

Research Article

Reduction and Heavy Metal Stabilization of River Sediment by Hydrothermal Treatment

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Received 7 May 2022; Revised 1 August 2022; Accepted 2 August 2022; Published 22 August 2022

Academic Editor: H C Ananda Murthy

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In this paper, hydrothermal treatment was used to treat river sediment. The physicochemical properties, chemical speciation, bioavailability, ecotoxicity, and leaching toxicity of heavy metals (Zn, Cu, Cr, Cd, Ni, Pb) in sediment under different hydrothermal treatment conditions were studied, and stabilization mechanisms of heavy metals were explained. The results showed that hydrothermal temperature and time had a huge impact on sediment reduction and heavy metal stabilization. The best reduction and stabilization of sediments were achieved at a hydrothermal temperature of 260°C and a hydrothermal period of 3 h. The hydrothermal treatment caused the sediment to undergo dehydration, dihydroxylation, decarboxylation, deamination, and aromatization with a gradual decrease in its H/C ratio, O/C ratio, and pH; a gradual increase in porosity and surface area; and a decrease in particle size. This facilitates the dehydration, reduction, and stabilization of the sediment. The bioavailable components of heavy metals in sediment were dramatically reduced following hydrothermal treatment, but the fraction of stable components rose significantly. This resulted in a marked decrease in the environmental bioavailability, ecotoxicity, and leaching toxicity of the heavy metals. Therefore, hydrothermal treatment might be an effective *ex situ* repairment way for reducing, stabilizing, and making river sediment harmless.

1. Introduction

Over the years, large volumes of industrial wastewater, domestic sewage, and agriculture-related sewage have been discharged into rivers [1, 2]. The pollutants in river water will be deposited into the sediment, making the sediment a “breeding ground” for water pollution. Meanwhile, sediments are also the “source” of pollution released to the overlying water [3]. It was reported that the release of nitrogen, phosphorus, and polycyclic aromatic hydrocarbons by river sediment will lead to eutrophication, and the presence of highly biotoxic heavy metals such as Zn, Cu, Cr, Cd, Ni, and Pb in river sediments will pose considerable toxicity threats to the ecosystem and human health when they migrate to water and soil [4, 5]. Therefore, there is an urgent need for the safe disposal of river sediments.

Current methods for the disposal of sediment include sediment dredging, acid washing, and chemical stabilization [6]. Sediment dredging is the most common practice in river sediment treatment, but it needs a very large land area to enable sediment filling. The river sediments are mainly composed of inorganic components with low calorific values that cannot be incinerated, which makes the disposal of the dredged sediment difficult [7]. Acid washing refers to technologies that use various acids to extract and precipitate the metals in the sediment [8]. Due to the complexity of the sediment components, the extract and precipitate reactions will always be complex and hard to regulate. In addition, the resulting secondary leachate is a hazardous waste and should be further disposed of. Chemical stabilization of heavy metals in sediments is primarily achieved by adding immobilizers and stabilizers, but there is still a chance that

the agents may fail and be released into the water column, reducing the stability effect [9].

Hydrothermal methods are chemical reactions carried out in a closed vessel with subcritical water as the solvent at a high temperature and pressure [10]. Hydrothermal heat can promote the dissolution of the dry sludge base, improve the dewatering properties of the sludge, and achieve sludge reduction [11]. In this process, pathogens and parasites can be killed, which will result in stabilization during the hydrothermal process [12]. Hydrothermal treatment can also change the morphology of heavy metals in sludge and promote their transformation from unstable to stable, thereby achieving stabilization and harmlessness of heavy metals in sludge. Many studies on the hydrothermal stabilization of heavy metals have been carried out by researchers. Huang et al. examined the danger of heavy metals in sludge after hydrothermal treatment to the environment, and the findings revealed [13] that the leaching rate of heavy metals in sludge was significantly reduced, as was the ecotoxicity. Shi looked into the movement of heavy metals in sludge after hydrothermal treatment and found [14] that the state of heavy metals such as Ni, Cr, Zn, Cu, Cd, and Pb in sludge changed from weakly bound to stable, and their ecological risk was greatly reduced. Li et al. [15] used subcritical water and supercritical water to gasify sludge and found that the bioavailability and ecotoxicity of heavy metals in the treated sludge were significantly reduced. In particular, the bioavailable content of Cu decreased by nearly 97%. Liu et al. [16] studied the distribution of heavy metals in the hydrothermal carbonization process of sewage sludge and found that hydrothermal treatment reduced the exchangeability/acid solubility and reduced states of heavy metals in the sludge, thus reducing the potential risk of heavy metals in the sludge. Those studies indicate that hydrothermal methods can significantly reduce the ecological risk of sludge land use [17]. At present, the research on hydrothermal technology mainly focuses on excess sludge, etc., and there are few reports of applying it to the treatment of river sediment. They have a great theoretical basis for the treatment of river sediments. The nature of river sediment is different from that of sludge, and it is of interest to further investigate the reducibility of hydrothermally treated river sediments, the stabilizing impact of heavy metals, and the associated mechanisms.

The goal of this research was to reveal the mechanisms of reduction of river sediments by an ex situ repairment way which is hydrothermal treatment and evaluate the bioavailability of heavy metals in river sediments after hydrothermal treatment. The effect of hydrothermal treatment on the physicochemical properties of river sediments was studied. Potential ecological risk indicators, environmental risk assessment indicators, and leaching toxicity are identified based on the chemical morphological distribution of heavy metals in the hydrothermal products. Besides, the behavior of heavy metals during hydrothermal treatment, as well as their migration and stabilization mechanisms, was also explored.

2. Materials and Methods

2.1. Experimental Materials. The river sediments utilized in the experiments came from a river in a district of Shanghai.

The dredged river sediment is stirred evenly and screened through 20 mesh screens to remove large stones, gravel, plant debris, and shellfish from the sediment. The sediment was collected in a refrigerator at a temperature of 4°C before being further processed and analyzed. The physicochemical characteristics of the river sediments were analyzed following centrifugation and freeze-drying prior to hydrothermal treatment.

