Synergistic effects of calcium peroxide and Fe_3O_4 @BC composites on AVS removal, phosphorus and chromium release in sediments

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Research Article

Keywords: Black-odorous sediment, Fe_3O_4 @BC composites, Calcium peroxide, AVS, Phosphorus, Chromium, Microorganisms

Posted Date: January 27th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1158138/v1>

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Abstract

Black-odorous sediment pollution in urban have received widespread attention, especially pollution caused by acidified volatile sulfide (AVS), phosphorus and heavy metals. Fe_3O_4 was loaded onto the biochar (BC) by coprecipitate method to synthesize $\text{Fe}_3\text{O}_4@\text{BC}$ composites, which were mixed with calcium peroxide (CP) to sediment pollution treatment. In this study, the removal of AVS was analyzed from three aspects: firstly, AVS was oxidized with oxygen produced by CP. And then, Fe^{2+} could activate H_2O_2 produced by CP to generate hydroxyl radicals which have strong oxidation property to oxidize AVS. Finally, AVS was removed by bacterial denitrification. The results showed that the AVS removal rate could reach 71% compared with the blank group on the 25th day. With the addition of CP and $\text{Fe}_3\text{O}_4@\text{BC}$, the content of overlying water remained at 0.1 mg/L, which was due to the conversion of $\text{NH}_4\text{Cl-P}$ and Fe/Al-P in sediments into Ca-P to inhibit the release of phosphorus. At the same time, the acid extractable state and the reducible state of Cr in the sediment also decreased to 0.58% and 0.97%, which inhibited the release and migration of the heavy metal Cr. In addition, the results of high-throughput genetic test showed that the $\text{CP}+\text{Fe}_3\text{O}_4@\text{BC}$ group had a great increase in the total number of microorganisms compared to other groups. The abundance of *Sulfurovum* increased while that of sulphate-Reducing Bacteria (SRBs) was inhibited. Moreover, an abundance of denitrifying bacteria (*Dechloromina*s, *Acinetobacter* and *Flavobacterium*) was increased. This study showed that the combined application of $\text{Fe}_3\text{O}_4@\text{BC}$ composites and CP had a remarkable effect on the urban sediment treatment, which provided a new way to remove sediment pollution.

1. Introduction

In recent years, with the rapid development of industry and agriculture in China, a large number of pollutants have been discharged into water bodies, doing serious harm to urban rivers and forming black-odorous sediment (DeFu et al., 2015; Yu et al., 2020; Zhu et al., 2017). The main pollutants include AVS, phosphorus and heavy metals. Among three types of pollutants, AVS mainly cause of black and odorous water (Mai et al., 2021). The release of phosphorus and nitrogen in sediments can lead to eutrophication (Waajen et al., 2016a), which will affect water quality and aquatic ecosystem. The migration of heavy metals will affect living things and thus human health. Among these heavy metals, chromium (Cr) is the major cause of water pollution by anthropogenic and natural sources. Therefore, the treatment for AVS, phosphorus and Cr become a research hotspot.

The current approaches to remove AVS are chemical methods (e.g., chemical oxidation, chemical precipitation and flocculation). AVS removal through denitrification enhanced by nitrate addition has been considered as a cost-effective technology for black-odorous sediments control (Yin et al., 2019). However, the addition of nitrate will lead to a great increase of nitrogen in the water, which leads to eutrophication and affects human health and safety (Alan R Townsend et al., 2003). At the same time, nitrate has a negative effect on the release of phosphorus and heavy metals from sediment (Ma et al., 2021). Calcium peroxide (CP) is another chemical substance that can remove AVS effectively, which

doesn't produce other pollutants and is environmentally friendly. CP can slowly liberate hydrogen peroxide (H_2O_2) and O_2 at a "controlled" rate when contacting with water (detailed as shown in Eqs. (1) and Eqs. (2)), during which H_2O_2 can further generate produce free radicals (Xu et al., 2020). Therefore, CP can effectively control black-odorous sediments (Nykänen et al., 2012; Wang et al., 2019). At the same time, for phosphorus and chromium pollution, we mainly inhibit their release from sediment (Yin et al., 2019; Mukwaturi & Lin, 2015).

