metals present in F1. This is important because this fraction introduced by anthropogenic activities is typified by the adsorptive, exchangeable and bound to carbonate fractions, which are weakly bonded metals that could equilibrate with the aqueous phase and thus become more rapidly bioavailable (Sundaray et al., 2011). The classification of risk has been categorized in terms of risk assessment code (RAC) and is tabulated in Table 4. There is no risk when the proportion of metals in F1 is lower than 1%, low risk for a range of 1–10%, medium risk for a range of 11–30%, high risk from 31% to 50% and very high risk for higher F1 percentages (Rodríguez et al., 2009).

3. Results and discussion

3.1. Leachable metal concentrations based on TCLP

Leachable metal concentrations determined with the TCLP test of SS and LR are given in Table 5. The results indicated that the metal concentrations in the leachate extracted from SS were 12.17, 87.38, 0.28 and 1.68 mg/kg for Cu, Zn, Cd and Ni, respectively. The leaching content of Cd and Ni were under the threshold values, while that of Zn exceeded the threshold value by about sixteen times. Meanwhile, Pb and Cr were not detected in the leachate derived from both SS and LR. However, the content of TCLP extractable heavy metals (Cu, Zn, Cd and Ni) in LR declined. Especially, leachable Zn concentrations were reduced from 87.38 mg/kg in SS to 17.93 and 6.83 mg/kg in LR1 and LR2, respectively. But they were still beyond the limit value for Zn (5.0 mg/kg). Therefore, Zn still had a potential risk to the environments.

Table 3
Indices and grades of potential ecological risk (RI) of heavy metal contamination.

Grade[a]	E_r^i value	Grades of ecological risk of single metal	RI value	Grades of potential ecological risk of the environment
A	$E_r^i < 5$	Low risk (LR)	RI < 30	Low risk (LR)
B	$5 \leqslant E_r^i < 10$	Moderate risk (MR)	30 ⩽ RI < 60	Moderate risk (MR)
C	$10 \leqslant E_r^i < 20$	Considerable risk (CR)	60 ⩽ RI < 120	Considerable risk (CR)
D	$20 \leqslant E_r^i < 40$	High risk (HR)	RI ⩾ 120	Very high risk (VHR)
E	$E_r^i \geqslant 40$	Very high risk (VHR)		

[a] Ren et al. (2007).

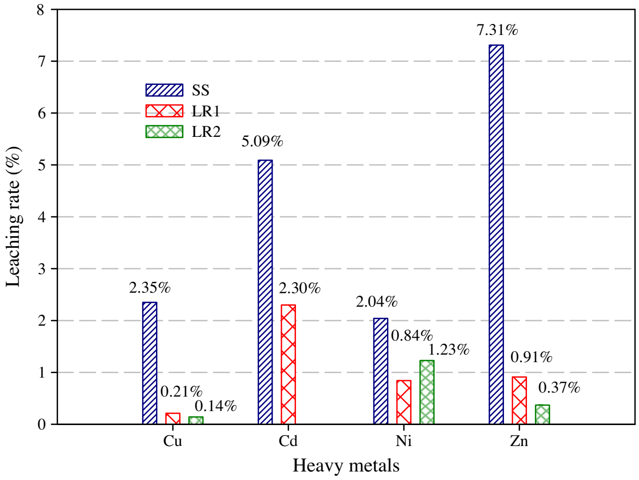

Fig. 1. The leaching rate of heavy metals in SS and LR.

The leaching rate (R_1) of heavy metals was proposed as one indicator for investigating the proportions of heavy metals bound to leachable fraction. R_1 was defined as the ratio of the leaching content of individual heavy metal to the total concentrations of each heavy metal. It can be calculated as follows:

$$R_1(\%) = \frac{LC_X}{TC_X} \times 100 \tag{5}$$

where X: one kind of heavy metal; LC_X: the leaching content of heavy metals (mg/kg) (Table 5); TC_X: the total concentrations of heavy metals (mg/kg) (Yuan et al., 2011).