2.2. Hydrothermal Experiment. The following steps were used to conduct hydrothermal experiments in this study: 60 g of river sediment (with around 85% moisture content) was placed into a YZHR 100 ml hydrothermal reaction kettle, and then, the sediment was heated to 180°C, 200°C, 220°C, 240°C, 260°C, and 280°C. After reaching the desired temperature, it was kept at 0.5 h, 1.5 h, 3 h, 4.5 h, 6 h, and 7.5 h. After the hydrothermal kettle cooled naturally to ambient temperature, the reactor was opened, the solid-liquid mixture was withdrawn for extraction, and the filtered solid-liquid combination was collected. The precipitated hydrothermal solid product was heated in an oven at 105°C for 12 hours before being placed in dry glassware for standby. The hydrolysate was put in a refrigerator below 4°C for standby. The original precipitate was denoted by RS, and the filtrate of the original precipitate was denoted by RL. The solid product after hydrothermal treatment was represented by HS, and “HS-Hydrothermal Temperature-Hydrothermal Time” represented the hydrothermal solid product of sediment under different conditions. The hydrolysate was denoted by HL, “HL-Hydrothermal Temperature-Hydrothermal Time,” representing the hydrolysate under different conditions. For instance, HS-180-3 represented the hydrothermal solid product of sediment obtained after hydrothermal treatment at 180°C for 3 h, while HL-180-3 represented the hydrolysate obtained by hydrothermal treatment of sediment at 180°C for 3 h.

2.3. Sample Processing and Analysis. An elemental analyzer (Elementar, Germany) was developed to analyze and determine the elemental (C, H, and N) content of the raw sediment and hydrothermal solid products. The ash content in the raw sediment and sediment hydrothermal solid products was determined by burning the sediment in a muffle furnace at 600°C. The elemental content of O was measured by the difference method [18], namely: $O\% = 100\% - C\% - H\% - N\% - \text{Ash}\%$. The chemical functional groups contained in the hydrothermal solid products of the original sediment and sediment were determined using a Nicolet 550 Fourier transform infrared spectrometer (Nicolet, USA). The specific surface area of the original sediment and the hydrothermal solid products of the sediment could be determined using the Brunauer-Emmett-Teller (BET) method. The surface morphology and structure of raw sediment and the hydrothermal solid products of the sediment were characterized by a scanning electron microscope (Zeiss Gemini SEM 300).

2.4. Determination Method of Organic Reduction Rate. The organic content of the original sediments was calculated as

follows:

$$m_3 = m_1 - m_2, \quad (1)$$

where m_1 is the mass of solid (S1) obtained after suction filtration dehydration and drying at 105°C, m_2 is the mass of solid (S1) burnt at 600°C in a muffle furnace to constant weight, and m_3 is the mass of organics contained in raw sediment.

The mass of organics in the hydrothermal solid product of the sediment was calculated as follows:

$$m_6 = m_4 - m_5, \quad (2)$$

where m_4 is the mass of solid (S2) obtained after suction filtration dehydration and drying at 105°C, m_5 is the mass of solid (S2) burnt at 600°C in a muffle furnace to constant weight, and m_6 is the mass of organics contained in raw sediment.

The organic reduction rate was calculated as follows:

$$\text{Organic reduction rate} = \frac{m_3 - m_6}{m_3} \times 100\%. \quad (3)$$

2.5. Analysis Method of Hydrothermal-Related Parameters. The chemical oxygen demand (COD) in the hydrolysate was determined analytically using the “dichromate method for determination of chemical oxygen demand in water quality” (HJ 828-2017). Inductively coupled plasma mass spectrometry (Thermo Scientific ICAP Q, USA) was used to assess the concentration of heavy metals and salt ions in the hydrolysate after it was filtered through a 0.45 μm membrane.

2.6. Analysis and Evaluation Methods of Heavy Metal

2.6.1. Determination of Total Amount and Form of Heavy Metals. Acid digestion [19] was used to determine the total amount of heavy metals Zn, Cu, Cr, Cd, Ni, and Pb in raw sediment and sediment hydrothermal solid products. The modified BCR four-step extraction method [20] was used to determine the forms of heavy metals Zn, Cu, Cr, Cd, Ni, and Pb in raw sediment and sediment hydrothermal solid products. Several procedures were used to continuously extract heavy metal components by the BCR method: exchangeable or acid-soluble components (T1), reducible components (T2), oxidizable components bound to organics and sulfides (T3), and residual components bound to the lattice (T4). Inductively coupled plasma mass spectrometry was used to determine the heavy metal content in the digestate.

2.6.2. Risk Evaluation Indicator. The environmental risks allied to heavy metals in the raw sediment and sediment hydrothermal solid products were evaluated by means of risk assessment codes (RAC), which are commonly utilized in the evaluation of heavy metal toxicity in the environmental sciences [21]. In this paper, the ratio of heavy metal content in exchangeable or acid soluble components (T1) to total heavy metals in primary sediments and sediment

hydrothermal solid products will be used as an evaluation indicator. The classification of the risk assessment indicator is as follows in Table 1.

2.6.3. Potential Ecological Risk Indicator. Potential ecological risk indicators (RI) [22] on the basis of heavy metal concentrations, toxicity, and sensitivity were utilized to study the potential ecological risk of heavy metal contamination in raw sediments and sediment hydrothermal solid products. The potential ecological risk indicator was calculated according to the following formulas.

$$\begin{aligned} C_f &= \frac{C_m}{C_n}, \\ E_r &= T_r \times C_f, \\ \text{RI} &= \sum E_r, \end{aligned} \quad (4)$$

where C_f is a single heavy metal pollution factor; C_m is the potential flow component of heavy metals (T1, T2, and T3); C_n is the stable component of heavy metals (T4); E_r is the potential ecological risk factor of a single heavy metal; T_r is the toxic reaction factor of a single heavy metal, of which Zn is 1, Cu and Pb are 5, Cr is 2, Cd is 30, and Ni is 6; and RI is the sum of potential ecological risk factors of pollutants.

The relationships between single heavy metal pollution factors, potential ecological risk factors, and potential ecological risk indicators with the degree of contamination are shown in Table 2.

2.6.4. Toxicity Leaching Test. The leaching concentrations of heavy metals in the sediments were measured according to the Toxicity Characteristic Leaching Procedure (TCLP) method of the US Environmental Protection Agency (EPA) [23]. A glacial acetic acid solution (pH = 2.88) was used as the leaching solution for the heavy metals, and a leaching experiment for the toxicity characterization of the raw sediment and sediment hydrothermal solid products was conducted on a leaching solution at a sample mass ratio of 20:1. The raw sediment and sediment hydrothermal solid products were mixed with the leaching solution and placed on an LCD CNC rotary mixer (MX RL Pro, Shanghai Shuangxu Electronics) and shaken at 30 r/min for 18 hours. At the end of the leaching procedure, the supernatant will be obtained by filtration. The content of heavy metals was evaluated using inductively coupled plasma mass spectrometry after passing through a 0.45 μm filter.