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Nowadays, nano-composites, especially Fe_3O_4 nano-composites are increasingly applied in environmental engineering. Nano- Fe_3O_4 composites contain iron in different valence states, which is an essential element for microbial growth and can promote the metabolic activity of the microbial community (Dimkpa & Bindraban, 2016; He et al., 2011). What's more, Nano- Fe_3O_4 is a high-performance catalyst of the Fenton reaction, which is widely used for H_2O_2 activation to degrade organic pollutants (Dimkpa & Bindraban, 2016; He et al., 2011). However, nano- Fe_3O_4 particles have a tendency to attract each other and aggregate into many larger-size particles, which causes a significant decrease in the specific surface area (Dong et al., 2015) and then reduces the catalytic performance. To address this issue, researchers have chosen different materials as a carrier to stabilize and scatter the nano- Fe_3O_4 particles. Compared with other support materials, biochar (BC) is a readily available porous carbon-rich material with a higher specific surface area (Dong et al., 2017). BC is widely applied in soil improvement (Ahmed et al., 2016; Huang et al., 2020), sediment treatment (Ahmed et al., 2016; Huang et al., 2020) and environment recovery (Ahmed et al., 2016; Huang et al., 2020). Humic acid is a carbon-rich material that contains a large number of functional groups, such as hydroxyl, carboxyl and aromatic groups. Biochar derived from humic acid not only has a larger specific surface area, but also retains organic functional groups, which can solidify heavy metals through cation exchange and complexation (Wang et al., 2021). Therefore, we consider that Fe_3O_4 loaded onto humic acid biochar can also solve the agglomeration problem of nano- Fe_3O_4 . At the same time, it can adsorb heavy metals to reduce the harm of heavy metals. Up to now, it has not been reported that the $Fe_3O_4@BC$ composite was produced, which was used to synergistically treat black and smelly sediment pollution with calcium peroxide.

In this study, humic acid was selected as the raw material to produce biochar at 600 °C. Nano- $Fe_3O_4@BC$ composites were successfully prepared by the coprecipitation method. The synergistic effect of CP and $Fe_3O_4@BC$ composites was used to treat the black-odorous sediment. This study mainly focused on the removal effect and mechanism of AVS, and the effects on phosphorus and Cr release. The change of microbial community in the sediment was also explored deeply. This research proposes a safe, high efficiency and eco-friendly method to treat black and odorous sediment pollution in the urban river.

2. Materials And Methods

2.1 Reagents and materials

Calcium peroxide was purchased from Zhoujian Animal Health Technology Co., Ltd. (Guangdong, China), and the content of calcium peroxide is above 60%. Humic acid was purchased from the Changbai Mountain Nutrient Soil Plant in Dalian, China. All the other chemicals used were analytical and purchased from Chengdu Kelong chemical company (Sichuan, China). Deionized water was applied throughout the experiment.

2.2 Material preparation

2.2.1 Preparation of biochar

The humic acid was first crushed and sieved, then put in a porcelain boat and heated in a tube furnace under N₂ atmosphere (200 mL/min) condition at 600 °C for 2 h, and the heating rate was kept at 10 °C/min.

2.2.2 Preparation of Fe₃O₄@BC

The Fe₃O₄@BC nanocomposites were synthesized by the co-precipitation method (Zhu et al., 2011; Zhuang et al., 2015). Firstly, 10.2 g FeCl₃·6H₂O and 4.975 g FeCl₂·4H₂O were dissolved in 200 mL ultrapure water, then 7 g of pre-prepared BC powder was added into the solution and continued to stir 24 h. A peristaltic pump was used to slowly drop 5 M NaOH into the reaction solution (4 mL/min) until the solution pH reached 11. The whole preparation process was purged with nitrogen gas (N₂) to eliminate the interference of dissolved oxygen in the water. Finally, the black material obtained was filtered and washed several times, and placed in the 65°C vacuum oven to dry 24 h.

2.2.3 Characterization of the biochar and Fe₃O₄@BC

The surface morphology of the biochar and the Fe₃O₄@BC composites were observed using scanning electron microscopy (SEM, JSM-7500F, JEOL). Energy dispersive X-ray spectroscopy (EDS) was coupled with SEM to examine surface elemental composition and obtain surface elemental distribution maps. The chemical structures were identified by Fourier-transform infrared spectroscopy (FT-IR, Nicolet 6700, USA). Analysis of the crystalline structures of the catalyst powders was performed by X-ray diffraction (XRD, EMPYREAN, UK).

2.3 Experiment design

The experiments were conducted in a series of 250-mL serum bottles and the total number of experimental serum bottles was 147. Seven sets of batch experiments were carried out simultaneously and the specific amount was shown in the following table (Table 1).

Table 1
Details of the experimental set-up.

