Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29577

295 (2023) 125–132
May

Ex-situ treatment of black and odorous sediments using chemical oxidation

Cong Huang[a], Qiang Lin[b], Shaokang Peng[c], Zheng Xu[a], Min Zhang[a], Dingli Chen[a], Haoming Sun[c], Jizhao Chen[c], Lei Miao[c], Zongping Wang[c,*]

[a]*PowerChina Huadong Engineering Co., Ltd., Hangzhou 311100, China, emails: huang_c@hdec.com (C. Huang), xu_z@hdec.com (Z. Xu), zhang_m9@hdec.com (M. Zhang), chen_dl@hdec.com (D. Chen)*
[b]*China Municipal Engineering Southwest Design Research Institute Co., Ltd., Chengdu 610213, China, email: lqbestlife@163.com (Q. Lin)*
[c]*College of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430070, China, emails: m202174065@hust.edu.cn (S. Peng), m202174069@hust.edu.cn (H. Sun), 1982055971@qq.com (J. Chen), miaolei@hust.edu.cn (L. Miao), zongpingw@hust.edu.cn (Z. Wang)*

Received 6 November 2022; Accepted 18 April 2023

ABSTRACT

The treatment of sediments is a key challenge with regards to the treatment of black and odorous water. At present, the sediments of black and odorous water bodies are mostly treated using dredging, and the sediments need to be effectively treated to reduce the secondary pollution to the environment. Chemical process is widely used in the treatment of black and odorous sediments due to its obvious and fast treatment effect. In this study, three chemical reagents, namely sodium persulfate, calcium oxide and hydrogen peroxide, were selected to find their optimal dosages to treat the sediments. The results show that persulfate had the most favorable treatment effect on sediments, and exhibited the optimum removal effect for water content, organic matter, total nitrogen, ammonia nitrogen, total phosphorus and heavy metal content of sediments. The optimal dosage of sodium persulfate and calcium oxide was 6 g/L each, while that of hydrogen peroxide was 30 mL/L. For the combination of different reagents, the combined effect of sodium persulfate and hydrogen peroxide was the most favorable. When the dosages of sodium persulfate and hydrogen peroxide were 4.5 g/L and 7.5 mL/L, respectively, the removal rates of total nitrogen, ammonia nitrogen, total phosphorus, cadmium, chromium, nickel, lead, water content and organic matter in sediments reached the values of 69.53%, 74.58%, 77.23%, 39.21%, 41.01%, 43.72% and 21.74%, 21.33% and 2.4%, respectively.

Keywords: Black and odorous water; Chemical process; Sediments; Persulfate; Hydrogen peroxide

1. Introduction

Nowadays, the existence of black and odorous water bodies is a huge challenge for the improvement of urban water environment [1]. China has put forward stringent requirements to mitigate the problem of black and odorous water bodies. These requirements include the "Water Pollution Prevention and Control Action Plan" and "Water Ten Articles" issued by China in 2015 and clearly state that black and odorous water bodies in urban built-up areas will be eliminated completely by 2030. As endogenous pollution of black and odorous water bodies, the bottom sediments is imperative to be treated. In this regard, sediment is often dredged [2] and need to be stabilized and harmless to avoid secondary pollution to the environment.

At present, the common treatment methods of sediment are divided into *in-situ* and *ex-situ* treatment methods [3]. Although *ex-situ* treatment is undertaken at large scale and has high cost, it is still widely used because of the advantages

* Corresponding author.

of obvious and quick treatment effect [4]. *Ex-situ* treatment mainly includes physical separation method, stable curing method, biodegradation method, leaching method, pyrolysis method, ultrasonic degradation method, electrodialysis and advanced oxidation process [5–8]. The most effective way to stabilize sediments is the chemical process [9]. Among various chemical processes, the most common application is the redox method. Chemical reagents such as calcium peroxide [10], hydrogen peroxide [11], potassium permanganate [11,12] and nitrate are commonly used to oxidize and remove pollutants in sediments. In recent years, more and more attention has been paid to persulfate-based oxidation technology [13,14], which has been widely used in sediments treatment [13] and soil remediation [14]. It is generally recognized that, persulfate has a certain degree of oxidation due to the peroxygen, and free radicals or other active oxidizing substances produced after activation further enhance its oxidizing ability [15]. Zhen et al. [13] found that the floc structure of sediments changed after the addition of persulfate, and the dewatering effect of sludge was significantly improved. Do et al. [14] used persulfate to treat diesel-contaminated soil, and activated persulfate through ferrous iron in the soil significantly removed organic pollutants from soil.

In order to explore the effect of persulfate and common chemical reagents on the treatment of black and odorous sediments and to find the optimum dosage of combined reagents, this study took the black and odorous sediments of a river in Wuhan (China) as the research object, and explored the treatment effect of individual reagents and composite reagents (consisting of calcium oxide, hydrogen peroxide, and sodium persulfate) on the sediments of black and odorous water. At the same time, the dosage of chemical reagents was varied, and the changes in water content, organic matter, total nitrogen, total phosphorus, ammonia nitrogen and heavy metal content in sediments were studied. Based upon the results, the optimum chemical reagent type and its corresponding dosage were determined, which provide theoretical guidance for the effective disposal of black and odorous water sediments.

