Experimental Study of Al-Modified Zeolite with Oxygen Nanobubbles in Repairing Black and Odorous Sediments in River Channels

Guo Chao (author.GCLRF@163.com)
Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Shaanxi Xi'an 710071 2.Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd.

Wang Huanyuan
Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources., Shaanxi Xi'an 710071

Wei Yulu
Shaanxi Provincial Land Consolidation Engineering Technology Research Center., Shaanxi Xi'an 710071

Peng Biao
Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Shaanxi Xi'an 710071

Shu Xiaoxiao
Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Shaanxi Xi'an 710071

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Abstract

As an extreme phenomenon of water pollution, black and odorous water not only causes ecological damage, but also severely restricts urban development. At present, the in-situ remediation technology of black and odorous sediment from river channels is still undeveloped, and there are many bottlenecks in the key technologies of black and odorous sediment pollution control and ecological restoration. In this study, three experimental tanks are used to explore the effects of Al-modified zeolite with oxygen nanobubbles on repairing black and odorous sediment from Shichuan river. Which one of the tanks plants *Typha orientalis* and *Canna indica L.* (TC), the other plants the same plants and adds Al-modified zeolite with oxygen nanobubbles (TC+AMZON), and the last used as comparison test is not processed (CS). The results show that Nitrogen(N) and phosphorus(P) in the sediment are released violently to the surrounding water. However, TC+AMZON can effectively inhibit the release of P. The amount of soluble reactive phosphorus (SRP) of pore water in the sediment released reaches the maximum at 40 d, and it is 122.97% and 74.32% bigger in TC and CS than that in TC+AMZON. The amount of total phosphorus (TP) of pore water in the sediment released reaches the maximum at 70 d, and it is 260.14% and 218.23% bigger in TC and CS than that in TC+AMZON, respectively. (2) TC+AMZON can significantly increase the dissolved oxygen (DO) and oxidation-reduction potential(ORP) of pore water in the sediment in the early stage of the test. On the 0 d, the DO content in TC+AMZON reaches 10.6 mg/L, and it is 112.0% and 178.95% bigger than that in TC and CS, respectively. The change laws of ORP in the sediment is consistent with that of DO. (3) TC+AMZON can significantly improve the transparency and reduce the content of $chlorophyll_a$ of the upper water, and can slightly reduce the N and P content of the upper water. The transparency of the upper water in TC+AMZON is increased by 130.76% and 58.73% compared with TC and CS, and the content of $chlorophyll_a$ is decreased by 55.6% and 50.0% compared with TC and CS.

1. Introduction

With the development of industrial and agricultural production and the acceleration of urbanization, more and more rivers have been polluted[1]. Rivers become "black and stinky", and they have a serious impact on the lives of residents and the surrounding environment. As an extreme phenomenon of water pollution, black and odorous water not only causes ecological damage, but also severely restricts urban development[2,3]. Remediation of black and odorous water has become one of the most difficult environmental problems in water environmental protection[4].

Many black and odorous water remediation projects have fallen into the strange phenomenon of " remediation every year, black and odorous every year", it is due to the focusing on remediation and short-term effects, but ignoring maintenance and long-term effects[5,6]. Therefore, in the current process of black and odorous water remediation, how to choose the appropriate black and odorous water treatment technology and optimize the integration is the main problem to be solved urgently[7]. In addition, how to effectively prevent its repeat and achieve the goal of long-term maintenance of good water quality is the key to completely eliminate the urban black and odorous water after the remediation[8,9]. At this stage, the main technical bottlenecks faced by the remediation of black and odorous water are the control of the sediments pollution in the river channel and the reconstruction of healthy river ecosystems.