Groups	Sediment (g)	Water (mL)	BC (g)	CaO ₂ (g)	Fe ₃ O ₄ (g)	Fe ₃ O ₄ @BC (g)
CK	75	150				
BC	75	150	4			
CP	75	150		12		
CP+BC	75	150	4	12		
CP+Fe ₃ O ₄	75	150		12	2	
CP+BC+Fe ₃ O ₄	75	150	4	12	2	
CP+Fe ₃ O ₄ @BC	75	150		12		6

All the groups were mixed and placed in the incubator (HWS-350) at 25°C under dark conditions. The sediment was sampled at days 2, 4, 6, 8, 13, 18 and 25. All the experiments were conducted in triplicate.

2.4 Measuring method

The pH and ORP were analyzed with a portable analyzer (Multi3610, WTW, Germany). For the determination of AVS, 2.0 g wet sediments were added into a round-bottom flask filled with N₂. Then the sediment suspension was stirred and acidified for 45 min with 20 mL of 6 mol HCl at room temperature. Finally, with N₂ as a carrier gas, the H₂S was absorbed by 0.5 mol NaOH solution and determined via the methylene blue method, using a Techomp UV1000 spectrophotometer. According to the four-step extraction method proposed by Hietjes and Lijklema (LIJKLEMA, 1980), different forms of P were extracted from the sediment and the content of P was analyzed by molybdate salt photometer (T3200, China).

The different fraction of Cr in the sediment was measured by BCR (LIJKLEMA, 1980) three-step extraction method and the Cr was detected by Atomic absorption spectrophotometer (AA-6880G, Japan). Ammonia nitrogen (NH₄⁺-N), nitrate-nitrogen (NO₃⁻-N) and nitrite-nitrogen (NO₂⁻-N) analyses were conducted according to national standard methods issued by the State Environmental Protection Administration of China (Wang et al., 2016).

The total DNA was extracted in the sediment using the E.Z.N.ATM Mag-Bind Soil DNA Kit (Omega, USA) while its completeness was tested by agarose gel electrophoresis. Then High-throughput sequencing was conducted with the Illumina MiSeq system (Li et al., 2021) (Shanghai, China) to determine the microbial in the sediment.

2.5 Statistical analysis

The results are presented as the means and standard deviations of three replicate samples. Significant differences among the means in different treatments were identified through one-way ANOVA, followed by Tukey's test.

All statistical analyses were performed using SPSS 21.0 (IBM, New York, USA), and significant levels were reported at $p < 0.05$.

3. Results

3.1 Characterization of $\text{Fe}_3\text{O}_4\text{@BC}$

3.1.1 SEM and EDS

As shown in Fig. 1 (a), the surface morphology of biochar mainly presents a flaky structure with a few porous structure. However, it could be clearly observed that the surface was loaded with many nano-particles when the Fe_3O_4 was loaded on the biochar in Fig. 1 (b).

The mass fraction of Fe in $\text{Fe}_3\text{O}_4\text{@BC}$ increased from 0.78–22.30% after loading Fe_3O_4 onto biochar (Fig. 1 (c, d)). The results showed that $\text{Fe}_3\text{O}_4\text{@BC}$ was successfully prepared and the Fe_3O_4 was loaded onto biochar in the form of nano-particles.

3.1.2 XRD and FT-IR

The crystalline properties of BC and $\text{Fe}_3\text{O}_4\text{@BC}$ were analyzed by XRD (Fig. 2a). The characteristic peaks at $2\theta = 21.2^\circ, 35.1^\circ, 41.4^\circ, 50.4^\circ$ and 67.2° were indexed as the (111), (220), (311), (400) and (511) planes of Fe_3O_4 , respectively (PDF#19-0629). Thus, the results of XRD were consistent with the SEM image which indicated that Fe_3O_4 are successfully loaded onto biochar.

The FT-IR spectra of the synthesized BC, Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@BC}$ are shown in Fig. 2b. Each band in the spectrum represents the vibration of functional groups in BC, Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@BC}$: -OH (3270 cm^{-1}), C=O (1630 cm^{-1}), C-O (1022 cm^{-1}) and Fe-O (555 cm^{-1}). The addition of Fe oxides to the biochar will make the biochar more hydrophilic, and the oxygen-containing functional group will be enhanced, so -OH was produced (Peng et al., 2019). The Fe-O stretching vibration peak also shows that Fe_3O_4 was successfully loaded onto biochar (Peng et al., 2019).

3.2 pH and OPR

The variations of pH in overlying water were presented in Fig. 3a. There was nearly no difference between the CK and the CP+ $\text{Fe}_3\text{O}_4\text{@BC}$ regarding pH value during the experimental study ($p > 0.05$). The pH of each group with BC or CP increased and finally remained at about 8.0. In the CP+BC+ Fe_3O_4 group, the pH remained stable in the early stage and began to rise after the 6th day, eventually reaching 8.3.

