

Article

Study on the Preparation of Biochar Ceramsite Based on Sewage Sludge and the Characterization of Its Properties

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Featured Application: Due to the particularity of the source, the sludge can be fired into biochar ceramsite without adding other auxiliary materials, and can be used as the padding of constructed wetland.

Abstract: Biochar ceramsite was prepared from residual sludge at different temperatures. Specific surface area, compressive strength, and toxic leaching tests were used to compare the properties. Through tests and scanning electron microscopy (SEM), it was found that with the increase of preparation temperature, the ceramsite showed higher porosity, larger specific surface area, and better compressive strength. The leaching amount of toxic heavy metals is low when the temperature is higher than 650 °C. According to X-ray diffraction (XRD) analysis, the main component of sludge is quartz. There were amounts of iron and aluminum in sludge, which were the main reason for its good adsorption efficiency. Through the adsorption experiment on Cr(VI), it was found that the adsorption efficiency of the ceramsite on Cr(VI) was better at low pH, and the adsorption isotherm fitted well with Langmuir and Freundlich types. The adsorption process had both monolayer adsorption and multilayer adsorption, and the adsorption process was in line with the pseudo-second-order kinetics.

Keywords: sludge; biochar; ceramsite; constructed wetland; padding; adsorption; Cr(VI)



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1. Introduction

Sludge is the solid waste generated in the process of sewage treatment. With the rapid development of the sewage treatment industry, the amount of sludge produced in the process is also increasing, and the problem of sludge treatment and disposal is becoming increasingly prominent. Sludge contains a large number of organic matter, insoluble inorganic substances, and bacterial micelles formed by various microorganisms, etc. Untreated sludge entering the environment will cause great harm to the environment [1]. There are many types of sludge, which can be roughly divided into three types according to their sources: water supply sludge, domestic sewage sludge, and industrial wastewater sludge [2]. Different sludges have different compositions and different disposal methods. At present, commonly used sludge disposal methods mainly include incineration, land-fill, composting, ocean discharge, and so on [3]. However, these methods have certain limitations, and the exploration of new methods for sludge disposal and new ways for comprehensive utilization of resources is of great significance in solving the problem of sludge disposal [4].

Considering that it contains a large number of viruses and bacteria, high temperature is a better treatment method, which can not only kill the viruses and bacteria in the sludge, but also achieve the effect of volume reduction [1]. At present, the common high-temperature treatment methods of sludge include incineration [5], high-temperature hydrolysis [6], preparation of ceramsite and activated carbon [1,2,7]. Due to the low calorific value and high moisture content of sludge, the traditional incineration needs to be mixed with household waste and coal or other high calorific value materials, and the heat

utilization rate is low, and at the same time, a large amount of fly ash, HCl gas, and dioxins are generated [8]. Ceramsite as a light aggregate possesses the porous, light weight, anti-seismic, heat preservation, sound insulation, and other advantages, and is widely used in construction, environmental protection, chemical industry, horticulture, and other industries. The sludge is rich in inorganic components such as SiO_2 , Al_2O_3 , and Fe_2O_3 , which can be used as filler or adsorbent to realize the resource utilization of sludge [9,10]. The use of sludge to prepare ceramsite can not only reduce a large amount of sludge but also produce lightweight material as water treatment filler or building supplies, which is the current research hotspot of sludge resource utilization [2]. There are more and more patents for making ceramics from sludge [2,4,6,11], but most of them are mixed with kaolin, fly ash, cement, gypsum, or other materials to increase the firing strength [2,7]. Sludge is rich in carbonaceous organic matter, which is the raw material required for the manufacture of activated carbon. The preparation of activated carbon with sludge as raw material can save coal and wood and other precious resources, and solve the environmental problem of sludge disposal, curb waste with waste, turn waste into resource, and realize the resource utilization of sludge [12].