2.7. Data Analysis. To ensure the accuracy of the data obtained through the experiment, all data generated during the analysis processes was measured repeatedly three times to avoid random errors, which were plotted with mean and error bars in the graph.

3. Results and Discussion

3.1. Influence of Hydrothermal Treatment on Physicochemical Properties of Sediment. As demonstrated in

TABLE 1: Risk assessment code of heavy metals.

No.	Risk level	RAC = T1/total × 100 (%)
1	Very high risk	>50
2	High risk	31~50
3	Medium risk	11~30
4	Low risk	1~10
5	No risk	<1

Figure 1(a), as the hydrothermal temperature increased, the rate of organic reduction in the sediment increased as well. The mass of organics in the sediment was reduced by 31.5% when the hydrothermal temperature reached 260°C, compared to prior hydrothermal treatment. This may be due to the fact that the increase in temperature intensified the reaction and destroyed the flocculent structure of the sediment. In the issue, macromolecular organics were released into the liquid phase and hydrolyzed to form small molecules, leading to a decrease in the mass of organics in the sediment. When the hydrothermal temperature was above 260°C, the change in the reduction rate of organic matter levelled off. The optimum hydrothermal temperature was 260°C. After hydrothermal treatment, most of the organics in the sediment would enter the liquid phase. The reduction of organics in sediment could be further confirmed by the change of COD in the hydrothermal solution.

Furthermore, it can be understood from Figure 1(a) that the COD in the hydrothermal solution increased as the temperature of the hydrothermal solution increased, and the trend was generally consistent with the organic matter reduction rate. As seen from Figure 1(b), the reduction ratio of organics in the sediment and the COD of the hydrothermal solution increased continuously as the hydrothermal time was extended. After 3 h of hydrothermal treatment, the mass of organics in the sediment decreased by 31.1% compared with that before hydrothermal treatment, while the COD in the hydrothermal phase of the sediment increased to 3093 mg/L. However, both changes levelled off when the time was further extended. This indicates that the hydrolysis of organics in the sediment has reached an equilibrium state and that the reduction is difficult to increase. Considering the energy consumption and cost, the optimal hydrothermal time was 3 h.

Table 3 shows the physicochemical properties of the sediment hydrothermal solid products obtained on the raw sediment and under different hydrothermal conditions.

As seen from Table 3, the proportions of C, H, ON, O/C, and H/C values in the hydrothermal solid products of the sediments continued to decrease with increasing hydrothermal temperature and time. This may be due to dehydration and decarboxylation during the hydrothermal reaction [24]. It exhibits high aromaticity and strong carbonation [25], which facilitates the dehydration reduction of the sediment.

Furthermore, the ash content in the hydrothermal solid products of the sediments showed an overall increasing trend as the hydrothermal temperature and time increased. This may be due to the hydrothermal heat causing the organic components in the sediment to be released into the

hydrothermal solution. It gave rise to a relative increase in the inorganic component content. Meanwhile, the pH of the sediment hydrothermal solid products decreased as the hydrothermal temperature and time increased [26].

3.2. Functional Group Changes of Raw Sediment and Hydrothermal Solid Products of Sediment. Figure 2 shows the infrared spectra of the raw sediment and sediment hydrothermal solid products under optimal hydrothermal conditions (260°C, 3 h).

In comparison to the raw sediment, the O-H stretching vibration absorption peaks for alcohols and phenols in the sediment hydrothermal solid products are at 3620 cm⁻¹. The N-H stretching vibration absorption peaks of amides and imines are at 3434 cm⁻¹, and the relative intensity of the O-H planar deformation vibration absorption peak for carboxylic acids at 1429 cm⁻¹ is reduced. This suggests that the decomposition of carbohydrates (-OH), proteins (-NH), and fatty acids (-COOH) in the sediment is due to hydrothermal-induced material. Simultaneous decomposition of unstable substances in the sediment and dissolution into the liquid phase due to dehydroxylation, decarboxylation, and deamination of other organic substances made the sediment more stable [27].

After hydrothermal treatment, the peak at 2925 cm⁻¹ and the relative intensity corresponding with the aliphatic CH_n group (C-H stretching vibration) decreased, suggesting that the organic aliphatic structures in the sediment were broken down into gaseous compounds. For example, methane and carbon dioxide are converted into aromatic structures during hydrothermal treatment. The peak at 1635 cm⁻¹ corresponds to the aromatic ring stretching (-CONH-) functional group, whose relative intensity decreases after hydrothermal treatment. The C-H out-of-plane deformation vibrational absorption peaks of aromatic hydrocarbons were slightly enhanced at 797 cm⁻¹ and 776 cm⁻¹. It indicates that the hydrothermal treatment caused some organic matter (alkanes, cycloalkanes, and so on) in the sediments to undergo aromatization reactions to form aromatic hydrocarbons [28].

3.3. Morphological Characteristics of Raw Sediment and Sediment Hydrothermal Solid Products. Scanning electron micrographs of raw sediment and hydrothermal solid products of sediment under the optimum hydrothermal conditions (260°C, 3 h) are shown in Figure 3.

As shown in Figure 3, the surface structure of the original sediment is flat. After hydrothermal treatment, the sediments showed an increase in the porosity of the hydrothermal solid products and exhibited some degree of fragmentation, resulting in smaller particle sizes.

BET characterization was carried out on raw sediment and hydrothermal solid products of sediment, and the results are shown in Table 4. After hydrothermal treatment, the specific surface areas of sediment increased from 12.648 m²/g to 32.616 m²/g, the pore volume increased from 0.075 cc/g to 0.107 cc/g, and the pore diameter decreased from 3.820 nm to 1.936 nm, which is consistent with the observation results of SEM. The increase in pore volume

TABLE 2: The relation between C_f , E_r , RI, and pollution degree.