2. Materials and methods

2.1. Sediment source and properties

The sediments used in the experiments was obtained from a river in Wuhan, China, which was seriously polluted and the water body was black and odorous. The sediment sampling depth was about 40 cm. In order to eliminate the influence of overlying water on sediments as much as possible, it is necessary to concentrate the samples using gravity sedimentation, so that the impurities mixed in the sediment samples could be removed. The sediment samples were sealed, refrigerated, and stored at 4°C. The properties of the sediments are summarized in Table 1.

2.2. Experimental device and method

2.2.1. Experimental device

In order to simulate the treatment process of black and odorous sediments in the actual project, a 10-mm thick acrylic plexiglass plate was used to make a micro sediment disposal site as an experiment device, as shown in Fig. 1.

2.2.2. Experimental methods

In this experiment, different individual chemical reagents and composite reagents were used to simulate the stabilization process of chemical reagents on the sediments of black and odorous water bodies in practical engineering. By studying the dynamic changes of various substances in the sediments of black and odorous water bodies under different reagent dosages, the optimal reaction conditions were determined, which are useful for practical engineering applications.

1 L of the sediments after gravity sedimentation and concentration treatment was put in six experimental apparatus, respectively. 0 (control group), 1, 2, 4, 6, and 8 g/L of sodium persulfate were then added to each of samples. After 6 h of static reaction at ambient temperature of 24°C, the water content, organic matter content, total nitrogen (TN), ammonia nitrogen (NH_3–N), total phosphorus (TP) and heavy metal (Cd, Cr, Ni, and Pb) in the sediments were measured. The experimental steps for various reagents, namely calcium oxide, hydrogen peroxide and composite reagents, were the same as mentioned above, wherein the calcium oxide dosage was varied through values of 0, 1, 2, 4, 6, and 8 g/L, whereas the hydrogen peroxide dosage was varied through values of 0, 10, 20, 30, 40, and 50 mL/L. The composite reagents consisted of sodium persulfate + hydrogen peroxide and sodium persulfate + calcium oxide. The composition of the composite reagent is presented in Table 2.

2.2.3. Experiment reagents

According to previous research, properties of the reagents and the preliminary experimental results, the chemical reagents of sodium persulfate, calcium oxide and hydrogen peroxide were selected for the current work. Sodium persulfate and calcium oxide were added in solid form and the concentration of hydrogen peroxide was 30%. The detailed information is shown in Table 3.

2.3. Analysis methods

The main detection indices of sediments included water content, organic matter content, TN, NH_3–N, TP and heavy metals. The extraction method for nitrogen and phosphorus

Table 1
Properties of experimental sediment

Index	Experimental sediment properties
Moisture content (%)	64.21
Organic matter content (%)	10.24
TN (mg/L)	63.25
NH_3–N (mg/L)	52.97
TP (mg/L)	1.36
Cd (mg/kg)	2.83
Cr (mg/kg)	103.50
Ni (mg/kg)	34.83
Pb (mg/kg)	75.33

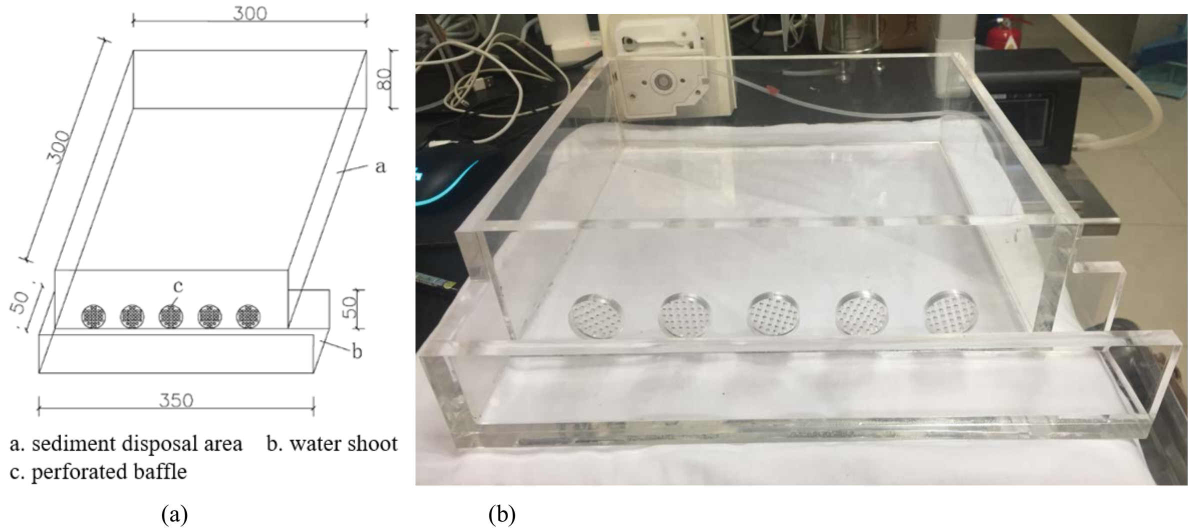

Fig. 1. Schematic of the experimental set-up (a) schematic diagram of the experimental device and (b) actual picture of the experimental device.