Wetland has a strong purification function, known as the lung of the earth. Constructed wetland is an environmental ecosystem constructed by an artificial simulation method. It uses the organic combination of packing matrix permeability, aquatic or marsh plants, and the microbial matrix attached on the padding to reach the effect of sewage purification, which is like a compound ecological system with physical (precipitation, filtration, adsorption), chemical (ion exchange), and the biological (plants extract nutrients, microbial metabolism) properties [10,13]. Constructed wetlands are widely used because of their advantages such as good pollutant purification efficiency, low cost, and easy maintenance [14]. Wetland padding is the crucial part of constructed wetland system. It not only provides the growth medium for plants and microorganisms, but also directly removes pollutants through the effects of precipitation, filtration, and adsorption. The adsorption capacity of paddings to pollutants determines the overall treatment effect of constructed wetland [15]. The general selection of constructed wetland padding should meet the following conditions: (1) high mechanical strength; (2) large specific surface area, high porosity, and good adsorption capacity; (3) good permeability, not easy to plug; (4) stable chemical properties, no secondary pollution; (5) reasonable price. The most commonly used padding substrates are gravel, zeolite, soil, pebble, coal cinder, fly ash, and so on [16].

The ceramsite fired by sludge is porous, with large specific surface area and good adsorption ability, which just meets the requirements of constructed wetland padding. There have been pieces of research on the ceramsite of constructed wetlands padding made by sludge [15–19]. The sludge from water works was used as raw material to fire the ceramsite. The surface porosity of the ceramsite was higher, and was more favorable to the growth of microorganisms. A constructed wetland system of “sludge ceramsite + plant” was constructed to treat domestic sewage. The removal effect of COD and TP was better than that of constructed wetland with coal cinder, shale, zeolite, and steel slag as paddings [15]. Ouyang et al. [16] made biochar with sludge as raw material to adsorb heavy metals in the bottom sludge. While supplemented by the plant to establish the constructed wetland, which was used to treat the water of Xiangjiang River. The biochar could be reused, and the heavy metals in the effluent reached the standard. It has the advantages of low cost, relatively simple access to raw materials, and high treatment efficiency of heavy metal pollutants. Liu et al. [17] used aluminum sludge as adsorbent to adsorb Cr(VI) in water through static experiments. Functional groups such as OH^- , SO_4^{2-} , and Cl^- on the surface of aluminum sludge can undergo ligand exchange with Cr(VI) to achieve the purpose of Cr(VI) removal. The sludge from drinking water plant was used as raw material to make ceramsite, and *Oenanthe javanica* was used to construct constructed wetland to treat rural domestic sewage. Removal efficiencies of 76.7% TP, 56.4% $\text{NH}_4\text{-N}$, and 60.8% TN were obtained [19].

But mostly, the ceramsite was fired by the aluminum sludge as raw material, because compared with residual activated sludge of sewage treatment plant, the amount of inorganic matter and heavy metals in aluminum sludge is relatively lower. As an adsorption material, heavy metals dissolution of the ceramsite is easy to be controlled in the standard range. And the sludge of sewage treatment plant is enrichment of inorganic elements such as nitrogen, phosphorus, and potassium; Cd, Cu, Pb, and other heavy metals; organic pollutants such as pesticides, antibiotics, and pathogenic microorganisms; and other pollutants. The concentration of the pollutants causes great limitations to sludge disposal. The change of conditions can easily lead to the dissolution of heavy metals [5]. If necessary, a stabilizer should be added for stabilization [11].

In this study, the residual activated sludge from Chaozhou No. 1 Sewage Treatment Plant was used as raw material to fire sludge-based biochar ceramsite under different sintering systems, and no other auxiliary material was added. Its physical properties were characterized, and the dual activity of ceramsite and biochar was explored to adsorb Cr(VI) from waste water. The feasibility of the ceramsite used as padding substrate in constructed wetland was discussed.

2. Materials and Methods

2.1. Materials and Reagents

The sludge was the residual activated sludge from Chaozhou No. 1 Sewage Treatment Plant. And all the reagents were analytical grade. K_2CrO_4 was purchase from Aladdin, and the Cr standard solution was purchased from National Standard Material Network.