As shown in Fig. 1, the leaching rates of heavy metals in LR were much lower than those in SS, which indicated that the release of heavy metals was well suppressed after liquefaction. These results can be explained by the fact that after liquefaction, the mobile and easily available heavy metal fractions (F1 and F2) were mainly transformed into the relatively stable heavy metal fractions (F3 and F4) (Yuan et al., 2011). As clearly shown in Table 1, the content of heavy metals associated with bioavailable fraction was significantly reduced after liquefaction. And an opposite trend was observed for the concentrations of heavy metals bound to non-bioavailable fraction.

3.2. Contamination degree based on I_{geo}

Geo-accumulation method I_{geo} was used to calculate metal contamination degrees in SS and LR. The I_{geo} results for heavy metals (Cu, Zn, Pb, Cd, Cr and Ni) in SS and LR are presented in Table 6. All of the I_{geo} values for Pb and Cr in both SS and LR were below 0, meaning uncontaminated level. In terms of SS, the I_{geo} values for heavy metals were in the increasing order of Ni (0.12) < Cu (0.52) < Zn (2.95) < Cd (4.65). It was implied that Ni and Cu none-moderately contaminated SS, while Zn polluted SS moderately-heavily and Cd heavily-extremely contaminated SS. Compared with I_{geo} numbers in SS, the values of LR were generally lower, showing lighter metal pollution in LR. Except Zn, I_{geo} values for Cu, Pb, Cd, Cr and Ni in LR were all under 0, corresponding to uncontaminated grade. Meanwhile, I_{geo} values for Zn were 1.65 and 0.01 in LR1 and LR2, respectively. It was indicated that Zn still polluted LR1 moderately, while LR2 was none-moderately contaminated by Zn.

On the whole, the pollution degrees of heavy metals were all mitigated after liquefaction. Cd in SS was classified as heavily-extremely polluted degree, but in LR, uncontaminated grade was suggested. The contamination degrees of Cu and Ni were transformed from none-moderately polluted grade to uncontaminated rank after liquefaction. Furthermore, the liquefaction process also relieved the pollution level of Zn. In SS, it belonged to moderately-heavily polluted class, but became moderately or none-moderately contaminated ranks in LR.

3.3. Potentially ecological risk assessment based on RI

The ecological risk assessment results of heavy metals in SS and LR are also listed in Table 6. It was found that the risk indices (E_r^i) of heavy metals in SS were ranked in the following order: Ni < Cu < Zn < Cd. E_r^i values for Cu and Zn were 10.76 and 11.35, respectively, revealing considerable risk. As regards Ni, E_r^i value was 8.16, indicating moderate risk. The monomial ecological risk

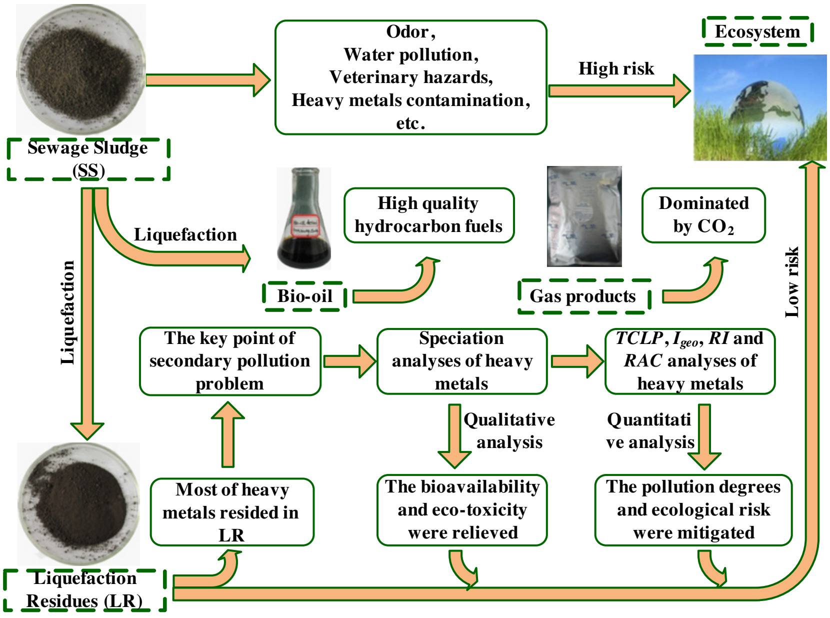

Fig. 2. Comprehensive evaluation of heavy metals' pollution hazards in LR of SS.