Table 2
Dosages of various composite reagents

Group number	Reagent combination	Reagent dosage ratio
0#	–	–
1#	$Na_2S_2O_8 + H_2O_2$	3 g/L + 15 mL/L
2#	$Na_2S_2O_8 + H_2O_2$	1.5 g/L + 22.5 mL/L
3#	$Na_2S_2O_8 + H_2O_2$	4.5 g/L + 7.5 mL/L
4#	$Na_2S_2O_8$ + CaO	3 + 3 g/L
5#	$Na_2S_2O_8$ + CaO	4.5 + 1.5 g/L
6#	$Na_2S_2O_8$ + CaO	1.5 + 4.5 g/L

from the sediments was as follows. First, a certain amount of sediments was taken in a 100-mL centrifugal tube. The supernatant was obtained by centrifugating the sample at a speed of 5,500 rpm for 15 min using a high-speed centrifuge. The contents of organic matter and water were measured using the weight difference method [16]. TN was measured using potassium persulfate oxidation-ultraviolet spectrophotometry [17]. Moreover, NH_3–N was measured using Nessler reagent spectrophotometry [18]. Furthermore, TP was measured using ammonium molybdate spectrophotometry [19]. Heavy metals were measured using inductively-coupled plasma spectrometry [20,21].

3. Results and discussion

3.1. Effect of single chemical reagent on the treatment of sediments

3.1.1. Effect of different dosages of sodium persulfate

After adding $Na_2S_2O_8$ and reacting for 6 h, the changes in the contents of water and organic matter of sediments were analyzed, and the corresponding results are shown in Fig. 2a. It can be seen from Fig. 2a that, with the gradual increase in the dosage of $Na_2S_2O_8$, the water and organic matter contents of the sediments gradually decreased from 60.25% and 9.98% to 57.45% and 9.02%, respectively. When the dosage of $Na_2S_2O_8$ reached the value of 6 g/L, the water and organic matter contents of the sediments stabilized. This is probably because the oxidative capability of $Na_2S_2O_8$ destroys the floc structure in the sediments, releases the water and organic matter, and improves the dehydration capability of the sediments. At the same time, $Na_2S_2O_8$ can also degrade organic matter, thereby improving the stability of sediments [22].

The changes in TN, NH_3–N and TP contents of sediments are shown in Fig. 2b. It can be seen from Fig. 2b that, with the gradual increase of $Na_2S_2O_8$ dosage, the removal rates of TN, NH_3–N and TP in the sediments gradually increased from 2.86%, 5.97%, and 2.94% to 27.21%, 32.64%, and 34.52%, respectively. When the dosage of $Na_2S_2O_8$ reached the value of 6 g/L, the removal rate gradually stabilized. This is probably because, after adding $Na_2S_2O_8$, the oxidative capability of the reagent could crack the microorganisms in the sediments, and promoted the release of nitrogen, phosphorus and other substances from sediments to interstitial water of the sediments [23]. Moreover, the interstitial water flowed along the device, thus reducing the contents of TN, NH_3–N and TP in the sediments.

The changes in heavy metal content in sediments are shown in Fig. 2c. It can be seen from Fig. 2c that, with the gradual increase of $Na_2S_2O_8$ dosage, the removal rates of heavy metals, including Cd, Cr, Ni, and Pb gradually increased from 2.47%, 2.18%, 2.04%, and 1.01% to 18.14%, 24.72%, 26.96%, and 8.13%, respectively. When the dosage reached the value of 6 g/L, the removal rates of Cd, Cr, and Ni in the sediments stabilized, while the removal rate of Pb tended stabilize and was lower than other heavy metals when the dosage reaches the value of 4 g/L, indicating that the removal effect of $Na_2S_2O_8$ for Pb was significantly lower than those of Cd, Cr and Ni. This is probably because the oxidative capability of $Na_2S_2O_8$ can cause some metals or their composites in the sediments to undergo a redox reaction, which is transformed into ionic state, dissolves into the interstitial

Table 3
Chemical stabilizing reagent

Name	Molecular formula	Purity	Manufacturer
Sodium persulfate	$Na_2S_2O_8$	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
Calcium oxide	CaO	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.
Hydrogen peroxide	H_2O_2	Analytically pure	Sinopharm Chemical Reagent Co., Ltd.

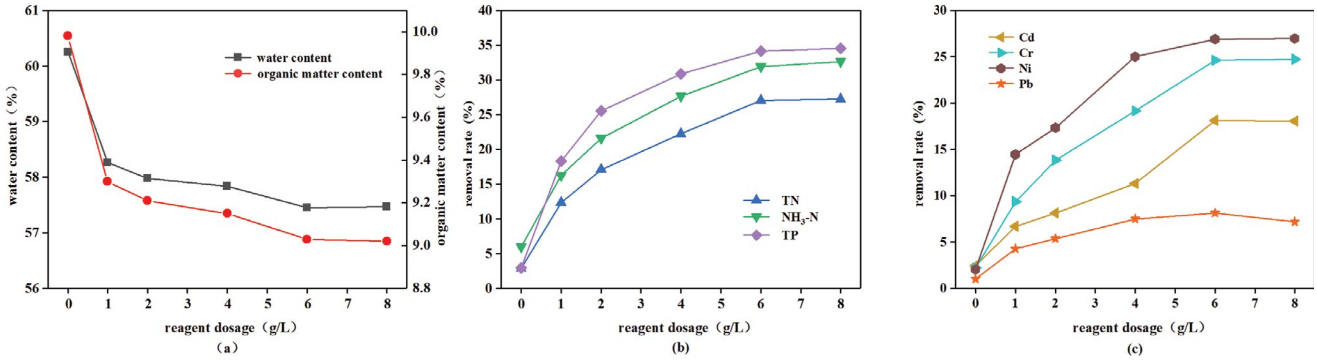

Fig. 2. Changes of in various indices of sediments for different $Na_2S_2O_8$ dosages. (a) Changes of water content and organic matter content in sediments for different $Na_2S_2O_8$ dosages, (b) effects of different $Na_2S_2O_8$ dosages on TN, NH_3–N and TP in sediments and (c) effect of different $Na_2S_2O_8$ dosages on heavy metals in sediments.

water of the sediments [24] and leaches away with the interstitial water. For Pb, one possibility is that, SO_4^{2-} appear in the sediments after the addition of $Na_2S_2O_8$, which reacts with part of Pb ions released in the interstitial water of the sediments to form stable $PbSO_4$ precipitates [24], thus restricting the transfer of Pb ions discharge with the interstitial water.