From Fig. 3b, it was found that the ORP of all groups (excluding the CP+Fe₃O₄@BC group) remained positive during the entire process of the experiment. But in the CP+Fe₃O₄@BC group, the ORP was negative in the first 8 days and then started to rise to a positive value after the 8th day.

3.3 Removal of AVS in the sediment

As shown in Fig. 4a, the content of AVS in the CP+Fe₃O₄@BC group decreased from 0.75 to 0.35 mg/g during the experiment and the AVS removal rate reached 52.77%. The AVS concentration in the sediment all of the CP, CP+BC, CP+Fe₃O₄, CP+BC+Fe₃O₄ groups decreased to 0.68 mg/g, 0.62 mg/g, 0.55 mg/g and 0.46 mg/g, respectively. There was no statistically significant difference between the CP group and CP+BC group during the experiment ($p > 0.05$). However, AVS in the CK and BC groups increased to 0.88 mg/g and 0.86 mg/g, respectively. Compared with the CK group, the removal of AVS in the CP+Fe₃O₄@BC group reached 71%, indicating that the combined CP and Fe₃O₄@BC can effectively reduce the formation of AVS in sediment.

3.4 Changes of TP content in the overlying water and the content of different fractions of phosphorus in the sediments

As shown in Fig. 5, the TP content in overlying water remained between 0.05 mg/L and 0.35 mg/L. In the CK group, BC group and CP group, the TP content increased in the early stage and reached the highest value on the 8th day, which were 0.331 mg/L, 0.288 mg/L and 0.296 mg/L, respectively. Then it began to slowly decrease. The total phosphorus content in the overlying water of the other four groups was relatively stable, ranging from 0.1 mg/L to 0.2 mg/L. However, the TP of CP+Fe₃O₄@BC group was maintained at 0.1 mg/L on average, which met the first class water standard (Su et al., 2017).

Phosphorus release from sediment is the main factor of overlying water eutrophication (Gao et al., 2005). The form of sediment P is divided into: weakly adsorbed phosphorus (NH₄Cl-P), iron/aluminum bound phosphorus (Fe/Al-P), calcium bound phosphorus (Ca-P) and Residual Phosphorus (Res-P). NH₄Cl-P and Fe/Al-P are easy to migrate, while Ca-P and Res-P are stable and difficult to migrate. On the 2th and 8th days, phosphorus morphological changes were shown in Fig. 6a and 6b. Although NH₄Cl-P and Fe/Al-P contents decreased in the CP+Fe₃O₄@BC group, Ca-P content increased to 27.86%. Therefore, TP content of overlying water in the CP+Fe₃O₄@BC group was maintained at 0.1 mg/L. However, the NH₄Cl-P content in the sediments of the CK group decreased from 23.25–10.61%, while the other contents remained unchanged, indicating that the release of NH₄Cl-P into water led to the increase of TP content in the overlying. The content of Fe/Al-P in the BC group also decreased from 28.14–12.96%, while the other contents remained unchanged, which increased the content of TP in the overlying water.

3.5 Changes of Cr content of different fractions in the sediments

The release of Cr in sediment is an important cause of heavy metals in water. The different forms of Cr in sediments are divided into: acid extractable state (exchangeable state and carbonate combined state), reducible state (iron-manganese oxide combined state), oxidizable state (organic state) and residue state. In each experimental group, the different fractions and contents of Cr in the sediment were shown in Fig. 7.

Among them, the acid extractable state and the reducible state are unstable and easily release and migrate, which are the main fractions released into the water (Cai et al., 2021; Du Laing et al., 2009). On the 6th day, the acid extractable state content of the CK group and the BC group was almost the same, accounting about for 8%, but the reducible state content was different, 10.31% and 5.20%, respectively. On the 25th day, the acid extractable state and reducible state in the CK and BC groups still remained at about 5%. However, the content of the acid extractable state and reducible acid in the CP+Fe₃O₄@BC group was 1.6% and 2.51% on the 6th day and decreased to 0.97% and 0.58% on the 25th day, respectively, which could greatly reduce the harm of Cr release and migration.

3.6 Changes in Nitrogen form

3.6.1 Variation of NH₄⁺-N, NO₃⁻-N and NO₂⁻-N in the sediment

The experimental changes of NH₄⁺-N, NO₃⁻-N and NO₂⁻-N in the sediment were shown in Fig. 8 (a)(c)(e). The content of NH₄⁺-N in the sediment showed a downward trend on the whole, but it could be seen that the content of CP+Fe₃O₄@BC group was lower than other groups. The content of NO₃⁻-N in the sediment also showed a downward trend during the experimental study and was finally maintained at 80 mg/kg. NO₂⁻-N showed a downward trend as a whole, but the content of the CP+Fe₃O₄@BC group was the lowest compared with other groups.