C_f	E_r	RI
$C_f \leq 1$	No risk	$E_r < 40$
$1 < C_f \leq 3$	Low risk	$40 \leq E_r < 80$
$3 < C_f \leq 6$	Medium risk	$80 \leq E_r < 160$
$6 < C_f \leq 9$	High risk	$160 \leq E_r < 320$
$C_f > 9$	Very high risk	$E_r \geq 320$

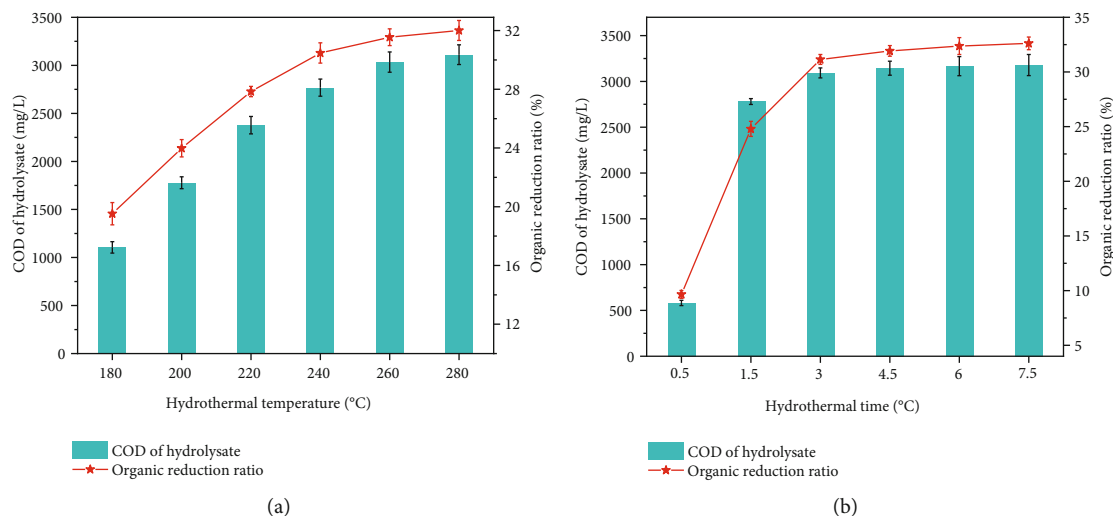


FIGURE 1: Influence of hydrothermal condition on organic reduction and COD of hydrolysate: (a) at 3 h of hydrothermal time, the hydrothermal temperatures were set at 180, 200, 220, 240, 260, and 280 °C; (b) at 260 °C of hydrothermal temperature, the hydrothermal times were set at 0.5, 1.5, 3, 4.5, 6, and 7.5 h.

TABLE 3: Properties of RS and HS.

Parameter	RS	HS-180-3	HS-220-3	HS-260-3	HS-260-0.5	HS-260-6
C%	3.25	2.69	2.37	2.33	3.16	2.32
H%	1.06	0.85	0.74	0.71	1	0.69
N%	0.15	0.08	0.07	0.06	0.12	0.06
O%	2.34	1.65	1.45	1.24	2.02	1.2
Ash%	92.2	93.73	94.37	94.66	92.7	94.73
O/C	0.54	0.46	0.46	0.4	0.48	0.39
H/C	3.91	3.79	3.75	3.66	3.8	3.57
pH	7.25	6.63	6.57	6.39	6.69	6.31

and specific surface area, as well as the decrease in pore diameter, facilitated the release of water from the sediments.

At the same time, the above changes are bound to cause the changes of sediment adsorption performance. Although some studies [29–31] have shown that titanate nanomaterials prepared by hydrothermal method can adsorb heavy metals from water, it remains to be further studied whether the hydrothermal products of the sediment prepared in this study can be used as nanoadsorbent materials.

3.4. Redistribution of Heavy Metals between Solid and Liquid Phases. At present, the traditional environmental risk assess-

ment methods are mainly based on the total concentration of heavy metals and are evaluated from the perspective of total quantity control. This index has always been the most basic basis for controlling the environmental risk of heavy metals [32]. The concentrations of heavy metals in the liquid-solid phase of the sediment before and after hydrothermal treatment are shown in Figure 4.

After hydrothermal treatment, a certain level of heavy metals in the sediment will be liberated or dissolved into the hydrolysate of the sediment, as shown in Figure 4(a). As for the amounts of heavy metals in the liquid phase of the sediment, they should not exceed 1% of the total amount

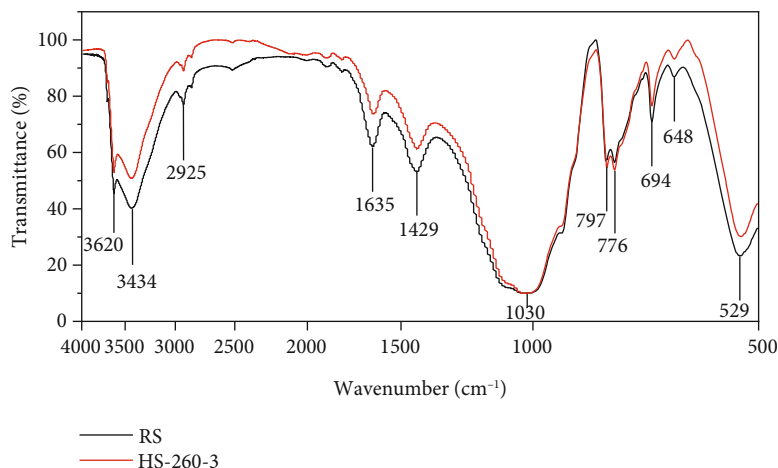


FIGURE 2: Fourier transform infrared (FTIR) spectra of RS and HS-260-3.

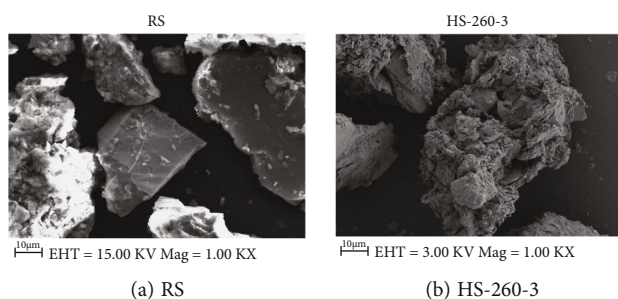


FIGURE 3: Scanning electron micrographs of RS and HS-260-3.

TABLE 4: BET of RS and HS-260-3.