Table 6
Quantitative assessment results of heavy metals' pollution degrees and ecological risk in SS and LR.

Sample	Item	Heavy metals					
		Cu	Zn	Pb	Cd	Cr	Ni
SS	I_{geo}	0.52/UMC	2.95/MHC	<0/UC	4.56/HEC	<0/UC	0.12/UMC
	RAC	1.28/LR	23.13/MR	<1/NR	<1/NR	<1/NR	32.09/HR
	E_r^i	10.76/CR	11.35/CR	<5/LR	1063.29/VHR	<5/LR	8.16/MR
	RI	1093.56/VHR					
LR1	I_{geo}	<0/UC	1.65/MC	<0/UC	<0/UC	<0/UC	<0/UC
	RAC	<1/NR	6.9/LR	<1/NR	<1/NR	<1/NR	<1/NR
	E_r^i	<5/LR	4.72/LR	<5/LR	<5/LR	<5/LR	<5/LR
	RI	4.72/LR					
LR2	I_{geo}	<0/UC	0.01/UMC	<0/UC	<0/UC	<0/UC	<0/UC
	RAC	<1/NR	1.54/LR	<1/NR	<1/NR	<1/NR	<1/NR
	E_r^i	<5/LR	1.51/LR	<5/LR	<5/LR	<5/LR	<5/LR
	RI	1.51/LR					

of Cd in SS (1063.29) denoted very high risk to the environments, which should be given rise to wide-spread concerns. However, in LR, the E_r^i values for Cu, Pb, Cd, Cr and Ni were all below five, suggesting no or low risk to the local ecosystem. Zn E_r^i values were 4.72 and 1.51 in LR1 and LR2, respectively. That was to say that Zn posed a low risk to the environments.

In order to quantitate the overall potential ecological risk of heavy metals in SS and LR, RI was calculated as the sum of the all six risk factors. Descriptive statistics of RI are summarized in Table 6, too. The RI of heavy metals in SS was as high as 1093.56, corresponding to very high risk. In other words, environmental pollution problems caused by heavy metals will be produced if SS is directly discharged to the environments without any pretreatment. It is interesting that the LR, as major by-product of SS liquefaction, had a much lower RI values (LR1: 4.72, LR1: 1.51), indicating low risk to the environments.RI could characterize sensitivity of local ecosystem to the toxic heavy metals and represent ecological risk resulted from the overall contamination (Shi et al., 2010). In SS, the element of Cd accounted for most of the total risks, which was followed by Zn, Cu and Ni. It can be concluded that the high ecological risk of SS was primarily dominated by metal of Cd.

3.4. Environmental risk assessment based on RAC

Table 6 presents the environmental risk assessment results according to RAC. It can be seen that the percentages of heavy metals in SS associated with the exchangeable and carbonate-bound fraction (F1) varied in the order of Ni (32.09%) > Zn (23.13%) > Cu (1.28%). In detail, Zn and Cu came under medium and low risk category, respectively. And Ni posed high risk to the ecosystem. The environmental risk values for Pb, Cd and Cr in both SS and LR were all less than 1, reflecting no risk to the environments. In addition, Ni and Cu in LR both came under no risk rank in contrast with their higher risk values in SS. However, Zn in LR still had a low risk, which was consistent with those evaluation conclusions made for Zn on the basis of other methodologies (TCLP, I_{geo} and RI).

3.5. Comparisons of assessment results based on I_{geo}, RI and RAC

As shown in Table 6, the comparisons of assessment results according to I_{geo}, RI and RAC indicated that there were several disagreements among the three classifications of heavy metal pollution in SS and LR. From the results of geo-accumulation evaluation, Cu in SS samples was classified as the none-moderately contaminated degree. However, ecological risk caused by Cu was considerable due to its high toxicity. Furthermore, according to I_{geo}, Ni in SS samples ranked in the none-moderately contaminated degree. However, Ni had a high risk based on RAC for its high percentages of acid soluble/exchangeable fraction (F1). The monomial ecological risk of Ni denoted moderate risk because of its high toxicity. Moreover, Cd in SS was considered to be no risk to the environments in the light of RAC. Some significantly opposite results were obtained that Cd polluted the SS samples heavily-extremely and had a very high risk to the ecosystem in accordance with I_{geo} and RI, respectively.