3.6.2 Variation of NH₄⁺-N, NO₃⁻-N and NO₂⁻-N in the overlying water

The experimental changes of NH₄⁺-N, NO₃⁻-N and NO₂⁻-N in the overlying water were shown in Fig. 8 (b) (d)(f). As shown in Fig. 8b, the content of NH₄⁺-N decreased gradually (except CP+Fe₃O₄@BC group) in all groups. The content of NH₄⁺-N in CP+Fe₃O₄@BC group increased from the 2nd day to the 11th day, with a peak at 2.4 mg/L followed by a slow drop. The overall nitrate nitrogen of each group in the experiment showed an upward trend and the final content remained at 2.5 mg/L, but the nitrate nitrogen content in the CK group was the least. As shown in Fig. 8f, the content of NO₂⁻-N in all experiment groups basically reached the highest value on the 8th day, and then began to decrease to nearly 0 mg/L (except CP+Fe₃O₄@BC group). However, the NO₂⁻-N content in the CP+Fe₃O₄@BC group was almost 0 mg/L in the early stage and slowly increased to 0.467 mg/L on day 8, then began to decrease to 0 mg/L.

3.7 Analysis of microbial changes in sediments

3.7.1 Microbial diversity

Table 2 shows the analysis of the biodiversity index. The coverage rate of the samples had reached 99%, which can truly reflect the microorganisms in the sediment. Chao index is commonly used in ecology to estimate the number of species. From the below table, it can be found that the Chao indexes between the experimental groups were 2900~3200. The Chao index in the CK group was only 2977.78, while the Chao index increased after adding CP, BC, Fe₃O₄ and Fe₃O₄@BC, which proved that the introduction of CP, BC, Fe₃O₄ and Fe₃O₄@BC can promote the growth of microorganisms.

Table 2
Diversity Index Statistics in sediments

	Sample	Shannon	Chao	Simpson	Shannoneven	Coverage
13 th days	CK	5.49	2977.78	0.03	0.70	0.99
	BC	5.63	3207.53	0.02	0.71	0.99
	CP+Fe ₃ O ₄	5.73	3030.68	0.02	0.74	0.99
	CP+BC+Fe ₃ O ₄	5.62	3068.40	0.03	0.72	0.99
	CP+Fe ₃ O ₄ @BC	5.97	3144.75	0.01	0.76	0.99

Shannon and Simpson represent the diversity of the community. The higher the Shannon index, the higher the community diversity, while the lower the Simpson index, the higher the community diversity. The Shannon index of the CP+Fe₃O₄@BC group was 5.97, which was larger than that of other experimental groups. And the value of Simpson 0.1 was smaller than the value of other experimental groups. It can be found that the adding of Fe₃O₄@BC material and CP can increase the diversity of the community. Shannoneven represents the uniformity of the species, the larger the value, the better the uniformity. The Shannoneven index of the CP+Fe₃O₄@BC group was larger than the value of other experimental groups, indicating that the uniformity pretty great.

3.7.2 Microorganisms in sediments

Figure 9 shows the relative abundance of genus-level microorganisms in different experimental groups. The main bacteria in the CK group were *Dechloromonas* (5.6%), *Arthrobacter* (7.3%), *Paenisporosarcina* (3.5%), *Sulfurovum* (0.5%), *Luteolibacter* (2.5%) and *Desulfobulbus* (0.45%).

Sulfurovum can obtain energy by oxidizing AVS (Sun et al., 2020). Compared with CK group, *Sulfurovum* abundance of the CP+Fe₃O₄ group, CP+BC+Fe₃O₄ group and CP+Fe₃O₄@BC group increased to 0.9%, 1.5% and 1.7%, respectively. Sulphate-reducing bacteria (SRBs) use oxidized sulfur compounds as electron acceptors and produce sulfide while oxidizing organics for energy generation. As a type of SRB,

Desulfobulbus content in the CK group and BC group were 0.45% and 0.31% respectively, but the *Desulfobulbus* content in the CP+Fe₃O₄ group, CP+BC+Fe₃O₄ group and CP+Fe₃O₄@BC group is 0.21%, 0.3% and 0.13%, respectively. Therefore, the introduction of CP and Fe₃O₄@BC composite materials can inhibit the growth of SRB and promote the growth of sulfur oxidizing bacteria, which can remove AVS (Purdy et al., 2001).