The primary task of the black and odorous water remediation is to recognize its causes and take effective control measures to eliminate the black and odorous. The main causes of black and odorous water in urban inland rivers are the input of exogenous pollutants, such as industrial wastewater, domestic sewage, garbage, and non-point source pollution on both banks, ect., and the released pollutants from river sediments[10]. The environmental factors that cause black and odorous mainly include organic pollutants, nitrogen, phosphorus, iron, manganese, sulfide and other pollutants. The lack of oxygen and poor fluidity of water can further accelerate the black and odorous. A lot of effective work on the control of exogenous pollutants have been done, which can basically be achieved by improving the sewage pipeline network, improving the efficiency of rain and sewage diversion, and concentrated sewage treatment and discharge. For example, upgrading or shutting down the key sewage enterprises, improving the efficiency of garbage removal and transportation, etc. However, there are still many bottlenecks in the technology for the treatment of endogenous sediment pollution.

Zeolite is an aluminosilicate mineral widely existing in nature. The main components are SiO_2, Al_2O_3 and iron oxides. Natural zeolite is one of the abundant reserves characterized by unique pore structure, large specific surface area, strong surface adsorption and ion exchange. Therefore, it is widely used in the adsorption of ammonia nitrogen and heavy metal ions[11]. However, the removal effect of natural zeolite on anions such as phosphate is poor, and it is affected by many factors such as temperature, particle size, etc.[12,13]. Modification of natural zeolite by different methods can effectively increase the removal efficiency of anions such as phosphate. Lin, J. *et al.*[14] showed that natural zeolite/hydrochloric acid modified zeolite and calcite composite can effectively reduce the release of N and P in sediments. The more the dosage and the smaller the particles, the better the phosphorus passivation effect, and the phosphorus passivation effect of adding zeolite is better than adding calcite[15,16]. Gibbs, M. *et al.*[17,18] compared the passivation effect of four passivators of modified zeolite Z2G1, phoslock, alum and allophane. The results show that Z2G1 can effectively inhibit the release of P in sediments, and pollutants such as heavy metal ions could not be released to the surrounding water from sediments. In additon, most of the oxygen in the river sediment is consumed by reducing substances, the amount of oxygen reaching the sediment-water interface is very small. Shi, M. *et al.*[19] showed that algae-induced anoxia/hypoxia could be reduced or reversed after oxygen nanobubbles (Diameter is less than 1μm) are loaded onto zeolite micropores and delivered to anoxic sediment. The manipulation of microbial processes using the surface Oxygen nanobubbles potentially served as oxygen suppliers. Therefore, oxygen nanobubbles have the advantages of good stability and high oxygen mass transfer rate, which provide great potential for the research and development of precise oxygenation technology at the sediment-water interface of river sediments.

Therefore, in this study, the Al-modified zeolite with oxygen nanobubbles is used to control the black and odorous sediment pollutants in the river channel through three groups of pilot test, and aquatic plants are used for restoration. It will provide a new technology for the remediation of black and odorous water in urban river channels.

2. Materials And Methods

2. 1 Materials

(1)Al-modified zeolite with oxygen nanobubbles

Natural zeolite is modified using aluminum salt, and an efficient, low-risk, low-cost in-situ passivation material for sediment pollution is developed. Namely Al-modified zeolite (natural zeolite 30% + aluminum salt 15% + Stone powder 55%). The main component of stone powder is $CaCO_3$, and it has a large specific surface area. After the zeolite is modified by aluminum salt, its Al^{3+} is hydrolyzed to form a positively charged $Al(OH)_3$ colloid. Oxygen nanobubbles are loaded onto zeolite micropores, and it could effectively increase the DO concentration at the sediment-water interface. Thus significantly inhibit the release of phosphorus from the sediment. Al-modified zeolite with oxygen nanobubbles oxidize the active Fe (Fe^{2+}) in the sediment to iron oxide (Fe^{3+}), and then form an iron oxide layer on the surface (1 ± cm) of the sediment, which can inhibit the release of Fe-P, and enhance the sediment P fixed capacity. Al-modified zeolite and the oxygen nanobubbles are seen in Fig. 1.

(2) Aquatic plants

The aquatic plants of *Typha orientalis* and *Canna indica L* are used, and they have excellent pollutant adsorption ability. Physical-biological-microbial methods are used to optimize the structure of the local water ecosystem, and to improve the primary productivity of water and convert nutrients in water into plant tissues.

