

Ceramsite preparation from sea sludge with sewage sludge biochar and its environmental risk assessment

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Abstract. Ceramsite were produced from sea sludge (SS) by adding different percentage of sewage sludge biochar (SSB). The characteristics of ceramsite including micrograph and elementary composition were analyzed. In addition, the heavy metals (HMs) fractions, leaching behaviour and potential environmental risk were also investigated. The microstructure of the ceramsite was slit pores and the main elements of the ceramsite were Si, Al and O. The residual fraction (F4) of Cu, Cr and Cd in ceramsite with 100% SS (SS100) reached the maximum (100%, 99% and 100%, respectively), while F4 of Zn and Ni in ceramsite with 80% SS and 20% SSB (SS80) reached the top value of 99.5% and 98%. Moreover, the HMs of feedstock can be immobilized after sintering as ceramsite and the leached amounts of HMs in all ceramsite were much lower than that stated by GB 5085.3-2007. Furthermore, ceramsite preparation from sea sludge with sewage sludge biochar will not bring HMs contamination and potential ecological risk.

1. Introduction

With the development of marine economy in coastal areas, a large amount of sea sludge (SS) has been generated from rapid construction of coastal ports, channel and estuary dredging since 1988 in China. The traditional methods for disposing the SS are dumping in the sea and stacking on the ground. The dumping of SS is a prevalent choice and more than 100 million tons of SS has been poured into the broad ocean since 2002 in China [1]. The improper disposition of SS may result in irreparable damage to the ocean environment. On the other hand, stacking SS on the ground not only takes up huge space, but also is a waste of resource. So it is urgent to find a feasible way to utilize the SS.

At the same time, there has been more than 60 million tons of sewage sludge (80% water content) produced since 2015 in China [2]. Increased concern about the environment has contributed to the development of new friendly technologies to minimize and reduce the environmental impact of sewage sludge. Pyrolysis technology, a thermal treatment process with mainly biochar production, has proved to be a promising method for reducing the volume of sewage sludge and destructing pathogens and organic pollutants in the sewage sludge [3, 4]. However, the high concentration of heavy metals (HMs) remained in the sewage sludge biochar (SSB) is a main factor impeding its application.

At present, it is a tendency to combine contamination control and utilization in the co-disposal of solid waste. Ceramics is considered to be one of the most promising and applied approaches for treating various hazardous wastes including sludge, slurries, contaminated soils, dusts and other



particulate matter because of its destroying organic matter and immobilizing HMs in a stable matrix. Previous research has reported that the SS as raw material can be used to produce ceramics [5]. On the other hand, we find that the SSB is mainly composed of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , K_2O , Na_2O and et al. [6], which is fit to adjust the composition of SS to prepare ceramsite. Recently, little work has been conducted to explore the mixing of SS with SSB as feedstock for producing ceramics and the migration of HMs in ceramsite.

In the present work, the SS by adding different percentage of SSB as feedstock was used to produce ceramsite. The change of HMs fractions and leaching characteristic before and after sintering as ceramsite was revealed, in turn the potential ecological risk of HMs in the ceramsite was assessed.

2. Materials and methods

2.1. Raw materials and ceramsite preparation

The sea sludge (SS) used in this study was obtained from Xinglin bay, Xiamen, Fujian province, China. The sewage sludge biochar (SSB) was produced at 600 °C for 30 min by pyrolyzing dewatered sewage sludge from the sludge pyrolysis production line in a wastewater treatment plant of Xiamen. The concentrations of HMs (Cr, Ni, Cu, Zn and Cd) are shown in table 1.

Table 1. Total concentrations of HMs in SS and SSB (mg/kg).