Based on the changes in water content, organic matter content, TN, NH_3–N, TP and heavy metals for different $Na_2S_2O_8$ dosages, the $Na_2S_2O_8$ dosage of 6 g/L produced the most favorable dewatering effect on the sediments. Meanwhile, it has a good removal effect for the organic matter, TN, NH_3–N, TP and heavy metals in the sediments. This conclusion is similar with the previous studies [25].

3.1.2. Effect of different dosage of calcium oxide

After adding CaO and reacting for 6 h, the changes in moisture and organic matter contents of sediments were analyzed and the corresponding results are shown in Fig. 3a. It can be seen from Fig. 3a that, with the increase of CaO dosage, the water and organic matter contents of sediments decreased from 60.29% and 10.21% to 58.71% and 9.47%, respectively. This is probably because the CaO can consume water in the sediments, and due to the exothermic reaction, the evaporation of the sediments increased, which further reduced the water content in the sediments. Meanwhile, CaO can also react with some organic substances in the sediments and convert them into inorganic calcium salts [26], thus resulting in a decrease in the organic matter content of the sediments.

After adding CaO and reacting for 6 h, the changes in TN, NH_3–N and TP contents in the sediments were analyzed and the corresponding results are shown in Fig. 3b. It can be seen from Fig. 3b that, with the increase of CaO dosage, the removal rates of TN, NH_3–N, and TP in the sediments gradually increased from 3.76%, 7.57%, and 3.68% to 25.09%, 31.09%, and 34.23%, respectively. When the dosage reached the value of 6 g/L, the removal rates of TN, NH_3–N and TP in the sediments stabilized. This may be because the addition of CaO promotes the release of nitrogen-containing substances in the sediments into the interstitial water of sediments [26], which flow away with the leached interstitial water. In addition, the added CaO reacts with water to produce $Ca(OH)_2$ that increases the pH value in the sediments and promotes the release of NH_3–N in the sediments [27]. With regards to TP in the sediments, one possibility is that, the calcium ions (Ca^{2+}) produced by the reaction of CaO with water interact with part of the phosphate ions (PO_4^{3-}) released into the interstitial water and form stable $Ca_5(PO_4)_3OH$ precipitates [28], which reduce the phosphorus content in the interstitial water of sediments.

After adding CaO and reacting for 6h, the changes in the contents of Cd, Cr, Ni and Pb were analyzed and the corresponding results are shown in Fig. 3c. With the increase of CaO dosage, the removal rates of Cd, Cr, Ni and Pb in the sediments fluctuated within the ranges of 0.42%–4.05%, 0.53%–4.83%, 0.25%–5.33%, and 0.90%–3.82%, respectively. This shows that there is no obvious correlation between the dosage of CaO and the removal rate of heavy metals in the sediments, whereas CaO has no significant removal effect for the heavy metals in the sediments. This conclusion is similar with the previous studies [29].

Based on various dosages of CaO, when the dosage of CaO was 6 g/L, the water content of sediments was low. Meanwhile, it has a good removal effect for the organic matter, TN, NH_3–N and TP in the sediments.

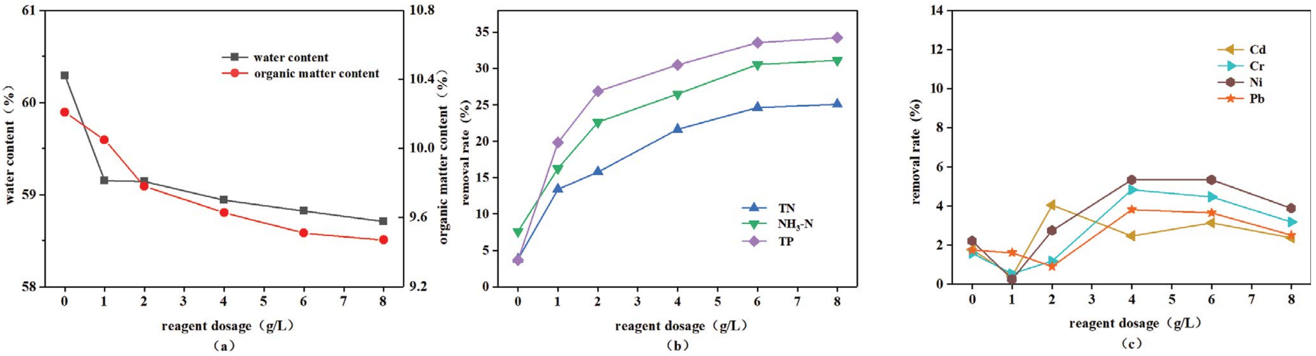

Fig. 3. Changes in various indices of sediments for different CaO dosages. (a) Changes in water and organic matter contents in sediments for different CaO dosages, (b) effects of different CaO dosages on TN, NH_3–N and TP in sediments and (c) effect of different CaO dosages on heavy metals in sediments.