Samples	Specific surface areas (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
RS	12.648	0.075	3.820
HS-260-3	32.616	0.107	1.936

of each heavy metal. The findings indicate that the hydrothermal treatment has some influence on the dissolving of the heavy metals in the sediment. This may be due to the fact that the hydrothermal treatment decomposes the organics in the sediment, thus releasing the combined heavy metals [33]. Nevertheless, the content of heavy metals entering the liquid phase through solid-liquid separation was very low, indicating that the hydrothermal method was difficult to effectively isolate the heavy metals from the sediment and the vast majority of the heavy metals remained in the solid phase.

As illustrated in Figure 4(b), the concentration of heavy metals in the hydrothermal solid phase of sediment increased as the hydrothermal temperature and time increased. On the one hand, the great majority of the heavy metals remained mainly in the solid phase of the sediment. On the other hand, the hydrolysis of organics during the hydrothermal treatment [21] led to an increase in the relative content of inorganic materials such as heavy metals, showing an enrichment and intensification effect. Nonetheless, whether this enrichment increases the potential risk of

heavy metals in the sediment needs to be further determined by changes in the chemical form of heavy metals.

3.5. Content Changes of Chemical Forms of Heavy Metals during Hydrothermal Treatment. The research results in recent years show that the environmental risk of heavy metals in sludge depends not only on the content of heavy metals in sludge but more importantly on the form of heavy metals in sediment [13, 34, 35]. The BCR extractable chemical form concentration of heavy metals in raw sediment and hydrothermal solid products of the sediment is shown in Figure 5.

As shown in Figure 5, most of the Zn in the sediment is exchangeable (T1: 47% and T2: 21%). After hydrothermal treatment, the proportion of heavy metals in the T1 form of Zn decreased significantly, and the proportion of heavy metals in the T3 and T4 forms increased significantly, reaching 41% and 25%, respectively. In contrast, the proportion of T2 heavy metals remained largely unchanged. This indicates that the morphology of Zn in the sediment changed from a

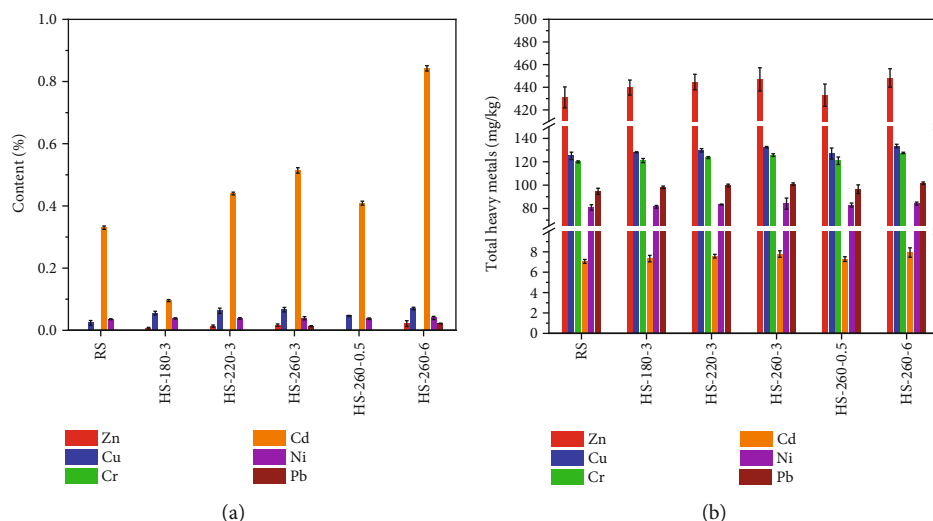


FIGURE 4: The redistribution of heavy metals between liquid phase (a) and solid phase (b) of sediment after hydrothermal treatment.

weakly bound condition to a rather stable state after hydrothermal treatment. The increase in hydrothermal temperature and time promoted the stability of Zn in the generated sediment hydrothermal solid products.

The highest proportion of Cu in the sediment was in the T3 form (47%), followed by T4 (31%). After hydrothermal treatment, Cu was transformed from the T1 form and T2 form into the T3 form and then fixed, with the proportion of heavy metals in T4 remaining largely unchanged. Therefore, as the hydrothermal temperature and duration rose, the fraction of stable components in the sediment grew dramatically, and the findings are consistent with earlier research. That is, Cu may be blind to stronger organic ligands and is contained in minerals with low bioavailability and mobility potential [36].

The proportion of heavy metals in the T1 form of Cr did not change significantly, whereas the proportion of heavy metals in the T3 form decreased somewhat, and the proportion of heavy metals in the T2 and T4 forms increased slightly. Although a rise in the proportion of heavy metals in the T2 form was harmful to the sediment's stability, the proportion of heavy metals in the T4 form increased substantially faster than the T2 form as hydrothermal temperature and duration increased. As a result, Cr is still stabilized by the hydrothermal treatment.

The proportion of heavy metals in the T1 form and T2 form of Cd decreased, so the proportion of heavy metals in the T3 form and T4 form increased significantly. Furthermore, after hydrothermal treatment, the status of Cd transformed from unstable to stable, and the higher the hydrothermal temperature and the longer the hydrothermal time, the more obvious the stabilization trend of Cd.

In terms of heavy metal Pb, the proportion of heavy metal in the T1 form, T2 form, and T3 form decreased significantly, and the proportion of heavy metal in the T4 form increased significantly, reaching about 43%. At the same time, the higher the hydrothermal temperature and the longer the hydrothermal time, the greater the proportion of heavy metals in the T4 state and the greater the stability of

Pb. Evidently, this indicates that hydrothermal heat has a strong stabilizing effect on Pb in sediments and can significantly reduce its bioavailability. These findings support earlier data showing Pb in sediment hydrothermal solid products being very stable and posing little damage to the environment [37].

With regard to the heavy metal Ni, the T1 form with the highest specific gravity did not change significantly before and after hydrothermal treatment. Only a handful of heavy metals in the T1 form were transformed into heavy metals in the T3 form. This indicates that the stabilizing effect of hydrothermal heat on Ni was not significant and that the influence of hydrothermal temperature and time on the morphological changes was limited.