Items	Cr	Ni	Cu	Zn	Cd
SS	964.38	405.50	3205.00	6806.25	5.50
SSB	3939.00	1098.00	9341.00	6519.00	1.67

The SS and SSB were smashed and sieved through 100-mesh before mixing with 35 wt.% water. The SS was mixed with SSB at different mass ratio. The mixture was stirred and poured into a pelletizer to get raw pellets with the globule size of about 10 mm. The raw pellets were dried at 105 °C in an air oven for 3 hours before sending to sinter at 1075°C for 30 min in a chamber electric furnace (QSH-1700M-1010T, China). After cooling down in the furnace, the ceramsite with different SS: SSB (10:0, 8:2 and 4:6, respectively) were produced and named as SS100, SS80 and SS40, respectively. The micrograph and elementary composition were analyzed using scanning electron microscopy and X-ray energy dispersive spectrum (SEM-EDS, S-4800, Hitachi, Japan). The flow chart of ceramsite preparation is showed in figure1.

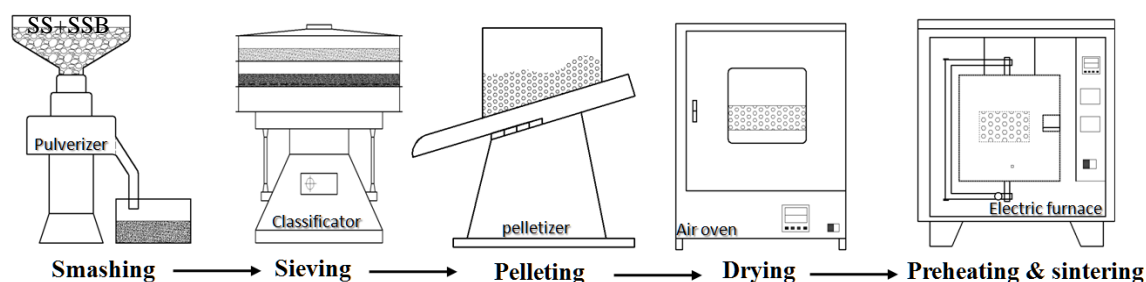


Figure 1. Flow chart of ceramsite preparation.

2.2. Fractionation and leaching procedure of HMs

The speciation of HMs (Zn, Cr, Ni, Cu and Cd) in raw material and ceramsite was analyzed by a three-step sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) which has been reported in a previous study [7]. A sequential acid soluble/exchangeable fraction (F1), a reducible fraction (F2), an oxidizable fraction (F3) and a residual fraction (F4) were obtained after extraction. The residual fractions and the total concentrations of metals in the samples were firstly digested in a microwave digestion system with an acid mixture (HNO_3 : HClO_4 : HF = 5: 5: 2, v/v) before detection [8].

The toxicity characteristics of HMs were determined by using the toxicity characteristic leaching procedure (TCLP). It is a standard method updated by USEPA for determining HMs leaching toxicity [4]. TCLP leachates of samples were extracted by a glacial acetic acid solution (pH: 2.88 and liquid/solid ratio: 20:1) in a shaking incubator (200 r/min) for 18 h and the liquid phase was subsequently separated by centrifugation at 4000 r/min.

All of the liquid phase samples were filtered through 0.45- μ m membrane filters before diluting to a constant volume with 2% HNO₃, and then stored in a refrigerator at 4 °C before analysis. The concentrations of Cu, Zn, Cr, Pb and Cd were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500cx, Agilent, USA).

2.3. Toxicity and ecological risk assessment of HMs

The chemical speciation of HMs is directly related to their bioavailability and eco-toxicity in the environment [9]. The non-residual fractions (F1, F2 and F3) of HMs had some toxicity to environment. F3 leaching in rigorous conditions (highly acidic conditions and oxidizing atmosphere), had potential toxicity and bioavailable fractionation (F1+F2) were easily prone to leaching, had directly toxicity [10]. Hence potential ecological risk index (*RI*) was used to assess the degree of potential risk of heavy metal pollution in SS and ceramsite. The equations are as follows [10]:

$$C_f = C_i/C_n \quad (1)$$

$$E_r = T_r C_f \quad (2)$$

$$RI = \Sigma E_r \quad (3)$$

Where C_f is the contamination factor of a heavy metal; C_i and C_n are the mobile (F1+F2+F3) and stable fractions (F4) of the heavy metals respectively; E_r is the potential ecological index for individual heavy metal; T_r is toxic factor of the individual heavy metal; RI is the potential ecological risk index of the solid (sea sludge/ceramsite). The T_r values used for calculation of potential ecological index of individual metal are Cr (2), Zn (1), Ni (6), Cu (5) and Cd (30). The indices for ecological risk assessment are shown in table 2.