Dechloromonas, *Acinetobacter* and *Flavobacterium* are all denitrifying bacteria. Compared with the CK group, the abundance of *Dechloromonas* (Duffner et al., 2021) in the CP+Fe₃O₄ group, CP+BC+Fe₃O₄ group and CP+Fe₃O₄@BC group increased to 6.8%, 7.3% and 7.5%, respectively. *Acinetobacter* content in the CK group was only 0.043%, while 0.059%, 0.079%, 0.103% and 0.106% for the BC group, CP+Fe₃O₄ group, CP+BC+Fe₃O₄ group and CP+Fe₃O₄@BC group, respectively. *Flavobacterium* mostly has the function of nitrogen and phosphorus removal (Hao et al., 2017). *Flavobacterium* content in the CK group was only 0.068%, while the BC group, CP+Fe₃O₄ group, CP+BC+Fe₃O₄ group and CP+Fe₃O₄@BC group were 0.097%, 0.079%, 0.098% and 0.103%, respectively. The introduction of BC and Fe₃O₄ can promote the growth of *Dechloromonas*, *Acinetobacter* and *Flavobacterium*, which can promote denitrification. *Nitrospira* is a kind of nitrite-oxidizing bacteria (NOB), which can oxidize ammonia nitrogen into nitrate nitrogen (Nakamura et al., 2006). According to the measurement data, the abundance of *Nitrospira* in the CP+Fe₃O₄@BC group was 0.12%, while that in the CK group was only 0.05%. The results showed that CP and Fe₃O₄@BC could promote the transformation of nitrogen and reduce nitrogen, one of the main components of eutrophication.

4. Discussion

4.1 AVS removal mechanism

The excessive accumulation of AVS in the sediment could poison biological growth and impact environmental health (Li et al., 2021). At the same time, AVS is the main cause of black and smelly water (Cao et al., 2020). More than 71% of the sediment AVS in the CP+Fe₃O₄@BC group had been removed, compared with the concentration of AVS in the CK group. The mechanism of AVS removal in this experiment is as follows:

Firstly, CP can slowly decompose to release O₂ at a “controlled” rate when in contact with hydrous media. AVS can be oxidized by oxygen to form SO₄²⁻ (Eq. (3)) (De Lange et al., 2008; Teuchies et al., 2011a; Zhang et al., 2020). The production of oxygen also led to the increase of Sulfurovum (Fig. 9), which promoted the removal of AVS. Therefore, the removal rates of AVS in the sediments of the CP group, CP+BC group, CP+Fe₃O₄ group, CP+BC+Fe₃O₄ group and CP+Fe₃O₄@BC group were 8.74%, 17.3%, 26.3%, 38.6% and 52.8%, respectively. However, AVS concentration increased in the experimental group without CP (Fig. 10a).

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Secondly, the hydroxyl radicals, which has a high standard oxidation potential (2.80 V) and exhibits high reaction rates, can oxidize AVS efficiently (De Lange et al., 2008; Teuchies et al., 2011a; Zhang et al., 2020) (Eq. (4)). In the CP+Fe₃O₄ group, CP+Fe₃O₄+BC group and CP+Fe₃O₄@BC group, the removal rate of AVS was as high, as 26.26%, 38.58% and 52.77%, respectively. It is probably attribute to the Fenton reaction between Fe²⁺ and calcium peroxide, which produced hydroxyl radicals (Fig. 10b) (Yang et al., 2021). Nano-Fe₃O₄ was loaded onto the BC by the coprecipitation method, which solved the agglomeration problem of nano-Fe₃O₄ and made it fully contact reaction. Therefore, the removal of AVS from sediments in the CP+Fe₃O₄@BC group was 14.19% more than that in the CP+BC+Fe₃O₄ group. At the same time, the by-product of the Fenton reaction would produce H⁺, which reacted with OH⁻ to maintain pH value (Jian et al., 2021), so the pH of the CP+Fe₃O₄@BC group was unchanged (Fig. 3a).

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Finally, the main theory of nitrate repairing AVS in sediment is that autotrophic sulfide drives denitrification (Li et al., 2019). The introduction of CP and Fe₃O₄@BC materials promoted the growth of nitrifying bacteria and transformed NH₄⁺-N and NO₂⁻-N into NO₃⁻-N in the sediment. At the same time, denitrifying bacteria also increased, which used nitrate to remove AVS (Fig. 10c).