Overall, the hydrothermal treatment led to a marked decrease in the proportion of bioavailable fractions (T1 and T2) and a crucial increase in the stable fraction (T4) of heavy metals in the sediment. The results indicate that the bioavailability of heavy metals decreases significantly after hydrothermal treatment and that heavy metals are more stable in the sediment. The conversion of the unstable heavy metal fractions (T1 and T2) to the reasonably stable fractions (T3) and stable fractions (T4) was significantly influenced by hydrothermal treatment (T4). The higher the temperature or the longer the time, the more pronounced the stabilization.

3.6. Environmental Risk Assessment of Heavy Metals. The environmental risk of heavy metals in sediments can be assessed by the RAC. Since heavy metals in the T1 form are most easily affected by changes in ionic strength and pH value in the environment, the content of this part directly determines the environmental risk of heavy metals [38]. The RAC values of Zn, Cu, Cr, Cd, Ni, and Pb in raw sediment and hydrothermal solid products are shown in Table 5.

Cu and Cr had RAC values of less than 10%, which meant they were at low risk levels and had low environmental toxicity. However, the risk indicator RAC for Zn was as

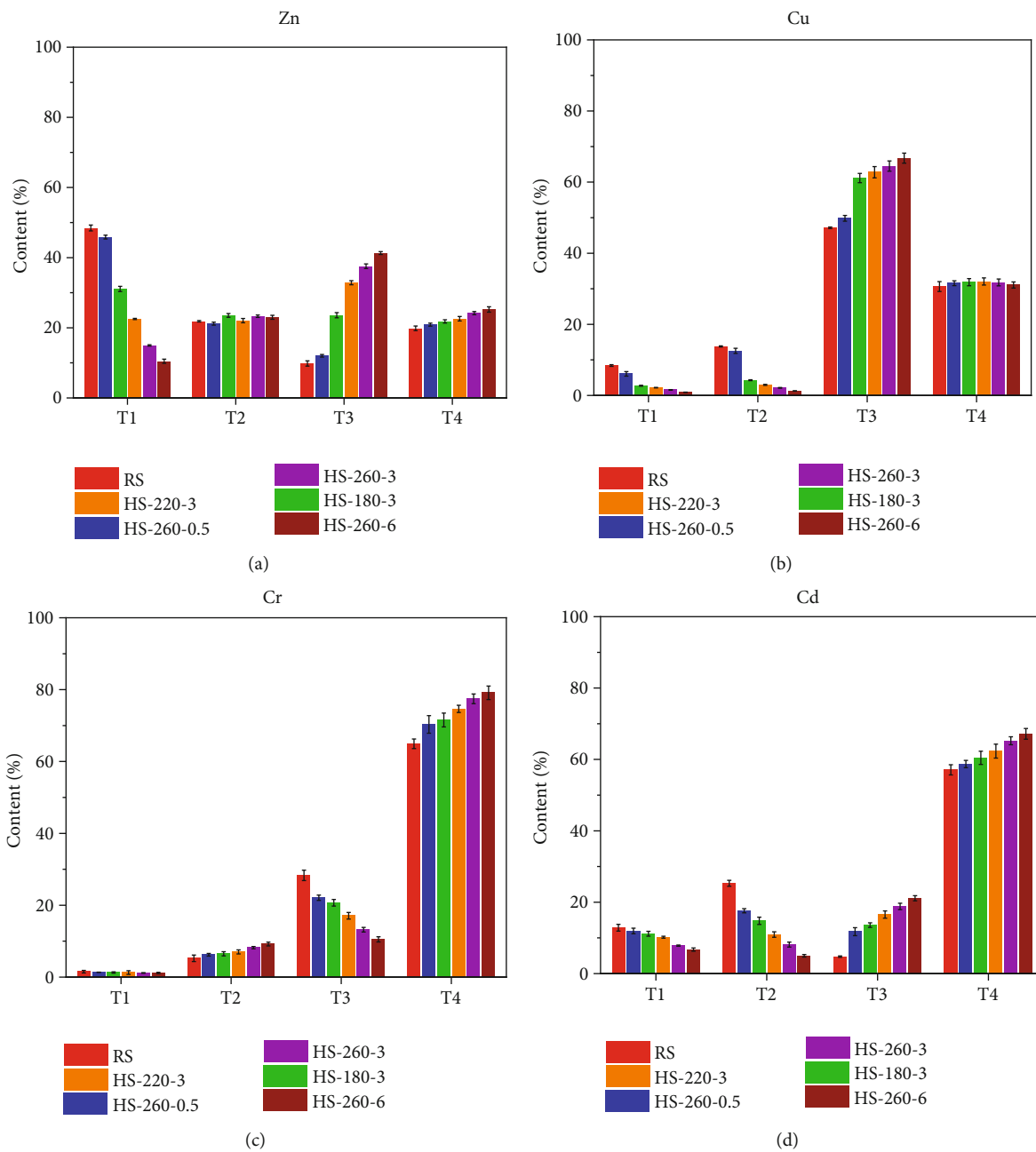


FIGURE 5: Continued.