Table 2. Indices for ecological risk assessment [10].

C_f	Metal contamination	E_r	Potential ecological risk	RI	Sea sludge/Ceramsite Contamination
$C_f < 1$	Clean	$E_r < 40$	Low	$RI \leq 50$	Low
$1 < C_f < 3$	Low	$40 \leq E_r < 80$	Moderate	$50 < RI \leq 100$	Moderate
$3 < C_f < 6$	Moderate	$80 \leq E_r < 160$	Considerable	$100 \leq RI < 200$	Considerable
$6 < C_f < 9$	Considerable	$160 \leq E_r < 320$	High	$RI > 200$	High
$C_f > 9$	High	$E_r \geq 320$	Very high		

3. Results and discussion

3.1. Characteristics of ceramsite

As shown in figure 2, it is evident that ceramsite can be generated successfully from SS by adding different percentages of SSB. Besides, the apparent appearance has some difference. The color of ceramsite changed from brown to black obviously when the SSB content increased from 0% to 60%. The surface of ceramsite with higher SSB content was more smooth and denser. It is probably caused by that the SSB is easier to be melt, and the adding of SSB may decrease the melting temperature of composition by adjusting the ratio of the elements. The contents of Ca and Mg increased with more SSB added (table 2), which probably narrows down the range of sintering temperature and reduces the expansibility of ceramsite [11]. The above results suggest that adding SSB probably makes the ceramsite easier to sinter, which will save energy during the producing ceramsite process. Furthermore, the microstructure was slit pores generated with the accumulation of lumps. It can be seen that the slit pores become less and bigger with increase of adding SSB, as well as the volume of the lumps. The

results can be explained by that the inorganic components in the mixture with higher SSB contents are much easier to melt, and then the melt phase will fill in the pores and integrate the lumps together [12].

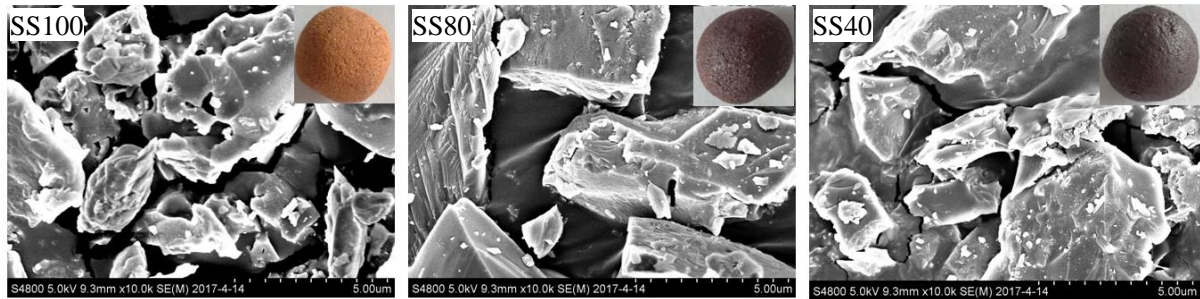


Figure 2. Apparent appearance and microstructure of ceramsite with different SS contents.

EDS was conducted to study the elementary composition of ceramsite surface (figure 3). The mass percents of various elements are given in table 3. The main elements of the ceramsite were Si, Al and O. And the mass percentage of Al fluctuated, and Si reduced with the elevation of SSB proportion. However, the content of O on the ceramsite surface rose after the adding SSB. There are some reductive elements (C, Fe and P et al.) in SSB which are obtained from pyrolysis [13], and the reductive elements may probably react with the O₂ during sintering process to increase the O content.