2.2. Experimental Methods

2.2.1. Partial Indexes of Sludge

The moisture content, combustion loss, and ash content of the fresh sludge were determined by differential weight method. Briefly, the fresh sludge was weighted (m_0), and then dried at 105 °C. The weight of dried sludge was denoted as m_1 . The dried sludge was fired at 950 °C. The weight of fired sludge was denoted as m_2 . The moisture content, combustion loss were calculated followed the equations:

$$\text{moisture content} = \frac{m_0 - m_1}{m_0} \times 100\% \quad (1)$$

$$\text{combustion loss} = \frac{m_1 - m_2}{m_1} \times 100\% \quad (2)$$

The ash content was what the remains after dry sludge was burned away. Another part of the sludge was digested by HNO_3 - HCl - $HClO_4$ - HF (complete wet digestion) to determine the contents of several main metal elements using atomic absorption spectrophotometer (WA2081, Beijing Ruilihentong, Beijing, China).

2.2.2. Preparation of Ceramsite Biochar

The sludge was kneaded into raw material balls with a diameter of 20–30 mm, and then the balls were put into an electric thermostatic air-drying oven, and dried at 105 °C for 4 h. Then, the dried raw material balls were put into a tube furnace (OTF-1200X, Kejing, China) to be calcined at a constant temperature for 30 min under the atmosphere of N_2 . The finished product after calcining was further tested.

2.2.3. Ceramsite Performance Test

The physical properties (porosity, cylinder compressive strength) of the ceramsite before and after calcining were tested according to “*Light Aggregates and Test Methods* (GB/T 17431.2-2010, Beijing, China)”, with some modifications. The porosity of the ceramsite was measured by vacuum water absorption meter (ZK-16, Tianjin Jianyi, Tianjin, China), and the cylinder compressive strength was measured by microcomputer controlled universal material testing machine (TFW-50S, Jinan Xinguang, Jinan, China). The leaching toxicity of

ceramsite before and after calcining was acquired according to “Leaching Method of the Solid Waste Leaching Toxicity-Horizontal Oscillation Method (HJ 557-2010, Beijing, China)”, although slightly modified, and the leaching agent was 1% nitric acid. The specific surface area of the ceramsite was measured by specific surface area meter (ASAP2460, Micromeritics, Georgia, GA, USA) at 77K of N₂.

The zero electric point (pH_{PZC}) of the sintered ceramsite was determined by solid addition method [20,21]. Adding 25 mL 0.01 mol/L KNO₃ solution into 10 beakers, and adjust the pH of the solutions between 3–12 with 0.1 M HNO₃ solution and NaOH solution, respectively. The initial pH of each beaker was recorded (recorded as pH₀), then 1.0 g of crushed ceramsite were added to each beaker. The beakers were sealed immediately and placed on the oscillator to oscillate for 24 h. After that, the pH of supernatant was measured and recorded as pH_e. The difference between the initial pH and the equilibrium pH ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_e$), the point at which the $\Delta\text{pH} = 0$, is the zero electric point.

2.2.4. Mineral Composition and Microscopic Morphology

The mineral composition of the ceramsite before and after calcining was tested by X-ray diffractometer (MiniFlex600, Rigaku Japan, Tokyo, Japan). The operating voltage was 40 kV, the electric current was 30 mA, the scanning rate was 8°/min, and the scanning range was 3–90°. The micromorphology was observed by field emission scanning electron microscope (Quanta 250 FEG, FEI, Hillsboro, OR, USA).

2.2.5. Adsorption Experiment

The ceramsite was weighed and put into a 250 mL conical flask. Cr(VI) solution with a concentration of 10 mg/L and a certain pH was added according to the ratio of solid to liquid of 1:40. The conical flask was sealed and put into a water bath oscillator to oscillate at 150 r/min and 25 °C. After a certain time, the supernatant was filtered through a 0.45 µm membrane and the concentration of Cr(VI) in supernatant was determined by atomic absorption spectrophotometer. The adsorption rate of Cr(VI) was calculated as Equation (1).

$$\varphi = \frac{c_0 - c}{c_0} \times 100\% \quad (3)$$

where φ is the adsorption rate (%), c_0 is the initial concentration of Cr(VI) (mg/L); c is the residual concentration of Cr(VI) in the solution after adsorption equilibrium (mg/L).

The adsorption amount of Cr(VI) was calculated as Equation (2).

$$Q = \frac{(c_0 - c) \times v}{w} \quad (4)$$

where Q is the adsorption capacity (mg/g); v is the solution volume (mL); w is adsorbent dosage (g).

The effect of pH on the adsorption was investigated, and the isotherm and kinetics of adsorption were fitted.