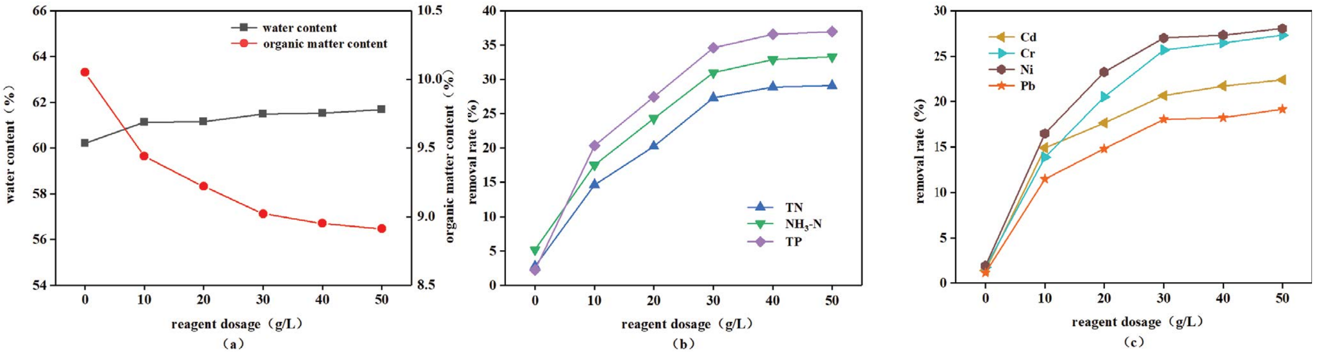

Fig. 4. Changes in various indices of sediments for different H_2O_2 dosages. (a) Changes in the contents of water and organic matter in sediments with different H_2O_2 dosages, (b) effects of different H_2O_2 dosages on TN, NH_3–N and TP in sediments and (c) effect of different H_2O_2 dosages on heavy metals in sediments.

3.1.3. Effect of different dosage of hydrogen peroxide

After adding H_2O_2 and reacting for 6 h, the changes in the contents of water and organic matter of the sediments were analyzed and the corresponding results are shown in Fig. 4a. It can be seen from Fig. 4a that, after adding H_2O_2 to the sediments, the water content of the sediments increased slightly from 60.18% to 61.68%. This is probably because the oxidation capability of H_2O_2 can destroy the floc structure of sediments and release water in them. However, due to the addition of H_2O_2 as a liquid, the water content in the sediments will increase accordingly with the increase in the dosage of H_2O_2. At the same time, H_2O_2 is partially decomposed into H_2O, due to which the reduction in water content becomes less obvious. With the increase of H_2O_2 dosage, the content of organic matter in sediments gradually decreased from 10.05% to 8.91%. This phenomenon was similar with the previous studies [30]. This may be due to the strong oxidation of H_2O_2, which oxidized and decomposed the organic matter in the sediments into inorganic matter [31], resulting in a continuous decrease in the content of organic matter in the sediments.

After adding H_2O_2 and reacting for 6 h, the changes in TN, NH_3–N and TP in the sediments were analyzed and the corresponding results are shown in Fig. 4b. It can be seen from Fig. 4b that, with the increase of H_2O_2 dosage, the removal rates of TN, NH_3–N and TP in sediments increased from 2.75%, 5.17%, and 2.21% to 29.07%, 33.28%, and 36.93%, respectively. When the dosage of H_2O_2 reached the value of 30 mL/L, the removal rates of TN, NH_3–N and TP stabilized. After adding H_2O_2, the oxidative capability of H_2O_2 will crack the bacteria and other microorganisms in the sediments [32], which promotes the release of nitrogen, phosphorus and other substances in the sediments into interstitial water of the sediments. These substances then flow away with the leached interstitial water, thus reducing the contents of TN, NH_3–N and TP in the sediments.

After adding H_2O_2 and reactions for 6 h, the changes in the contents of Cd, Cr, Ni and Pb in the sediments were analyzed and the corresponding results are shown in Fig. 4c. It can be seen from Fig. 4c that, with the increase of H_2O_2 dosage, the removal rates of Cd, Cr, Ni, and Pb in the sediments gradually increased from 1.41%, 1.73%, 1.92%, and 1.13% to 22.38%, 1.13%, 27.31%, 28.03%, and 19.15%, respectively. When the dosage of H_2O_2 reached the value of 30 mL/L, the removal rates of heavy metals in the sediments gradually stabilized. This phenomenon was similar with the previous studies [33]. Because of the strong oxidation capacity of H_2O_2, the exchangeable and carbonate heavy metals in the sediments, as well as the relatively stable organic matter bound to heavy metals and their sulfides can be oxidized and dissolved into the interstitial water of the sediments [34], thus reducing the heavy metal content in the sediments.

Based on the changes of moisture content, organic matter content, TN, NH_3–N, TP and heavy metal content in the sediments for different H_2O_2 dosages, the H_2O_2 dosage of 30 mL/L exhibited the most favorable removal effect for organic matter, TN, NH_3–N, TP and heavy metals in the sediments.

In general, $Na_2S_2O_8$, CaO and H_2O_2 have a stabilizing effect on black and odorous sediments, and can reduce the contents of organic matter, nitrogen and phosphorus in the sediments. The optimum individual reagent was found to be the $Na_2S_2O_8$. Moreover, $Na_2S_2O_8$ and CaO can significantly reduce the water content of sediments, while H_2O_2 has no obvious effect on reducing the water content of the sediments. However, H_2O_2 has the most favorable effect on the removal of Cd, Cr, Ni and Pb. In addition, $Na_2S_2O_8$ exhibits its good removal of Cd, Cr and Ni; however, the removal of Pb was not extraordinary. Furthermore, CaO has no significant removal effect for heavy metals in the sediments.