2. 2 Test device

In March 2021, three test tanks with length×width×height = 2m×1m×1m is made in Fuping pilot test base of Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Black and smelly mud with a thickness about 10 cm is laid in the bottom, and the mud is taken from Shichuan River, Fuping County, Shaanxi Province. Then add water about 20 cm, and the water needs to be placed for about 10 days to discharge the chlorine gas. A week later, one of the tanks plant aquatic plants such as *Typha orientalis* and *Canna indica L*, then add Al-modified zeolite with oxygen nanobubbles with a thickness of about 2 cm, and it is marked as TC + AMZON. The particle size of the zeolite is about 2 ~ 3mm. The other tank is only planted *Typha orientalis* and *Canna indica L*, and it is marked as TC. The last used as comparison test is not processed, and it is marked as CS. The test process is shown in Fig. 2. The test device is completed in May 2021.

2. 3 Sample Collection

On May 16th, 2021, Al-modified zeolite with oxygen nanobubbles is added into the device. On May 26th, the upper water and sediment samples are collected. The water samples are taken from 5 cm below the water surface, and the sediment samples are taken within 2 cm below the sediment surface. After the samples are collected, the Al-modified zeolite is supplemented at the sampling point. Water and sediment samples are collected in three tanks every 10 days in the early stage, and they are collected every 15 or 20 days in the later period. The collected water and sediment samples are stored at -4°C, and the analysis is completed within one week. The test indicators and methods are shown in Table 1.

2. 4 Test methods

Table 1
Test indicators and methods

Indicators	Test methods
DO	Test in-siut
COD	Determination of the chemical oxygen demand-Dichrom method
Transparency	Methods of monitoring and analysis of water and wastewater[20]
NH_4^+-N	Air and exhaust gas-Determination of ammonia-Nessler's reagent spetcrophotomatry
TN	Alkaline potassium persulfate digestion UV spectrophotometric method
TP	Ammonium molybdate spectrophotometric method
SRP	Analysis of water used in boiler and cooling system- Determination of phosphate
$Chlorophyll_a$	Determination of $chlorophyll_a$- spectrophotometric method
ORP	Test in-siut

3. Results And Analysis

3. 1 N and P of pore water in sediment

It can be seen from Fig. 3 that before 130 d, the contents of TP and SRP of pore water in the sediment in CS and TC show an increasing trend, and maintain a high level of P content. It indicates that with the increase of temperature, and the P in the sediment releases to the surrounding water. The amount of SRP released reaches the maximum at 40 d. At this time, the content of SRP in the CS and TC is 122.97% and 74.32% bigger than that in TC + AMZON, respectively. The amount of TP released reaches the maximum at 70 d, and the content of TP in the CS and TC is 260.14% and 218.23% bigger than that of TC + AMZON, respectively. The contents of TP and SRP in TC + AMZON increased slightly before 70 days, but both are less than those in the CS and TC. The main reason is that during the anaerobic period in summer, Fe-P in the sediment is reduced to form a large amount of SRP, resulting in the strong release of P in the sediment[21]. However, the addition of the Al-modified zeolite with oxygen nanobubbles makes the sediment locally aerobic, and oxidizes Fe (Fe^{2+}) in the sediment to iron oxide (Fe^{3+}). Then it forms an iron oxide passivation layer, and Fe^{2+} is converted into Fe^{3+}. SRP/Fe-P is strictly fixed in the sediment, and effectively reduces the release of P. However, CS and TC is under the anaerobic conditions without the addition of Al-modified zeolite with oxygen nanobubbles, and a very high concentration gradient of Fe-P is on the sediment surface, so it leads to a strong release of P in the sediment. When the Al-modified zeolite with oxygen nanobubbles in TC + AMZON is added to the surface of the sediment, the nanobubbles continuously releases oxygen and forms an oxide layer on the surface of the sediment, which not only reduces the concentration of P and Fe but also greatly reduces the concentration gradient of P on the sediment surface. Thereby the release of P in the sediment is inhibited. Fortunately, the oxygen nanobubble on Al-modified zeolite plays an important role. In addition, zeolite has a large specific surface area and strong adsorption[22,23]. The natural zeolite is rich in Al^{3+} after modification with aluminum salt, and the Al^{3+} is hydrolyzed to form $Al(OH)_3$ colloid, which plays an important role for the adsorption of PO_4^{3+} in the water[24,25]. It can reduce the release of P in sediment and improve the water quality of the upper water. Therefore, it achieves the dual purpose of controlling P pollution and preventing eutrophication of upper water. At the same time, the available P in the pore water is absorbed by the aquatic plants, so that the P in the sediment is effectively removed. The river sediment in-situ passivation with phytoremediation is a P pollutant treatment technology with high efficiency, low cost, environmental protection and aesthetics[26].