3. Results and Discussion

3.1. Main Characteristics of Residual Sludge

The main physicochemical indexes of residual sludge are shown in Table 1.

Table 1. The main physicochemical characteristics of residual sludge.

pH	Moisture Content (%)	Loss on Ignition (%)	Ash Content	Percentage of Contraction (%)	
				Wet→Dry	Dry→Product
6.78 ± 0.12	76.7 ± 1.4	25.7 ± 0.9	74.3 ± 0.9	50.7 ± 0.5	2.5–11.3 ± 0.2

Note: The value is the average of 10 samples.

As can be seen from Table 1, the pH of the residual sludge is close to neutral, the burning loss is low, and the ash content is high, which indicates that the content of organic matter in the sludge is relatively small, which will lead to the low porosity of the ceramsite obtained after calcining and the low content of available biochar, thus affecting its adsorption effect. However, the high content of inorganic substances increased the compressive strength of ceramsite.

The content of major metal elements in the residual sludge is shown in Table 2.

Table 2. Contents of main elements in surplus sludge mg/kg dried basis.

Elements	Content	Elements	Content
Fe	1612.8 ± 8.7	Ni	79.3 ± 1.7
Al	3143.5 ± 10.2	Cr	187.6 ± 0.9
Zn	937.7 ± 5.8	Cd	21.7 ± 0.5
Cu	134.3 ± 2.3	Pb	52.2 ± 0.2

As illustrated in Table 2, the content of Al and Fe is high in the residual sludge, among which, Al is mainly from the flocculant used in sewage treatment, Fe may come from soil minerals, while the content of Cr is significantly higher than other heavy metals.

3.2. Main Performance Characteristics of Ceramsite

The main performance indexes of ceramsite before and after calcining are shown in Table 3.

Table 3. The main performance characteristics of ceramsite.

Firing Temperature (°C)	Porosity (%)	BET (m ² /g)	Compressive Strength (MPa)	Point Zero Charge (pH _{pzc}) *
105	-	201.1729 ± 10.3	11.33 ± 1.14	6.77 ± 0.11
350	6.3 ± 0.2	186.2960 ± 8.7	6.77 ± 1.10	6.21 ± 0.05
650	7.9 ± 0.2	401.7924	8.25 ± 0.83	5.34 ± 0.03
950	12.7 ± 0.3	292.6853	10.77 ± 0.55	8.12 ± 0.03

"-" not detected; "*" simple measurement method, for reference only.

It can be seen from Table 3 that the overall porosity of the ceramsite is small, which is related to the determination method. The vacuum water absorption meter is easy to measure the macropore, while it is not easy to obtain the micropore and mesopore. With the increase of calcining temperature, the porosity of the ceramsite is increasing, the reason is that in the calcining process, the water and volatile substances in the billet gradually volatilize, which has a certain pore-forming effect. At 950 °C, the volatiles in the sludge will be decomposed, and the billet will show partial melting and shrinkage. Moreover, CaO and MgO produced by calcination will be dissolved in water resulting in a certain amount of pores.

It can be seen from the BET data that the specific surface area of the ceramsite increases at first and then decreases with the increase of calcining temperature. High temperature can greatly increase the specific surface area. Wang et al. [22] roasted the waterworks sludge to make ceramsite, which was used to purify sewage. Although the specific surface area of the ceramsite is only 6.07 m²/g, the roasting make the specific surface area increase by 34.27%, and had a good removal rate on COD. The specific surface area increases with the increase of temperature for the same reason as the increase of porosity, which is mainly due to the pore formation of water and volatile components. While at 950 °C, the components in the ceramsite show partial melting, although macropores are generated, but the fluid will also make the micropores and mesopores disappear.