3

Desulfobulbus is a type of SRB that can transform sulfate into sulfide under anoxic environment. *Desulfobulbus* content in the CK and BC groups was 0.45% and 0.31%, respectively, thus increasing AVS content (Feng et al., 2014; Qiu et al., 2017). However, the *Desulfobulbus* content in the CP+Fe₃O₄@BC group is only 0.13%, proving that the addition of CP and Fe₃O₄@BC composite materials can inhibit SRBs and can effectively repair AVS for a long time.

In summary, there were three removal mechanisms of AVS by adding CP and Fe₃O₄@BC composite materials into sediments. The synergism of CP and Fe₃O₄@BC can not only can remove effectively the content of AVS in sediments and can not lead to the accumulation of NH₄⁺-N and NO₂⁻-N in sediments, but also can inhibit SRB growth and achieve long-term effective treatment of black odorous sediment.

4.2 Mechanism of phosphorus and Chromium change in different fractions in the sediment

4.2.1 Phosphorus

Phosphorus is an important nutrient, but excessive P will also lead to eutrophication of the water body, thereby destroying the water environment (Li et al., 2021). NH₄Cl-P and Fe/Al-P are referred to as

migrating phosphorus in this study because of their easy migration and release (Ribeiro et al., 2008; Rydin, 2000).

As shown in Fig. 11, the phosphorus migration state decreased from the 2nd day to the 8th day, but Ca-P content increased (except the CK group and the BC groups). The content of phosphorus migration state in the CK group and BC group decreased from 0.301mg/g and 0.273mg/g to 0.225mg/g and 0.16mg/g, while the content of Ca-P remained unchanged. This was attributed to the release of the phosphorus migration state in sediment, which led to the increase of phosphorus content in overlying water (Fig. 5) (Kaiserli et al., 2002; Liu et al., 2018; Wang et al., 2013). The Ca-P is relatively stable and difficult to release into water bodies. In the CP+Fe₃O₄@BC group, the pH value remained stable and the introduction of calcium ions led to the transformation of NH₄Cl-P and Fe/Al-P into Ca-P, which led to low TP content in overlying water (Fig. 10) (Han et al., 2015). Thus, adding CP and Fe₃O₄@BC composite in the sediment could effectively control internal phosphorus release by increasing the concentrations of Ca-P. At the same time, according to the ORP of the overlying water, the transformation between ammonia nitrogen and nitrate nitrogen and the change of the nitrite content of the intermediate product can be acquired (Fig. 8). In the reduction environment, the dissimilatory nitrate reduction to ammonium (DNRA) was prone to occur (Zhu et al., 2018). In the oxidizing environment, ammonia nitrogen is converted to nitrite nitrogen by microorganisms and eventually to nitrate nitrogen (nitrification reaction) (Xiao et al., 2010). In addition, denitrifying bacteria increased in the CP+Fe₃O₄@BC group, which promoted denitrification.

In conclusion, the introduction of CP and Fe₃O₄@BC composite materials can effectively inhibit the release of phosphorus in sediment and promote denitrification, which can effectively inhibit the eutrophication of water bodies (Waajen et al., 2016b).

4.2.2 Chromium

Cr is a well-known carcinogenic element present in drinking water. The high concentration of Cr also exerts strong toxic effects as it can diffuse through the cell membranes, oxidize biological molecules and create a potential risk of living being healthy. At the same time, Cr also is responsible for skin tumors in animals (Lal et al., 2020).

As shown in Fig. 12, the contents of acid exchangeable Cr (Ex-Cr) and reducible Cr (Reducible-Cr) in the CK and the BC groups were high, which were easy to release and migrate to water bodies. The content of Ex-Cr and Reducible-Cr in the experimental group with CP was lower than 0.5mg/kg. It was possible that O₂ was produced by CP, leading to the change of Cr morphology (Teuchies et al., 2011b). Adsorption, ion exchange, complexation and precipitation are the major mechanisms involved in the conversion of soluble and potentially soluble forms of heavy metals to geochemically stable solid phases by biochar (Shentu et al., 2022). However, the content of Ex-Cr and Reducible-Cr in the BC group did not decrease, which may be ascribed to that the BC had no effect on Cr fixation. When Fe₃O₄ was loaded onto BC by coprecipitation method, -OH functional groups were formed, which can solidify Cr (Fig. 2b). Therefore, the

Ex-Cr and Reducible-Cr contents in the CP+Fe₃O₄@BC group were only 0.157mg/kg and 0.0942mg/kg at 25 days, respectively, which were far lower than those in other experimental groups (Fig. 12).

In general, the introduction of CP and Fe₃O₄@BC composites can change the easily migrating state of Cr into a stable state, thus reducing the harm of heavy metal Cr.