3.2. *Effect of different composite reagents on the black and odorous sediments*

In order to further improve the treatment effect, reagents were combined into composite reagents. Based on the optimal dosage of each reagent determined in Section 2.1 – Sediment source and properties, the composite reagent was produced with different percentages of the optimal dosages of each reagents.

The removal effects for the contents of water and organic matter in sediments treated by different groups of composite reagents are shown in Fig. 5a. It can be seen from Fig. 5a that the water and organic matter contents were lower in case of treatment using composite reagents than those of the control group. The reduction effects for various composite reagents for water and organic matter contents were not much different from each other. Among them, the highest water content reduction was observed for the composite reagent 5#, which exhibited water content of 54.07%. Moreover, the highest organic matter reduction was observed for the composite reagent 3#, for which the organic matter content was 8.71%. Compared with the individual reagents, the composite reagents of $Na_2S_2O_8$ + H_2O_2 and $Na_2S_2O_8$ + CaO showed better performance for reducing the water and organic matter contents than the individual reagents. For the composite reagent of $Na_2S_2O_8$ + H_2O_2, the optimum dosage was the composite reagent 3#. After the reaction, the water content was reduced to 54.87%, whereas the organic matter content was reduced to 8.71%. For the composite reagent of $Na_2S_2O_8$ + CaO, the optimum dosage was the composite reagent 5#. After the reaction, the water and organic matter contents were reduced to 54.07% and 8.93%, respectively.

The removal effects for TN, NH_3–N and TP are shown in Fig. 5b. It can be seen from Fig. 5b that the removal effects of six groups of composite reagents for TN, NH_3–N and TP in sediments were all better than those of the control group, and the removal effect of the composite reagent $Na_2S_2O_8$ + H_2O_2 was better than that of the composite reagent $Na_2S_2O_8$ + CaO. This may be due to the reason that both $Na_2S_2O_8$ and H_2O_2 have good oxidative capability, which makes the oxidation capability of the composite reagent ($Na_2S_2O_8$ + H_2O_2) stronger than the composite reagent $Na_2S_2O_8$ + CaO. At the same time, there were significant differences in the removal effects of TN, NH_3–N and TP in the sediments for each group of composite reagents. For the $Na_2S_2O_8$ + H_2O_2 composite reagent, the optimum dosage for the removal of TN, NH_3–N and TP in the sediments was the composite reagent 3#, and after the reaction, the corresponding removal rates were 32.44%, 42.86% and 45.2%, respectively. For the composite reagent of $Na_2S_2O_8$ + CaO, the optimum dosage for the removal of TN, NH_3–N and TP was the composite reagent 5#, in which after the reaction, the corresponding removal rates reached 31.06%, 41.72% and 42.84%, respectively.

The removal effects of Cd, Cr, Ni and Pb in sediments are shown in Fig. 5c. It can be seen from Fig. 5c that the removal effects of the six groups of composite reagents for heavy metals in the sediments were better than those of the control group, and the removal effects of the composite reagents in each group for different heavy metals were significantly different from each other. Among them, for the composite reagent $Na_2S_2O_8$ + H_2O_2, the optimum dosage for the removal of Cd, Cr and Ni in the sediments was obtained for the composite reagent 3#, in which after the reaction, the corresponding removal efficiencies were 21.54%, 27.03% and 29.3%, respectively. However, the removal effect of this composite reagent for Pb was the worst. The most favorable reagent ratio for the removal of Pb was obtained in the composite reagent 2#, in which, after the reaction, the removal rate was 18.60%. This is probably because, $Na_2S_2O_8$ will react with some free Pb ions in the sediments to form lead sulfate precipitates, which is not conducive to the removal of Pb. However, the removal effect of H_2O_2 for Pb was better than that of $Na_2S_2O_8$. For the $Na_2S_2O_8$ + H_2O_2 composite

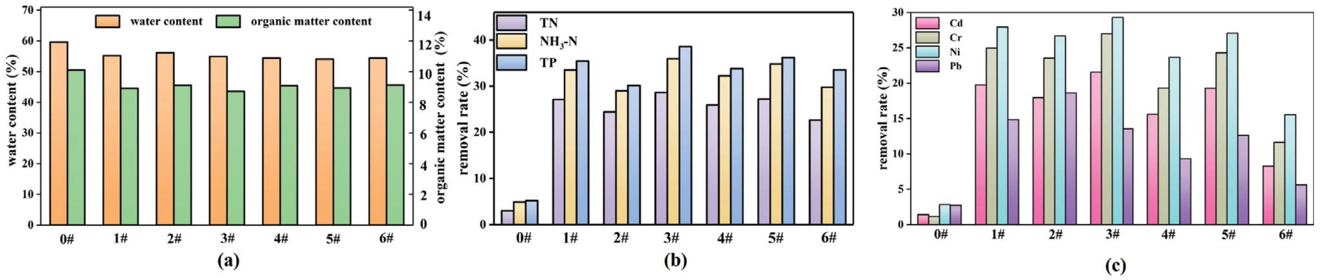

Fig. 5. Changes in the contents of water and organic matter in sediments. (a) Changes in water and organic matter contents in sediments, (b) changes in TN, NH_3–N and TP removal rates in sediments and (c) change in heavy metal contents in sediments.

reagent, the highest proportion of $Na_2S_2O_8$ was observed in the composite reagent 3#, and the highest proportion of H_2O_2 was found in the composite reagent 2#. Therefore, the composite reagent 3# exhibited the highest removal effect for the Pb, whereas the composite reagent 2# was the worst. For the $Na_2S_2O_8$ + CaO composite reagent, the optimum dosage ratio for the removal of Cd, Cr, Ni, and Pb in the sediments was the composite reagent 5#, for which, the corresponding removal rates reached the values of 19.28%, 24.29%, 27.07% and 12.62%, respectively.