The unfired sludge has fine particles, complex composition, good cohesiveness, and high compressive strength. There are large amounts of organic matters in the unfired sludge, which can serve as the organic binder. So when mixed with the fine particles, it will

become a dense agglomeration, similar to the cementation. At 350 °C, water volatilization, organic components start to volatilize, and porosity begins to increase. At this temperature, the organic components either evaporate or carbonize, and the clay components (kaolin, Illi, etc.) serve as inorganic binder that has not been crystal transformation through the removing of the structural water. Thus, this is a critical point; at this time, the ceramsite is at the worst stage of compressive degree. When the temperature rises to 650 °C, the inorganic components begin to porcelain, and the compressive strength increases with the cohesiveness increasing. When the temperature rises to 950 °C, some components of the sludge begin to become liquid phase and play the role of bonding particles, and the mechanical strength is greatly increased. As illustrated in the previous study [23], the ceramic granules made from sludge, with a compressive strength of 8 MPa, can be used as the building material.

In the pH_{pzc} obtained by the simple method as shown in Table 3, pH_{pzc} of unfired sludge is close to neutral. With the increase of temperature, the organic matter in the sludge begins to carbonize and decompose, forming carboxyl group or phenolic hydroxyl group on the surface, showing certain acidity, which results the dropping of pH_{pzc} . When the temperature rises to 950 °C, the organic matter is almost completely carbonized and decomposed, and the carbonates in the sludge are also decomposed into metal oxides (CaO, MgO, etc.), which can hydrolyze and make the surface with negative charge.

3.3. Dissolution of Heavy Metals

Toxic leaching experiments were carried out on the ceramsite at different temperatures with 1% nitric acid, and the leaching quantities of several heavy metals were mainly investigated. The results are shown in Table 4.

Table 4. Toxic leaching of ceramsite fired at different temperatures mg/g dried basis.

	Fe (±0.005) *	Zn (±0.005)	Cu (±0.002)	Ni (±0.002)	Pb (±0.002)	Cr (±0.002)	Cd (±0.002)
105 °C	0.081	0.065	0.009	0.023	0.009	0.012	0.005
350 °C	0.098	0.089	0.010	0.029	0.009	0.008	0.003
650 °C	0.026	0.021	0.005	0.007	0.001	0.001	0.001
950 °C	0.015	0.007	0.003	0.00	0.003	0.001	0.001

* Individual errors are lower than the displayed value, and the maximum value is set here.

As can be seen from Table 4, with the increase of temperature, the molten liquid phase on the ceramsite surface will clad the surface and form a layer of dense enamel layer, so that the leaching amount of various metals is gradually reduced. The contents of several metals in lixivium were much lower than the limits of the national standards—“*Hazardous Wastes Distinction Standard-Leaching Toxicity Distinction*” (GB 5085.3-2007, Beijing, China). Wu, et al. [24] used dried sewage sludge and used the raw materials to fire the ceramsite, which was used for pharmaceutical advanced wastewater treatment. After the mixed raw materials were sintered at 1150 °C, the leaching amounts of toxic heavy metals were also far less than the standards mentioned above. This was due to the coating of the molten material.

3.4. XRD Phase Analysis

It can be seen from XRD (Figure 1) that the main component of sludge before and after calcination is quartz. And there is also a small amount of kaolin and mica, which is closely related to the economic development of Chaozhou, which is the largest production location for daily ceramic. Chaozhou No.1 Sewage Treatment Plant is also located in the same place. Therefore, the components of the wastewater are related to ceramic raw materials, which may be the reason why the sludge can be fired with well compressive strength without adding other clay components. When the temperature is 950 °C, hematite appears in the mineral phase, which indicates that there is a large amount of iron in the sludge,

but it belongs to the iron minerals with weak crystallinity, such as ferrihydrite, hydroxyl ferric oxide, and so on, which are difficult to be observed in XRD. With the increase of temperature, these iron-bearing minerals change into hematite after removing structural water, which can be observed in phase retrieval. These iron and aluminum components in sludge have strong capacity of adsorption and catalytic oxidation, which play an important role in wetland padding [25–28].