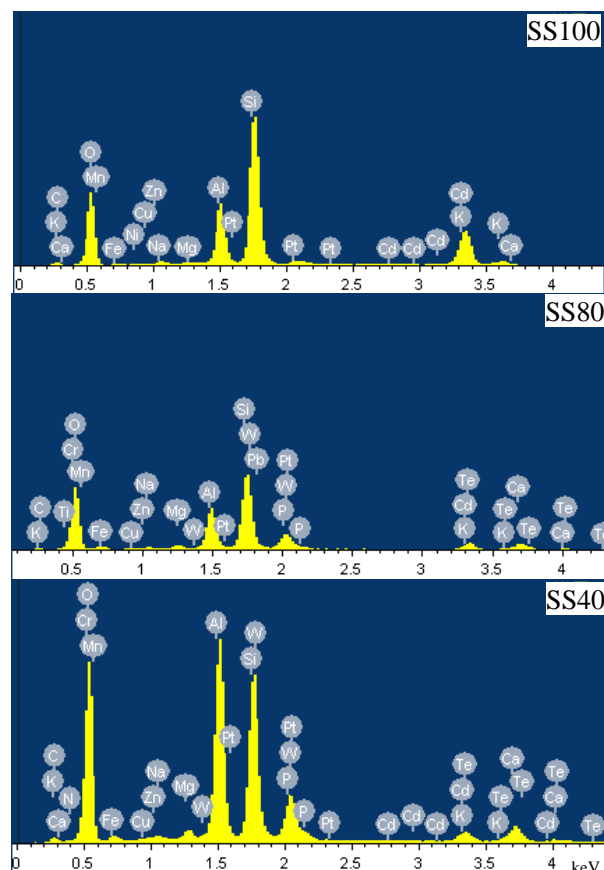


Figure 3. X-ray energy dispersive spectrum analysis of ceramsite with different SS contents.

Table 3. Elements on the surface of ceramsite with different SS contents (wt.%).

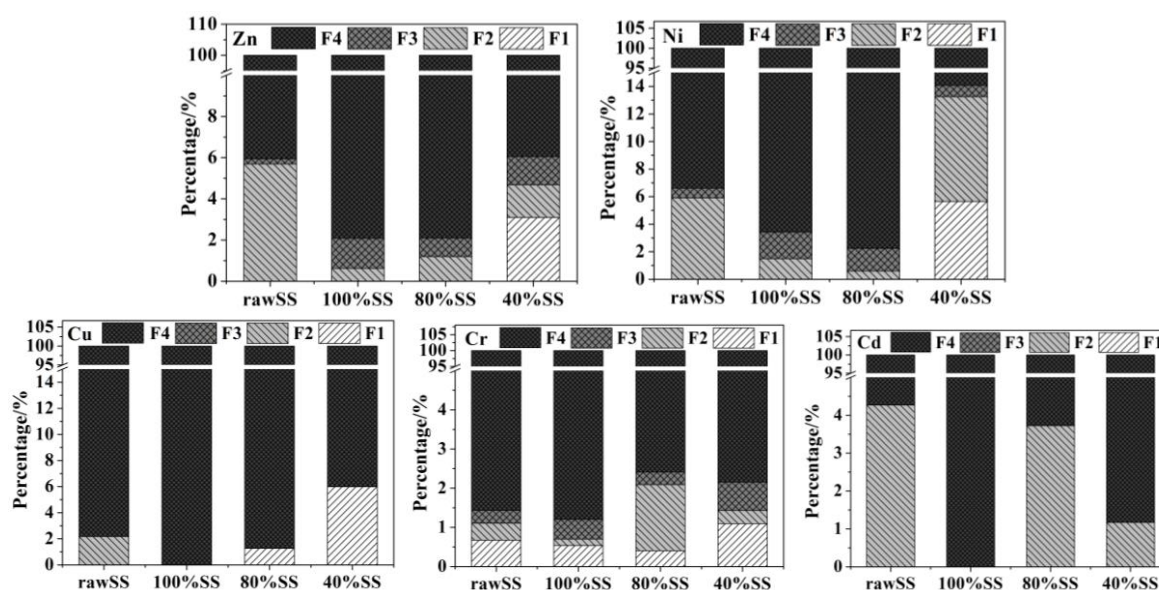
Items	C	O	Na	Mg	Al	Si	P	K	Ca	Cr	Mn	Fe	Cu	Zn	Cd
SS100	0.11	55.70	0.67	0.04	8.57	24.87	0.00	8.23	0.20	0.00	0.06	0.28	0.21	0.04	1.03
SS80	1.89	55.92	0.52	0.92	8.13	15.89	3.38	1.97	2.00	0.22	0.12	5.85	0.29	0.20	0.61
SS40	2.57	58.02	0.33	0.67	13.92	13.12	3.89	1.02	1.89	0.28	0.28	5.50	0.37	0.02	0.22