According to the changes in sediment water content, organic matter content, TN, NH_3–N, TP and heavy metals content under different concentrations of two groups of composite reagents, the optimum dosage for the composite reagent $Na_2S_2O_8$ + H_2O_2 was found in the composite reagent 3#, which was 4.5 g/L $Na_2S_2O_8$ + 7.5 mL/L H_2O_2. The optimum dosage for $Na_2S_2O_8$ + CaO was found in the composite reagent 5#, with 4.5 g/L $Na_2S_2O_8$ + 1.5 g/L CaO. The optimum composite reagent for stabilizing the sediments was $Na_2S_2O_8$ + H_2O_2. Although its effect on reducing the moisture content was not as good as $Na_2S_2O_8$ + CaO, the difference between the two reagents was not that obvious.

4. Conclusions

In this study, the stabilization effect of individual chemical reagents and composite reagents on the sediments of black odorous water was studied. Based upon the changes in water content, organic matter content, TN, NH_3–N, TP and heavy metal content of black and odorous water's sediments under different reagent types and reagent dosages, following conclusions are drawn.

- $Na_2S_2O_8$, CaO and H_2O_2 have a certain stabilization effect on black odorous sediments. The optimum dosage of $Na_2S_2O_8$ and CaO was 6 g/L, whereas the optimum dosage of H_2O_2 was 30 mL/L. The most favorable single reagent for sediments' stabilization was $Na_2S_2O_8$.
- The optimum dosage ratio of $Na_2S_2O_8$ + H_2O_2 was 4.5 g/L $Na_2S_2O_8$ + 7.5 mL/L H_2O_2, whereas the optimum dosage ratio of $Na_2S_2O_8$ + CaO was 4.5 g/L $Na_2S_2O_8$ + 1.5 g/L CaO. The optimum composite reagent for sediments' stabilization was $Na_2S_2O_8$ + H_2O_2. Although its effect on reducing the water content was not as good as $Na_2S_2O_8$ + CaO, the difference between the two composite reagents was not obvious.

Acknowledgements

This work was financially supported by Project of Research Collaboration on Chemical Bioremediation Technology of Sediment in Urban Black and Odorous Water. In addition, we acknowledge support of the Huazhong University of Science and Technology Analytical and Testing Center.

References

[1] X. Wang, Y.G. Wang, C.H. Sun, T. Pan, Formation mechanism and assessment method for urban black and odorous water body: a review, Chin. J. Appl. Ecol., 27 (2016) 1331–1340.

[2] L. Bi, L. Qiu, Treatment technologies of remediation for contaminated sediment in rivers, China Environ. Prot. Ind., 11 (2010) 32–35.

[3] T. Bo, M. Ji, The advance of control techniques for internal pollution, Ecol. Environ. Sci., 3 (2017) 514–521.

[4] Y. Yu, Z. Liang, J. Ma, X. Liang, X. Liu, H. Zhao, Sediment remediation technology and application prospects, Environ. Sci. Technol., 1 (2014) 3–5.

[5] D. Xia, H. Zhao, S. Kobayashi, Q. Mi, A. Hao, Y. Iseri, Effect of remediation reagents on bacterial composition and ecological function in black-odorous water sediments, Arch. Microbiol., 204 (2022) 280, doi: 10.1007/s00203-022-02871-4.

[6] X. Dong, Q. Lin, Y. Lin, S. Xi, B. Cheng, L. Chen, D. Zhang, Z. Wang, G. Guo, Effects of different electrolytes on acidogenic fermentation of waste activated sludge for volatile fatty acids production via electrochemical pretreatment, Environ. Eng., 12 (2022) 71–78.

[7] Z. Wang, Y. Chen, L. Chen, S. Xi, Y. Liu, S. Dong, L. Miao, *Ex-situ* treatment of sediment from a black-odor water body using activated sludge, Sci. Total Environ., 713 (2020) 136651, doi: 10.1016/j.scitotenv.2020.136651.

[8] Y. Li, F. Yang, S. Miao, D. Wang, Z. Li, X. Yuan, L. Yuan, Q. Liu, Achieved deep-dewatering of dredged sediments by Fe(II) activating persulfate pretreatment: filtrating performance and mechanistic insights, Chem. Eng. J., 405 (2021) 126847, doi: 10.1016/j.cej.2020.126847.

[9] C. Zhang, Y. Wang, X. Tan, L. Wang, C. Li, Study on stability standard of sludge treatment in municipal wastewater treatment plant, Water Wastewater Eng., 53 (2017) 137–140.

[10] A. Nykänen, H. Kontio, O. Klutas, O. Penttinen, S. Kostia, J. Mikola, M. Romantschuk, Increasing lake water and sediment oxygen levels using slow release peroxide, Sci. Total Environ., 429 (2012) 317–324.

[11] E. Ferrarese, G. Andreottola, I.A. Oprea, Remediation of PAH-contaminated sediments by chemical oxidation, J. Hazard. Mater., 152 (2008) 128–139.