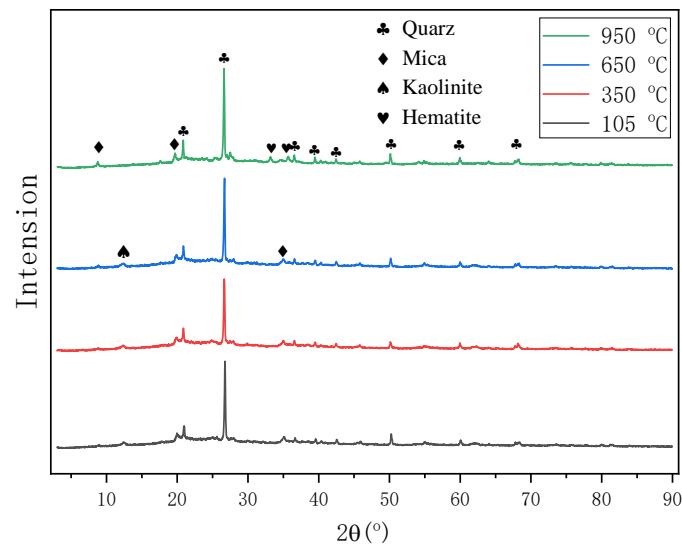


Figure 1. XRD images of ceramsite at different temperatures (from the bottom to the top, the temperature goes up).

3.5. SEM

Figure 2a is the ceramsite at 105 °C, which is relatively dense on the whole. Fibrous organic matter constitutes the aggregate, which is also one of the reasons for the high compressive strength. When the temperature rises to 350 °C, the volatile substances in the sludge start to volatilize, the sludge begins to expand, and the pores begin to increase. When the temperature rises to 650 °C, the volatile components evaporate completely, and the gas erosion pits appear on the surface of the particles. At this temperature, the specific surface area should be the maximum. The appearance and microstructure of the ceramsite was suitable for the attached growth of microorganisms [29]. When the temperature rises to 950 °C, parts of the material begin to melt, and the spherical particles condensed after melting appear on the surface. At this temperature, the porosity is high, but the micropore structure has been blocked, so the specific surface area is not large.

3.6. Adsorption Experiments

In combination with the previous characterization, it can be seen that when the calcining temperature is 650 °C, the specific surface area, compressive strength, and dissolution of heavy metals of the biochar ceramsite have met the basic requirements of wetland padding. At 950 °C, although with higher strength and lower heavy metal dissolution, the cost increases, therefore, 650 °C maybe the optimal temperature. The adsorption experiments were performed on the ceramsite fired at this temperature.

3.6.1. Influence of pH on Adsorption

The pH values of 10 mg/L Cr(VI) solutions in ten beakers were adjusted to 3, 4, 5, 6, 7, 8, 9 and 10, respectively, with 0.1 M HNO₃ and NaOH solution. The ceramsite fired at 650 °C was added into Cr(VI) solutions with different pH according to the ratio of solid to liquid of 1:40, and the total Cr concentration was measured after reaction according to the method of 2.2.5. The removal qualities of Cr by ceramsite at different pH are shown in Figure 3.