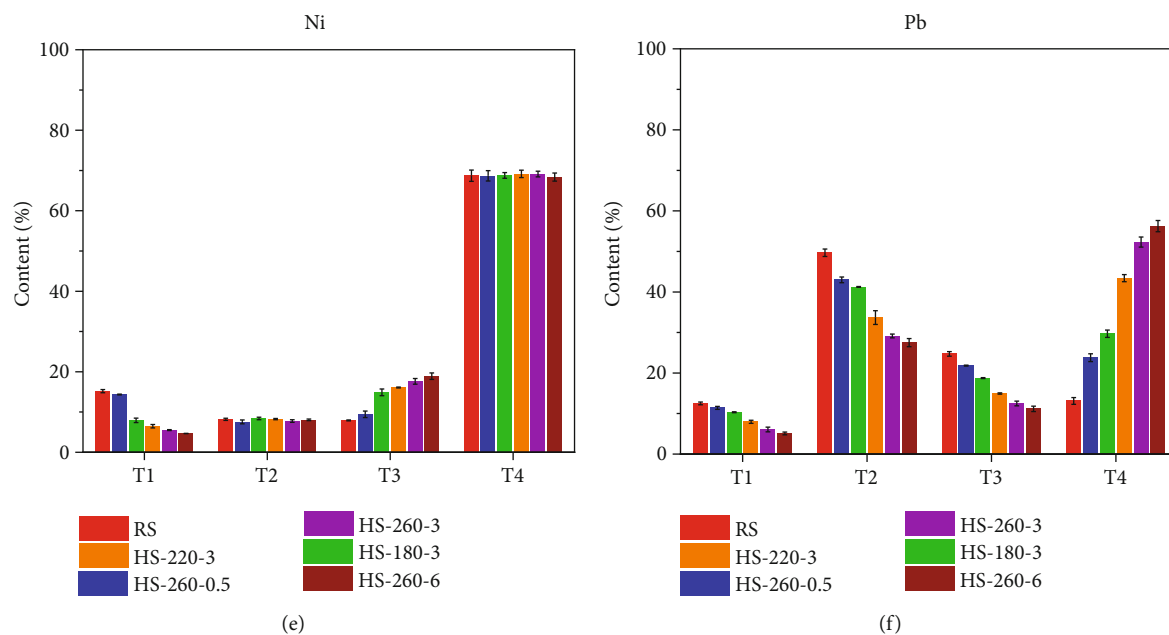


FIGURE 5: The chemical speciation changes of (a) Zn, (b) Cu, (c) Cr, (d) Cd, (e) Ni, and (f) Pb in RS and HS.

TABLE 5: RAC of heavy metals in RS and HS.

Samples	RAC					
	Zn	Cu	Cr	Cd	Ni	Pb
RS	48.45/HR	8.42/LR	1.53/LR	12.88/MR	15.19/MR	12.50/MR
HS-180-3	31.08/HR	2.72/LR	1.28/LR	11.17/MR	7.93/LR	10.32/LR
HS-220-3	22.51/MR	2.20/LR	1.27/LR	10.20/LR	6.48/LR	7.96/LR
HS-260-3	14.98/MR	1.56/LR	1.16/LR	7.83/LR	5.51/LR	6.05/LR
HS-260-0.5	45.87/HR	6.07/LR	1.36/LR	11.94/LR	14.35/MR	11.39/MR
HS-260-6	10.46/LR	0.90/NR	1.15/LR	6.74/LR	4.67/LR	5.10/LR

Note: NR: no risk, representing there is risk free; LR: low risk, representing there is a low risk; MR: medium risk, representing there is a medium risk; HR: high risk, representing there is a high risk.

TABLE 6: Ecological risk assessment of the heavy metals in RS and HS.

Sample	C_f						E_r						RI
	Zn	Cu	Cr	Cd	Ni	Pb	Zn	Cu	Cr	Cd	Ni	Pb	
RS	4.04	2.26	0.54	0.75	0.46	6.63	4.04	11.32	1.08	22.56	2.73	33.14	74.87
HS-180-3	3.59	2.14	0.40	0.65	0.45	2.37	3.59	10.70	0.80	19.61	2.72	11.84	49.26
HS-220-3	3.43	2.12	0.34	0.60	0.45	1.30	3.43	10.60	0.68	18.14	2.67	6.52	42.04
HS-260-3	3.14	2.15	0.29	0.53	0.45	0.91	3.14	10.73	0.58	16.00	2.68	4.56	37.68
HS-260-0.5	3.78	2.17	0.42	0.70	0.46	3.20	3.78	10.84	0.84	21.11	2.74	16.02	55.32
HS-260-6	2.96	2.22	0.26	0.49	0.46	0.78	2.96	11.10	0.53	14.67	2.78	3.89	35.92

high as 48.45%, which was at a high risk level with high environmental risk and ecotoxicity. The risk indicator RACs for Cd, Ni, and Pb were 12.88%, 15.19%, and 12.50%, respectively, which were at a medium risk level and harmful to the environment. After hydrothermal treatment, the RACs of the six heavy metals in the hydrothermal solid products of the sediments all decreased to varying degrees, and the degree of decline increased as the hydrothermal temperature and duration increased. The risk levels of all heavy metals

decreased, except for chromium, which remained at a low level before and after hydrothermal treatment. Zn was reduced from high to low risk after 6 hours of hydrothermal treatment at 260°C. Cu went from being a minimal risk to being completely risk-free. Cd, Ni, and Pb all went from a medium to a low danger level. Meanwhile, the risk indicators for Zn, Cu, Cr, Cd, Ni, and Pb decreased by 78.41%, 89.31%, 24.84%, 47.67%, 69.26%, and 59.20%, respectively, after 6 hours of hydrothermal treatment at 260°C. Combined with

TABLE 7: Leaching toxicity of heavy metals in RS and HS.

Sample	Zn (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	Ni (mg/kg)	Pb (mg/kg)
RS	163.72 ± 5.21	3.45 ± 0.07	0.51 ± 0.01	0.44 ± 0.02	9.60 ± 0.05	5.58 ± 0.07
HS-180-3	102.37 ± 1.96	1.40 ± 0.02	0.45 ± 0.01	0.38 ± 0.01	2.34 ± 0.03	2.00 ± 0.06
HS-220-3	72.47 ± 3.23	0.74 ± 0.01	0.42 ± 0.02	0.28 ± 0.01	1.67 ± 0.03	0.91 ± 0.03
HS-260-3	38.69 ± 2.91	0.62 ± 0.01	0.36 ± 0.01	0.20 ± 0.01	1.12 ± 0.02	0.84 ± 0.02
HS-260-0.5	148.30 ± 1.96	2.51 ± 0.03	0.49 ± 0.02	0.40 ± 0.01	8.57 ± 0.04	3.60 ± 0.08
HS-260-6	22.90 ± 1.47	0.55 ± 0.01	0.34 ± 0.01	0.18 ± 0.01	0.87 ± 0.02	0.66 ± 0.01
International permissible leaching limits	25	—	5	0.5	1	5

TABLE 8: Concentration of salt ions in RL and HL.

Sample	NH ₄ ⁺ -N (mg·L ⁻¹)	K ⁺ (mg·L ⁻¹)	Na ⁺ (mg·L ⁻¹)	Ca ²⁺ (mg·L ⁻¹)	Mg ²⁺ (mg·L ⁻¹)
RL	21.12 ± 0.18	9.72 ± 0.19	20.53 ± 0.66	27.22 ± 1.15	3.23 ± 0.13
HL-180-3	88.78 ± 0.73	24.52 ± 0.84	43.35 ± 0.98	38.74 ± 0.54	4.78 ± 0.09
HL-220-3	119.76 ± 0.54	26.27 ± 1.18	59.98 ± 2.11	40.44 ± 0.61	6.45 ± 0.15
HL-260-3	142.57 ± 2.66	28.31 ± 2.21	62.72 ± 2.65	41.20 ± 2.12	9.08 ± 0.10
HL-260-0.5	32.34 ± 0.97	14.43 ± 0.71	23.92 ± 0.38	30.78 ± 0.35	5.69 ± 0.17
HL-260-6	143.82 ± 1.43	29.72 ± 1.63	63.09 ± 2.34	41.61 ± 0.77	9.28 ± 0.28

previous research and findings, the hydrothermal treatment procedure has a practical impact on decreasing the risk levels of heavy metals in sludge [37]. The foregoing findings suggest that hydrothermal treatment can effectively lower the ecotoxicity of heavy metals in sediment, stabilize them, and reduce their risk to the environment and humans.