The TN and NH_4^+-N contents of the pore water in CS and TC sediments also show a trend of first increasing and then decreasing. The influence of TC + AMZON on TN and NH_4^+-N contents is great, and they are significantly lower than those in CS and TC. It shows that the N in the sediment is also released to the surrounding water, and Al-modified zeolite with oxygen nanobubbles inhibits the release of N in the sediment. Studies have shown that nanobubbles have negative charges at the gas-liquid interface, which can interact with positively charged pollutants in water, and the free radicals and vibration waves generated when they burst can promote the removal of pollutants[27]. Therefore, the pollutants discharged from urban non-point source pollution to rivers and lakes can be repaired by in-situ Al-modified zeolite + phytoremediation technology in the sediment, which can achieve the effect of pollutant control and beautify the city. It is the most effective technical means at present.

3.2 DO and ORP of pore water in sediment

It can be seen from Fig. 4 that the addition of Al-modified zeolite with oxygen nanobubbles can significantly increase the dissolved oxygen(DO) content of the pore water in the sediment. During the experimental period, the DO in the CS is kept between 2.9 and 4.3 mg/L, and it is varied from 5.3 to 7.5 mg/L in TC. However, the DO in the TC + AMZON is kept at 6.2–10.6 mg/L. Before 60 days, the DO content in TC + AMZON is significantly bigger than that in the CS and TC. On the 0th day, the DO content in TC + AMZON reaches 10.6 mg/L, which is 178.95% and 112.0% bigger than that in the CS and TC. With the experimental continual, the DO content of the pore water in the TC + AMZON is gradually decreased, which is mainly caused by the continuous oxygen consumption of reducing substances and microbial activities in the sediment. 60 days later, the DO concentration in TC + AMZON decreases to below 5.5 mg/L, and it is consistent with that of the TC, and gradually becomes stable. The results show that the Al-modified zeolite with oxygen nanobubble has a good ability to increase the oxygen at the sediment-water interface. Therefor the addition of Al-modified zeolite with oxygen nanobubbles is beneficial to increase the DO content in the pore water of the sediment.

The oxidation-reduction potential (ORP) on the sediment surface of the CS is maintained at -35-20 mV, and it is maintained at 5–35 mV in the TC, however the ORP in TC + AMZON is maintained at 12–95 mV. Therefore, the ORP of pore water in the TC + AMZON is significantly increased. Moreover, the change process of ORP in the sediment is consistent with that of DO, and it indicates that the distribution of DO content in the sediment affects the level of ORP. Which is consistent with the research results of Shi M. *et al*[19]. The transformation and diffusion of most dissolved substances in sediments are affected by their ORP.

3. 3 N, P and COD in upper water

It can be seen from Fig. 5 that the TP content in the upper water decreases with the time. The TP content in the three tanks is in the order of CS > TC > TC + AMZON, and TP content in the TC and TC + AMZON is all smaller than that in the CS. It shows that the release of P in the sediment will not increase the P content in the upper water. The main reason is that the Al-zeolite particles rapidly adsorb the dissolved active P in the sediment. Relevant studies have shown that aluminum ions in modified zeolites are hydrolyzed to form positively charged $Al(OH)_3$ colloids, which can strongly adsorb negatively charged bacteria and ions in water[28,29], such as PO_3^{4-}. At the same time, $Al(OH)_3$ colloids is the suspended matter with light weight and is not easy to precipitate[30,31]. But the $Al(OH)_3$ can increase its mass after adsorbing ions in water, and gradually settle to the bottom of the water, reducing the possibility of resuspension. In addition, the hydrolyzed product $Al(OH)_3$ provides bridging adsorption to adsorb suspended solids in water[32,33]. Al^{3+} is hydrolyzed to form a high molecular polymer with a linear structure, one side of the high molecular polymer can adsorb a particle far away, and the other side extends into the water to absorb another particle. The particle is bridged by the polymer adsorption that make the particles gradually become bigger and bigger[34]. With the increasing of the particle adsorbed by Al^{3+}, it gradually moves to the bottom of the water, and it can absorb the suspended particles in the water during the sinking process[35]. After the colloid settles to the surface of the sediment, a covering layer is formed on the surface of the sediment to prevent the pollutants in the sediment from being released to the upper water.