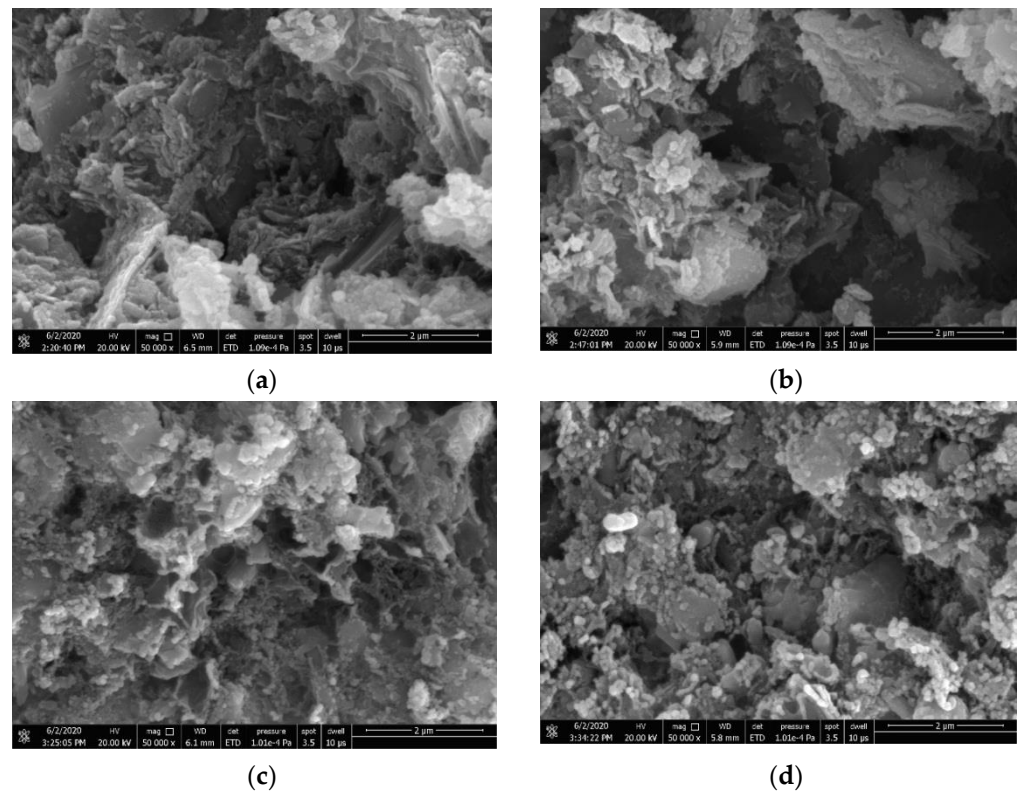


Figure 2. SEM images of ceramsite at different temperatures (a) 105 °C; (b) 350 °C; (c) 650 °C; (d) 950 °C.

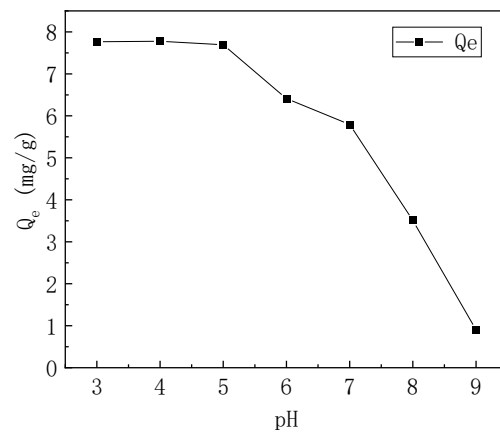


Figure 3. Graph of removal quantity as pH changes.

It can be seen from Figure 3 that when $\text{pH} < 7$, the removal quantity of Cr(VI) is higher. In this case, the surface is positively charged, and the electrostatic interaction with Cr(VI) is favorable for adsorption. After the point zero charge, the adsorption rate drops sharply. Because the surface of the ceramsite is negatively charged, which produces electrostatic repulsion to Cr(VI). Therefore, the subsequent adsorption experiments were carried out at $\text{pH} = 5$.

3.6.2. Adsorption Isotherm

Cr(VI) solutions with different concentrations were prepared, and the pH was adjusted to 5. A certain amount of ceramsite was added to each concentration solution according to the experimental method of 2.2.5. After reaction, the concentration of total chromium

in the supernatant was determined. The Langmuir and Freundlich adsorption isotherm model were used for fitting (Figure 4).

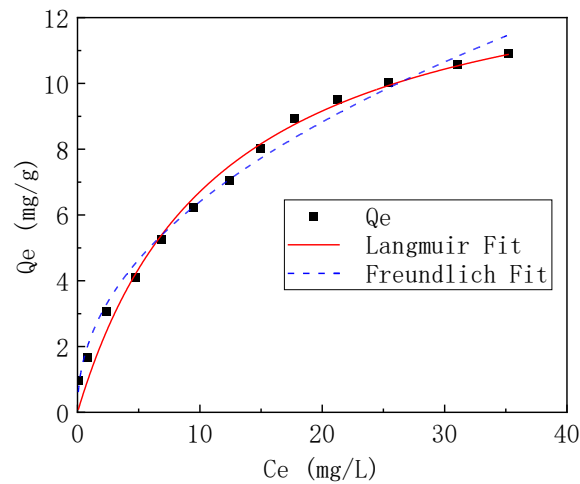


Figure 4. The fit of Langmuir and Freundlich adsorption isotherm model.

The parameters after fitting are shown in Table 5. The correlation coefficients of the two models are 0.9832 and 0.9981, respectively, which are very close, indicating that the adsorption of Cr(VI) by ceramsite is very complex. There is monolayer adsorption with adsorbates attached to the surface of the adsorbent and non-uniform multilayer adsorption with adsorbates accumulated on the surface of the adsorbent [30]. However, the n of the Freundlich model is greater than 2, which indicates that this adsorption model is not easy to conduct [31].