3.7. Ecological Risk Assessment of Heavy Metals. For single heavy metals in raw sediments and sediment hydrothermal solid products, C_f values for contamination factors, E_r values for potential ecological risk factors, and RI values for the total of potential ecological risk factors are reported in Table 6.

The C_f value of Pb in the raw sediment was 6.63, suggesting a high level of heavy metal contamination. Zn has a C_f value of 4.04, suggesting moderate heavy metal pollution. Cu has a C_f value of 2.26, reflecting a moderate amount of heavy metal pollution. As shown in Table 6 and Table 2, the C_f values for Cr, Cd, and Ni were less than 1, suggesting that they were not contaminated with metals. After hydrothermal treatment, the C_f value of heavy metals in the hydrothermal solid products of the sediment decreased significantly, except for Cu and Ni. Moreover, the higher the hydrothermal temperature and the longer the hydrothermal time, the lower the C_f value. For example, Zn decreased from 4.04 to 2.96, representing a change in risk from moderate to low, and Pb was the most pronounced, decreasing from 6.63 to 0.78, representing a change in risk from high to zero. After hydrothermal treatment, the RI value of river sediment decreased from 74.87 to 35.92. The lower the RI value of hydrothermal solid product sediments, the lower the potential ecological risk level. Further, the potential eco-

logical risk decreases significantly as the hydrothermal temperature and time increase.

3.8. Leaching Toxicity of Heavy Metals. The environmental risks of heavy metals are tightly linked to their leaching characteristics and leaching toxicity. The leaching characteristics are such that leachable heavy metals have direct toxicity to plants and soils during leaching [39]. The leaching concentrations of heavy metals in raw sediment and in the hydrothermal solid products of the sediment are shown in Table 7.

After hydrothermal treatment, the leaching concentrations of all six heavy metals decreased to some extent. At the same time, the higher the hydrothermal temperature or the longer the hydrothermal time, the greater the range of decrease, as shown in Table 6. In particular, the leaching concentration of Zn changed from 163.72 mg/kg to 22.90 mg/kg after 6 hours of hydrothermal treatment at 260°C, which was only 13.99% of the original, below the internationally permitted leaching limit. The leaching concentrations of Cu, Ni, and Pb also decreased to varying degrees and were below the internationally permitted leaching limits. The leaching concentrations of Cr and Cd had reached the internationally permitted leaching limit before hydrothermal treatment and decreased to some extent after hydrothermal treatment. In conclusion, the leaching rates of the various heavy metals did not exceed the internationally permitted leaching limits after the sediment was heated at 260°C for 6 hours. Concurrently, the change in leaching concentration was largely compatible with the change in RI values of heavy metals in the sediment. This is further evidence that hydrothermal treatment can actually lower the environmental risk of heavy metals in sediments by stabilizing them and reducing the risk to the environment and humans.

3.9. Stabilization Mechanism of Heavy Metals. The concentrations of some ions in raw sediment filtrate and the hydrothermal phase of sediment are shown in Table 8.

As the hydrothermal temperature and time increased, the amount of salt ions in the liquid phase increased significantly, as shown in Table 8. This intensified the competition for adsorption sites on the sediment, resulting in some of the weakly bound heavy metals entering the liquid phase after analysis. In addition, the hydrothermal treatment also facilitated the solubilization of heavy metals by facilitating their migration in the sediment, providing an opportunity for them to form more stable minerals in the liquid phase through precipitation and complexation with anions.

According to infrared spectrum analysis (Figure 2), the hydrothermal treatment resulted in the removal of oxygen-containing functional groups (-OH, -COOH) from the sediment, and the ability of the heavy metals to adsorb organic matter via hydroxyl and carboxyl groups was severely disrupted and released into the liquid phase. The heavy metals were then finally immobilized in the minerals by complexation, precipitation, or other means, namely, the transition from the unstable state (T1, T2) to the stable state (T3, T4), and finally, the stabilization of heavy metals in the sediments was achieved [10, 40, 41]. Studies by Huang et al. [13] and Wang et al. [37] also showed that the dehydroxylation and decarboxylation of macromolecules in organics during hydrothermal treatment might play an indispensable role in the reduction of bioavailability or immobilization of heavy metals.

Meanwhile, the C-H out-of-plane deformation vibration absorption peaks of aromatic hydrocarbons were slightly enhanced at 797 cm^{-1} and 776 cm^{-1} after hydrothermal treatment of the sediments. While the peak at $600\text{--}800\text{ cm}^{-1}$ corresponded to aromatic groups and heteroaromatic compounds, aromatic groups have π electrons and high potential energy, which form strong bonds with heavy metal cations [42]. Therefore, another possible reason for the reduction of the bioavailability or stabilization of heavy metals in sediments after hydrothermal treatment is that hydrothermal treatment causes aromatization of some organics (alkanes, cyclic hydrocarbons) in the sediment. The resulting aromatic groups combine with partially dissolved heavy metals or heavy metals in sediments to form strong bond compounds, which are finally fixed in minerals [43].

4. Conclusion

Hydrothermal treatment can significantly improve the dewatering performance of the sediment and remove the organic matter in the sediment to achieve the reduction and stabilization of the sediment. Hydrothermal treatment reduces the bioavailability components of heavy metals in sediments and converts them into more stable components, so that their environmental bioavailability, ecotoxicity, and leaching toxicity are significantly reduced, thereby achieving heavy metal stabilization in sediments. This study provides a new method for the treatment of sediment and provides a certain basis for the subsequent green land use of sediment.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

This study was supported by the National Key R&D Program of China (No: 2019YFD1100502) and the Project of Shanghai Science and Technology Commission (No: 19DZ1207903).

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