Thus it can be seen that I_{geo} method mainly focused on the accumulation levels of individual metal without regard to the toxic response factor. Potential ecological risk index could describe both ecological risk caused by single pollutant and overall risk or contamination from varied pollutants (Shi et al., 2010). Meanwhile, the classification of RAC only considered the percentages of F1 ignoring the proportions of reducible fraction (F2). In contrast with RAC, both I_{geo} and RI paid attention to the amounts of metals bound to F2. Thus, all of three assessment methods should be integrated when the environmental quality was evaluated. Consequently, more comprehensive and accurate assessment results can be gotten.

All of these assessment results including speciation analyses of heavy metals in previous work (Yuan et al., 2011) are summarized in Fig. 2. The heavy metals' pollution hazards in LR have been comprehensively evaluated from both qualitative and quantitative aspects. A consistent conclusion could be made that this liquefaction technology not only converts SS into target product (bio-oil), but also mitigates the mobility of heavy metals resulting in no or low risk to the local ecosystem. Rational explanations for the substantial decrease in heavy metals' bioavailability might be that the physicochemical properties of LR were markedly different from those of SS. Specifically, the changes in pH, EC and organic matter content (Yuan et al., 2011) might be reasons for the immobilization of heavy metals. In addition, liquefaction is a thermal process, which may enhance the transformation of thermodynamically unstable fractions, such as the reducible fraction (F2).

3.6. Comparisons between LR1 and LR2

NaOH was adopted as a kind of catalyst for enhancing the conversion of SS to bio-oil during liquefaction process (Huang et al., 2010). Comparisons of evaluation results between LR1 and LR2 indicated that the addition of NaOH also had an influence on the ecological risk and pollution degree of heavy metals. Compared with LR1, the leaching rates (R_1) of Cu, Cd and Zn in LR2 were further reduced. Accordingly, lower I_{geo}, RAC and E_r^i values for Zn in LR2 were obtained, which suggested lower pollution degree and ecological risk. With respect to Ni, an opposite trend was observed.

The R_1 of Ni in LR2 was higher than that in LR1. The possible explanation for these differences might be that the addition of NaOH changed the distribution of heavy metals' speciation and physicochemical properties of LR including pH and EC (Yuan et al., 2011). The species of catalyst needs to be further investigated for finding some ideal catalysts which could enhance the conversion of SS into bio-oil and immobilization of heavy metals at the same time.

4. Conclusions

Obvious decrease in leaching rates (R_1) of heavy metals indicated that the liquefaction process well suppressed the mobility/leachability of heavy metals. According to I_{geo} results, the pollution degrees of heavy metals were significantly relieved after liquefaction. The overall risk index caused by the six toxic metals in SS was 1093.56, revealing very high risk. However, in terms of LR, only low risk was suggested. The environmental risk values of heavy metals based on RAC were lowered to a relatively safe level. Attention should also be paid to the fact that Zn still had a low risk to the environments.

Acknowledgements

This research was supported by the Key Project for Science and Technology Research, Ministry of Education of China (No. 108100), the National Natural Science Foundation of China (No. 50978087), the Hunan University Graduate Education Innovation Project (531107011019), and the Hunan Province Innovation Foundation for Postgraduate (CX2010B157).

References

Abrahim, G., Parker, R., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ. Monit. Assess. 136, 227–238.

Cao, J.P., Zhao, X.Y., Morishita, K., Wei, X.Y., Takarada, T., 2010. Fractionation and identification of organic nitrogen species from bio-oil produced by fast pyrolysis of sewage sludge. Bioresour. Technol. 101, 7648–7652.

Hakanson, L., 1980. Ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975–1001.

Huang, H.J., Yuan, X.Z., Zeng, G.M., Li, H., You, Q., Zhou, M., 2010. Thermochemical liquefaction characteristics of sewage sludge in the sub- and supercritical acetone. China Environ. Sci. 30 (2), 197–203 (in Chinese).