Table 5. Adsorption parameters of Langmuir and Freundlich adsorption isotherms.

Langmuir			Freundlich		
b	Q_{max}	R^2	k	n	R^2
0.0866	14.45	0.9832	2.20	2.16	0.9881

3.6.3. Adsorption Kinetics

According to the method of 2.2.5, the ceramsite with a certain mass was added to a beaker containing Cr(VI) solution with a pH of 5 and a concentration of 10 mg/L according to the ratio of solid to liquid of 1:40. After sealing, it was put into a water bath at 25 °C for shock reaction. At certain intervals, 1.5 mL solution was taken out by a syringe, and then filtered with 0.45 μ m filter membrane. The concentration of Cr in filtrate was determined. Thus, the change of Cr removal rate with time is calculated, and the pseudo-second-order kinetic equation is used for fitting:

$$\frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where, k_1 is a pseudo-second-order adsorption rate constant, and q_t is the adsorption capacity of the adsorbent on metal ions at time t (mg/g).

As can be seen from Figure 5, the kinetics of adsorption reaction are relatively fast in the early stage, and then tend to reach equilibrium. The entire process fits well with the pseudo-second-order dynamics equation, the correlation coefficient is 0.9937. The adsorption of biochar ceramsite to Cr (VI) belongs to the chemical adsorption. The adsorption rate is related to the active sites on the surface of the adsorbent. At the initial stage of the reaction, there are abundant active sites on the surface of the adsorbent and the adsorption rate is

fast. As the active sites were occupied by Cr(VI), the rate gradually decreases until the adsorption equilibrium is reached [32].

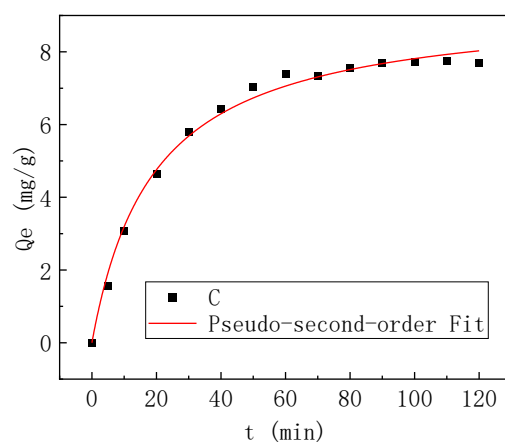


Figure 5. Pseudo-second-order adsorption kinetics fit.

4. Conclusions

Biochar ceramsite was prepared from the residual sludge of Chaozhou No. 1 Sewage Treatment Plant at different temperatures.

- (1) BET, compressive strength, and toxic leaching tests show that the prepared ceramsite has larger specific surface area and better compressive strength without additional auxiliary materials. The leaching amount of toxic heavy metals is low when the temperature is higher than 650 °C.
- (2) According to SEM, with the increase of calcining temperature, the volatile substances in the sludge begin to volatilize, the sludge starts to expand, and the pores begin to increase. When the temperature rises to 650 °C, the volatile components are completely consumed, and the specific surface area should be the maximum. When the temperature rises to 950 °C, part of the material begins to melt. Although the porosity is high, the micropores have been blocked, so the specific surface area decreases.
- (3) According to XRD, the main component of sludge is quartz, with a small amount of kaolin and mica, which can prepare high-strength ceramsite. Calcination converts the weak crystalline iron minerals to hematite.
- (4) The large amount of iron and aluminum in the sludge is the main reason for its good adsorption effect. According to the adsorption performance test of Cr(VI), the adsorption effect of ceramsite on Cr(VI) is well at low pH, and the adsorption isotherm fits well with Langmuir and Freundlich types. The adsorption process has both monolayer adsorption and multilayer adsorption, and the adsorption process conforms to the pseudo-second-order kinetics.

In general, the biochar ceramsite prepared by the residual sludge meets the basic requirements of wetland padding. The following experiment is to simulate the constructed wetland with ceramsite as padding to test the sewage purification effect.

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Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: Not applicable.

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Conflicts of Interest: The authors declare no conflict of interest.

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