The TN content in the upper water shows a decreasing trend with the test time, and the NH_4^+-N shows a trend of increasing first and then decreasing gradually. The TN and NH_4^+-N contents in the TC and TC + AMZON is all smaller than that in the CS. Before 60 days, the contents of TN and NH_4^+-N in the TC + AMZON are slightly lower than those in TC, and the differences gradually decreased 60 days later. The main reason is that zeolite has an adsorption effect on NH_4^+-N, which reduces the N content in the upper water. In addition, the absorption of available N by aquatic plants can also reduce the N content in water. Therefore, when using Al-modified zeolite to remediate pollutants in sediment, it is necessary to plant aquatic plants to absorb pollutants in sediment and water[36].

Al-modified zeolite has little effect on COD in the upper water. In the early stage of the experiment, there is minor differences of COD in the upper water among the three tanks. In the later stage, the COD content of the upper water in the TC + AMZON and TC is slightly lower than those in CS. It is mainly because the adsorption of soluble organic pollutants by plants that reduce the COD content. Therefore, the application of Al-modified zeolite has no obvious improvement effect on COD in black and odorous water.

3. 4 Transparency and chlorophyll$_a$ in upper water

It can be seen from Fig. 6 that the transparency of the upper water in the TC + AMZON and TC gradually increases with the experimental time, while it shows a trend of decreasing first, then remains stable in the later period in the CS. And the difference become bigger and bigger 60 days later. According to statistics, the transparency in the TC + AMZON remains at 17.6–30 cm 60 days later, and it varies from 15.5 to 22.4 cm in the TC. However, the transparency in the CS remains at 11.6–15.7 cm. Thus compared with the CS and TC, the transparency of the upper water in the TC + AMZON is increased by 130.76% and 58.73%, respectively at the sampling same. Therefore, the application of Al-modified zeolite with oxygen nanobubbles has a significant effect on water purification.

The content of chlorophyll$_a$ in the upper water generally increases at first and then decreased, and keeps stable finally. Tt begins to increase 30 days later, and reach the maximum value 50 days later. The main reason is that the experiment starts at the end of May. 30 days later, the temperature is high. There are more prokaryotic blue-green algae (cyanobacteria) and eukaryotic algae in the test tanks except for the green plants. The algae can synthesize some organic substances through photosynthesis, which converts light energy into chemical energy. Thereby increasing the content of chlorophyll$_a$ in water[37,38]. 80 days later, the content of chlorophyll$_a$ of the upper water in the TC + AMZON is significantly less than those in TC and CS. And the content of chlorophyll$_a$ in the TC + AMZON remaines between 15 and 21 μg/L, but it varies from 22 to 32 μg/L and and from 29 and 36 μg/L in the TC and CS, respectively. The content of chlorophyll$_a$ in the TC + AMZON is decreased by 50.0% and 55.56% compared with TC and CS at the same sampling time. It shows that the content of chlorophyll$_a$ in water can be reduced by the addition of Al-modified zeolite with oxygen nanobubbles. 105 days later, the chlorophyll$_a$ content in the three tanks gradually becomes stable.

Conclusion

Al-modified zeolite with oxygen nanobubbles is used to repair the black and odorous sediments in this study, and it demonstrates that:

(1) The P of the river sediment is strongly released to the surrounding water, and N has a certain release. However, the addition of Al-modified zeolite with oxygen nanobubbles can inhibit the release of P and N, and the effect is very obvious.