[12] L. Ji, H. Zhang, The progress in soil and groundwater remediation by *in-situ* chemical oxidation, Tech. Equip. Environ. Pollut. Control, 4 (2003) 37–42.

[13] G. Zhen, X. Lu, Y. Zhao, X. Chai, D. Niu, Enhanced dewaterability of sewage sludge in the presence of Fe(II)-activated per-sulfate oxidation, Bioresour. Technol., 116 (2012) 259–265.

[14] S.-H. Do, Y.-J. Kwon, S.-H. Kong, Effect of metal oxides on the reactivity of persulfate/Fe(II) in the remediation of diesel-contaminated soil and sand, J. Hazard. Mater., 182 (2010) 933–936.

[15] X. Duan, H. Sun, Z. Shao, S. Wang, Nonradical reactions in environmental remediation processes: uncertainty and challenges, Appl. Catal., B, 224 (2018) 973–982.

[16] C. Jiang, H. Chen, Y. Zhang, H. Feng, M. Shehzad, Y. Wang, T. Xu, Complexation electrodialysis as a general method to simultaneously treat wastewaters with metal and organic matter, Chem. Eng. J., 348 (2018) 952–959.

[17] T. Gea, R. Barrena, A. Artola, A. Sánchez, Monitoring the biological activity of the composting process: oxygen uptake rate (OUR), respirometric index (RI), and respiratory quotient (RQ), Biotechnol. Bioeng., 88 (2004) 520–527.

[18] J. Kong, Summarization of ammonia nitrogen analysis method and influencing factors in environmental monitoring in China, China Resour. Compr. Util., 36 (2018) 83–85.

[19] X. Jiang, Determination of total phosphorus in water by ammonium molybdate spectrophotometry, Sci. Technol. Innovation, 9 (2018) 134–135.

[20] Y. Xu, C. Yu, Z. Wang, Determination of heavy metals in soil by inductively coupled plasma emission spectrometry, Chem. Manage., 22 (2020) 47–48.

[21] Qingdao Urban Drainage Monitoring Station, Determination Method for Municipal Sludge in Wastewater Treatment Plant (CJ/T 221-2005), Ministry of Construction of China, Beijing, 2005, pp. 34–84.

[22] C. Gong, J. Jiang, S. Yang, Effects of Fenton oxidation with ultrasonic coupling on sludge particle size and soluble substances, China Environ. Sci., 33 (2013) 293–297.

[23] H. Liang, D. Sun, H. Zheng, C. Ma, X. Zhang, J. He, M. Xue, Treatment of excess sludge with sulfate free radical, J. Dalian Polytechnic Univ., 32 (2013) 47–50.

[24] W. Zhang, Z. Xiao, B. Ma, Q. Zeng, Effects of persulfate oxidation on dewatering performance and removing heavy metals in municipal sludge, China Environ. Sci., 37 (2017) 4605–4613.
[25] E. Doğan, F. Accoe, N. Boon, L. Bastiaens, W. Dejonghe, Impact of chemical oxidants on the heavy metals and the microbial population in sediments, Water Air Soil Pollut., 224 (2013) 1–12.
[26] G. Robin, Low aqueous solubility electron donors for the reduction of nitroaromatics in anaerobic sediments, J. Contam. Hydrol., 36 (1999) 91–104.
[27] D.S. Baldwin, M. Fraser, Rehabilitation options for inland waterways impacted by sulfidic sediments – a synthesis, J. Environ. Manage., 91 (2009) 311–319.
[28] L. Wang, Y. Zhong, G. Yu, X. Long, Temperature effect on and microbial community structure dynamics during *in-situ* oxidation of black and odorous sediment by calcium nitrate, J. Agro-Environ. Sci., 34 (2015) 1187–1195.
[29] X. Guo, Z. Wei, F. Xie, Q. Wu, Effect of lime and superphosphate on maize production and heavy metals uptake by low-accumulating maize, Chin. J. Environ. Eng., 6 (2012) 1374–1380.
[30] Q. Tang, M. Sheng, G. Wang, X. Wu, J. Yuan, B. Liu, Oxidative stability of the organic matter in sediments of polluted urban rivers, Environ. Chem., 34 (2015) 489–496.
[31] G. Zhang, D. Zhang, Experimental study on the treatment of heavy metal in electroplating wastewater by chemical precipitation method, Shandong Chem. Ind., 45 (2016) 215–216.
[32] R. Bai, Q. Li, J. Li, M. Hao, Research and application of Fenton and Fenton-like process in wastewater treatment, Sci. Technol. Chem. Ind., 18 (2010) 69–73.
[33] L. Wang, X. Yuan, H. Zhong, H. Wang, Z. Wu, X. Chen, G. Zeng, Release behavior of heavy metals during treatment of dredged sediment by microwave-assisted hydrogen peroxide oxidation, Chem. Eng. J., 258 (2014) 334–340.
[34] T. Zhang, Q. Wang, L. Ye, D. Batstone, Z. Yuan, Combined free nitrous acid and hydrogen peroxide pre-treatment of waste activated sludge enhances methane production via organic molecule breakdown, Sci. Rep., 5 (2015) 16631, doi: 10.1038/srep16631.
[35] Editorial Board of Water and Wastewater Monitoring and Analysis Method, State Environmental Protection Administration, Analytical Methods for Water and Wastewater Monitoring (4th ed.), China Environmental Science Press, Beijing, 2002.