Kim, Y., Parker, W., 2008. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. Bioresour. Technol. 99, 1409–1416.

Liu, H.L., Li, L.Q., Yin, C.Q., Shan, B.Q., 2008. Fraction distribution and risk assessment of heavy metals in sediments of Moshui Lake. J. Environ. Sci. 20, 390–397.

Lu, X., Li, L., Wang, L., Lei, K., Huang, J., Zhai, Y., 2009. Contamination assessment of mercury and arsenic in roadway dust from Baoji. China Atmos. Environ. 43, 2489–2496.

Li, H., Yuan, X.Z., Zeng, G.M., Huang, D.L., Huang, H.J., Tong, J.Y., You, Q., Zhang, J.C., Zhou, M., 2010. The formation of bio-oil from sludge by deoxy-liquefaction in supercritical ethanol. Bioresour. Technol. 101, 2860–2866.

Müller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. GeoJournal 2, 108–118.

Müller, G., 1981. Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chem. Ztg. 105, 157–164.

Mondala, A., Liang, K., Toghiani, H., Hernandez, R., French, T., 2009. Biodiesel production by *in situ* transesterification of municipal primary and secondary sludges. Bioresour. Technol. 100, 1203–1210.

Nair, A., Juwarkar, A.A., Devotta, S., 2008. Study of speciation of metals in an industrial sludge and evaluation of metal chelators for their removal. J. Hazard. Mater. 152, 545–553.

Ren, F.M., Zhou, Y.S., Niu, M.C., Xu, Z.Y., 2007. Characteristics analysis and environmental assessment on heavy metals in the sludge of sewage. J. Beijing Jiaotong University 31 (1), 102–105 (in Chinese).

Rodríguez, L., Ruiz, E., Alonso-Azcárate, J., Rincón, J., 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. J. Environ. Manage. 90, 1106–1116.

Shi, G., Chen, Z., Bi, C., Li, Y., Teng, J., Wang, L., Xu, S., 2010. Comprehensive assessment of toxic metals in urban and suburban street deposited sediments (SDSs) in the biggest metropolitan area of China. Environ. Pollut. 158, 694–703.

Sun, Y.B., Zhou, Q.X., Xie, X.K., Liu, R., 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang. China. J. Hazard. Mater. 174, 455–462.

Sundaray, S.K., Nayak, B.B., Lin, S., Bhatta, D., 2011. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments – A case study: Mahanadi basin. Indian J. Hazard. Mater. 186, 1837–1846.

Tian, Y., Zuo, W., Ren, Z.Y., Chen, D.D., 2011. Estimation of a novel method to produce bio-oil from sewage sludge by microwave pyrolysis with the consideration of efficience and safety. Bioresour. Technol. 102, 2053–2061.

Vardon, D.R., Sharma, B.K., Scott, J., Yu, G., Wang, Z.C., Schideman, L., et al., 2011. Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anerobic sludge. Bioresour. Technol. 102, 8295–8303.

Wang, X.J., Chen, L., Xia, S.Q., Zhao, J.F., 2008. Changes of Cu, Zn, and Ni chemical speciation in sewage sludge co-composted with sodium sulfide and lime. J. Environ. Sci. 20, 156–160.

Xu, C.B., Lancaster, J., 2008. Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. Water Res. 42, 1571–1582.

Yuan, X.Z., Huang, H.J., Zeng, G.M., Li, H., Wang, J.Y., Zhou, C.F., Zhu, H.N., Pei, X.K., Liu, Z.F., Liu, Z.T., 2011. Total concentrations and chemical speciation of heavy metals in liquefaction residues of sewage sludge. Bioresour. Technol. 102, 4104–4110.

Zhang, L.H., Xu, C.B., Champagne, P., 2010. Energy recovery from secondary pulp/paper-mill sludge and sewage sludge with supercritical water treatment. Bioresour. Technol. 101, 2713–2721.

Zuo, W., Tian, Y., Ren, N.Q., 2011. The important role of microwave receptors in biofuel production by microwave-induced pyrolysis of sewage sludge. Waste Manage. 31, 1321–1326.