(2) The addition of Al-modified zeolite with oxygen nanobubbles can significantly increase the DO and ORP in the sediment pore water in the early stage of the test. 60 days later, the DO concentration in TC+AMZON is reduced to below 5.5 mg/L, which is consistent with the TC. The same variation of ORP and DO in sediment pore water are observed.

(3) P and N released from sediment does not impact their increase in upper water. There is minor difference of TN, TP and NH_4^+-N contents of the upper water in the TC+AMZON and TC, and they were all smaller than that in CS. The addition of Al-modified zeolite with oxygen nanobubbles has little effect on COD in the upper water. In the early stage of the experiment, the difference of COD content in the three tanks is small, however, it is slightly less in the TC+AMZON and TC than that in the CS in later stage.

(4) The transparency of the upper water is significantly improved by adding the Al-modified zeolite with oxygen nanobubbles. 40 days later, the difference of the transparency in TC+AMZON is more and more obvious compared with the TC and CS. Moreover, the addition Al-modified zeolite with oxygen nanobubbles can reduce the content of chlorophyll_a in the upper water. 80 days later, the chlorophyll_a content of the upper water in the TC+AMZON is significantly less than that in the TC and CS.

Declarations

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Author contributions statement

Guo C. and Wang H. Y. conceived the experiments and analyzed the results, Wei Y. L. and Peng B. conducted the experiments, Shu X. X. analysed the date. All authors reviewed the manuscript.

Declaration of date

The authors declare that the datasets generated during and analyzed during the current study are not publicly available due to the reasons that the data is confidential, and it is the basis for further research, but are available from the corresponding author on reasonable request"