3.2. Speciation evolutions of HMs

The BCR method was used to explore the chemical speciation of Cu, Zn, Ni, Cd and Cr in this work. The HMs speciation distributions are shown in figure 4. The migration of chemical speciation of Zn and Ni exhibited the same tendency after sintering as ceramsite with increase of SSB contents. F4 of Zn and Ni elevated to the maximum after sintering as SS80, which was 99.5% and 98%, respectively. And then, the F4 decreased and the F1+F2 rose obviously when the SSB was added to 60%. The results indicate that high adding contents of the SSB can lead to the increase of unstable states proportion of Zn and Ni. The reason may be that there are some unstable states in the high concentration of Zn and Ni in the SSB [14]. 20% SSB adding in the SS had the best effect on the immobilization of Zn and Ni in the ceramsite.

As for Cu, the speciation in SS was mainly F4 fraction. After sintering as SS100, all the Cu existed as the form of F4 which was stable. While, with adding SSB in the raw material, the F1 of Cu appeared and increased to 5% in the SS40 probably due to the high content of Cu in the SSB (Table 1).

The Cr and Cd had similar change trend in chemical speciation. The migration tendency of chemical speciation of Cr and Cd fluctuated with the increase of SSB contents in raw material after sintering as ceramsite. The F4 of Cr and Cd in SS100 was 99% and 100%, which increased compared to the SS. In addition, with the change of SSB proportion from 0% to 60% in feedstock, the F4 elevated firstly and then declined. It can be explained that the feedstock with increase of SSB is easy to melt at high sintering temperature and tend to integrate after cooling down, which can enhance the ability preventing the Cr and Cd from being washed out. Literature has reported that Cd and Cr could be stabilized by means of replacing other elements in the structure of crystal phase in high sintering temperature [15].

**Figure 4.** HMs speciation distributions.

3.3. Leaching characterization of the HMs

Table 4 shows the TCLP leaching results of ceramsite, SS and SSB, and threshold values described in GB 5085.3-2007 of China [16]. For Zn, Ni and Cu, their leaching concentrations increased obviously with the elevation of adding SSB proportion due to the high leaching concentration of Zn, Ni and Cu in SSB (Table 1). As to Cr, the leaching concentration increased after sintering as SS100, and decreased with the SSB content increasing. One reason may be that the concentration of Cr in ceramsite is lower after adding SSB. Another reason is that the adding of SSB can enhance sintering and make ceramsite dense, leading to the prevention of Cr being washed out [17]. While the leaching concentration of Cd increased with the adding SSB proportion though the content Cd in SSB was less than those in SS. That is because Cd is easy to migrate with the melting phase, and most of Cd may be left on the surface of ceramsite for its low boiling point [18]. The Cd on the surface probably was unstable and leached easily, leading to the increase of its leaching concentration.