5. Conclusions

The synergistic treatment of black-odorous sediments with CP and Fe₃O₄@BC composites was researched in this study. The addition of CP and Fe₃O₄@BC composites into the sediment could effectively remove AVS. The results showed that the removal rate of AVS in sediments reached 52.77% on the 25th day. Compared with the CK group, the removal rate of AVS by CP and Fe₃O₄@BC reached 71%. The removal mechanism could be divided into three aspects: firstly, oxygen produced by CP could oxidize AVS. And then, CP produced H₂O₂, which was activated by Fe²⁺ to produce hydroxyl radical oxidation to oxidize AVS. Finally, the addition of CP and Fe₃O₄@BC could promote the growth of denitrifying bacteria (*Dechloromonas*, *Acinetobacter* and *Flavobacterium*) and strengthen denitrification to remove AVS. The addition of CP and Fe₃O₄@BC could transform the NH₄Cl-P and Fe/Al-P into a stable Ca-P complex, which greatly reduced the release of phosphorus. At the same time, the increase of denitrifying bacteria (*Dechloromonas*, *Acinetobacter* and *Flavobacterium*) promoted the denitrification reaction, which could promote the conversion of nitrogen. Therefore, the addition of CP and Fe₃O₄@BC could effectively inhibit the eutrophication of the water body. After CP and Fe₃O₄@BC composites were added, the content of the Ex-Cr and the reducible-Cr decreased to 0.157 mg/kg and 0.0942 mg/kg on the 25th day, respectively, which were lower than those in other groups. Thus, the harm of heavy metal Cr reduced. The addition of Fe₃O₄@BC composites could increase the total number of microorganisms and promote the growth of *Sulfurovum* and inhibit SRBs, which could effectively inhibit the production of AVS for a long time. Therefore, this study can be used to reference the restoration of sediments. It can be applied to practical engineering and provides a new idea to deal with black-odorous sediment.

Declarations

Acknowledgements The authors would like to acknowledge the financial support from the Major Scientific and Technological Special Program of Sichuan Province, China (2018SZDZX0027 and 2019-YF09-00081-SN).

Author contribution Naiwen Li and Chao Liu contributed to the conception of the study and provided financial support.

Yintian Li, Xueying Wang and Ge Gou performed the experiment.

Yintian Li and Yanchun Huang contributed significantly to analysis and manuscript preparation.

Yintian Li performed the data analyses and wrote the manuscript.

Bo Lai, Jun Li, Yuxin He and Naiwen Li helped perform the analysis with constructive discussions.

Funding This study was funded by Major Scientific and Technological Special Program of Sichuan Province, China (2018SZDZX0027 and 2019-YF09-00081-SN).

Data availability Some data generated or analysed during this study are included in this published article. The other raw or processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

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Figures

Figure 1

SEM images of (a) BC, (b) Fe₃O₄@BC; EDS spectrum of (c) BC, (d) Fe₃O₄@BC

Figure 2

(a) XRD patterns of BC and Fe₃O₄@BC; (b) FT-IR spectra of BC and Fe₃O₄@BC

Figure 3

The variation of pH and ORP in overlying water during the experimental study: (a) pH.(b) ORP

Figure 4

(a) The variation of AVS in the sediment during the experimental study; (b) The proportion of AVS in each group relative to the initial sediment on the 25th day

Figure 5

The variation of TP in overlying water during the experimental study.

Figure 6

The variation of P in different forms in sediments: (a) the 2nd day. (b) the 8th day.

Figure 7

The variation of heavy metal Cr in different groups during the experimental study; (a) the 6th day; (b) the 25th day

Figure 8

The variation of NH₄⁺-N, NO₃⁻-N and NO₂⁻-N in overlying water and sediment during the experimental study: (a) NH₄⁺-N in the sediment. (b) NH₄⁺-N in the overlying water. (c) NO₃⁻-N in the sediment. (d) NO₃⁻-N in the overlying water. (e) NO₂⁻-N in the sediment. (f) NO₂⁻-N in the overlying water.

Figure 9

The relative abundance of microbial communities

Figure 10

Synergistic reaction mechanism of $\text{Fe}_3\text{O}_4@\text{BC}$ and CaO_2 ; (a) Oxygen oxidizes AVS. (b) Hydroxyl radical oxidizes AVS.

(c) Autotrophic sulfide drives denitrification.

Figure 11

(a) The Phosphorus migration state changes on the 2nd day and the 8th day; (b) The Ca-P changes on 2nd day and 8th day

Figure 12

(a) The Ex-Cr fraction changes on the 6th day and the 25th day; (b) The reducible-Cr fraction changes on the 6th day and the 25th day