Compared with the threshold values recommended by the China standard named “identification standard for hazardous wastes-identification for extraction toxicity” (GB 5085.3-2007), it is concluded that the leaching amounts of HMs for all ceramsite were found to be much lower than the threshold values even though the leached amount of Cu and Zn in SSB (1784 and 1174 mg/kg) that exceeded the permissible limits. The results indicate that the ceramsite made from SS with SSB can be applied safely.

Table 4. Concentrations of HMs leached in TCLP tests (mg/kg).

Items	Zn	Ni	Cu	Cr	Cd
SSB	1174.00	12.71	1784.00	0.401	0.066
SS	0.00	0.18	0.00	4.21	0.12
SS100	0.00	0.00	0.00	8.38	0.01
SS80	0.02	0.00	30.64	4.73	0.05
SS40	113.03	11.38	119.83	3.73	0.09
GB 5085.3-2007	1000.00	50.00	1000.00	150.00	10.00

3.4. Toxicity and ecological risk assessment of HMs

The chemical speciation of HMs is directly related to their bioavailability and toxicity in the environment [9]. The C_f , E_r and RI were determined to identify the risk level of the metals in the SS, SS100, SS80 and SS40 (table 5). The C_f of Cu, Cr and Cd had the lowest values in SS100, and the minimums C_f of Zn and Ni were obtained in SS80. According to the HMs speciation distributions in figure 4, it can be found out that the C_f values of HMs in SS and ceramsite showed negative correlation with the F4 contents of HMs. The high content of F4 contributed to low C_f value of HMs. As for the E_r of HMs in SS and ceramsite, it had the same trend with C_f . The values of RI could clarify the potential ecological risk of SS and ceramsite which were obtained by adding the potential ecological index of each heavy metal. Compare to the SS, the RI values were much lower after sintering as SS100. Besides, the RI values increased with the adding amount of SSB increasing. It means that the addition of SSB may enhance the potential ecological risk of ceramsite due to the high concentration of HMs in it. The potential ecological risk of HMs in SS and ceramsite was found to follow the sequence SS> SS40>SS80>SS100.

Table 5. Ecological risk assessment of heavy metal toxicity.

Items	C_f					E_r					RI
	Zn	Ni	Cu	Cr	Cd	Zn	Ni	Cu	Cr	Cd	
SS	0.063	0.071	0.022	0.015	0.045	1.839	0.425	0.111	0.029	1.338	3.74
SS100	0.021	0.035	0.000	0.012	0.000	0.891	0.213	0.000	0.024	0.000	1.13
SS80	0.021	0.023	0.013	0.025	0.039	0.891	0.138	0.064	0.049	1.161	2.32
SS40	0.064	0.164	0.064	0.022	0.012	1.073	0.983	0.318	0.044	0.356	2.77

Based on the indices for the ecological risk assessment of C_f , E_r and RI in Table 2, although the values of C_f , E_r and RI in different ceramsite had some difference, the C_f values were lower than 1, the E_r values lower than 40 and the RI values were lower than 150 in ceramsite. It can be concluded that there is no metal contamination and potential ecological risk for ceramsite.

4. Conclusions

Ceramsite can be produced successfully from SS with different SSB addition. The adding of SSB can make the ceramsite easy to sinter and bring energy conservation during the production process. The microstructure of ceramsite was slit pore which became less and bigger with the increase of SSB content, and the main elements of the ceramsite were Si, Al and O. Compared to the SS, F4 of Cu, Cr and Cd were increased obviously to 100%, 99% and 100% in ceramsite of SS100. F4 of Zn and Ni reached to the relative maximum values of 99.5% and 98% after sintering as SS80. Moreover, the leached amounts of HMs in all of ceramsite were much lower than threshold values permitted by GB 5085.3-2007. Furthermore, the HMs risk in the SSB can be also weakened after sintering as ceramsite by mixing with SS as the feedstock. More importantly, ceramsite preparation from sea sludge with sewage sludge biochar will not bring HMs contamination and potential ecological risk and could be applied safely for environment.

Acknowledgment

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