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Figures

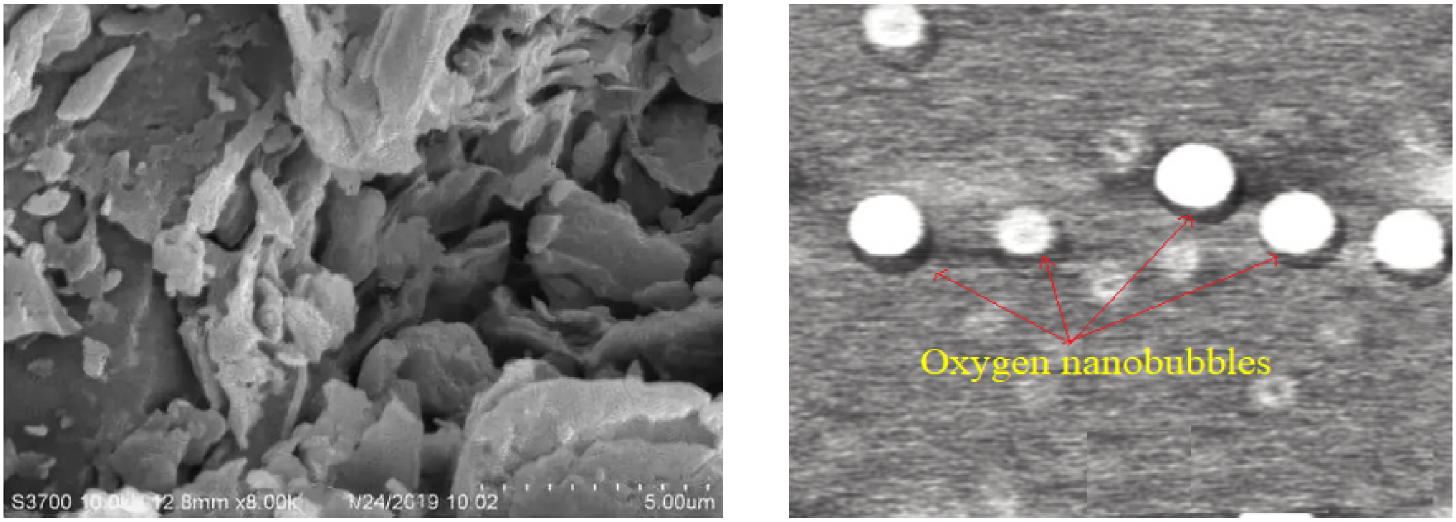


Figure 1

Al-modified zeolite and the oxygen nanobubbles

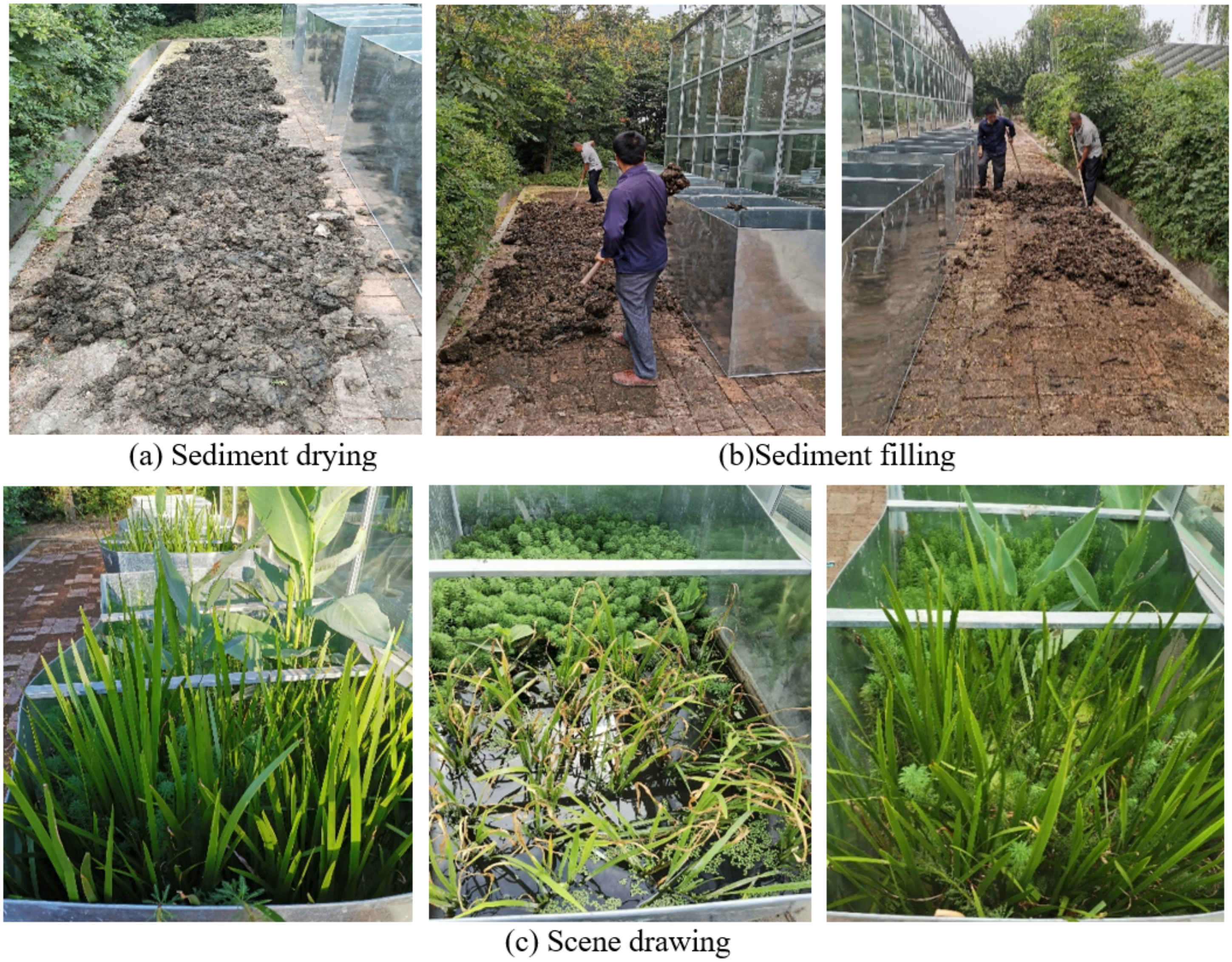
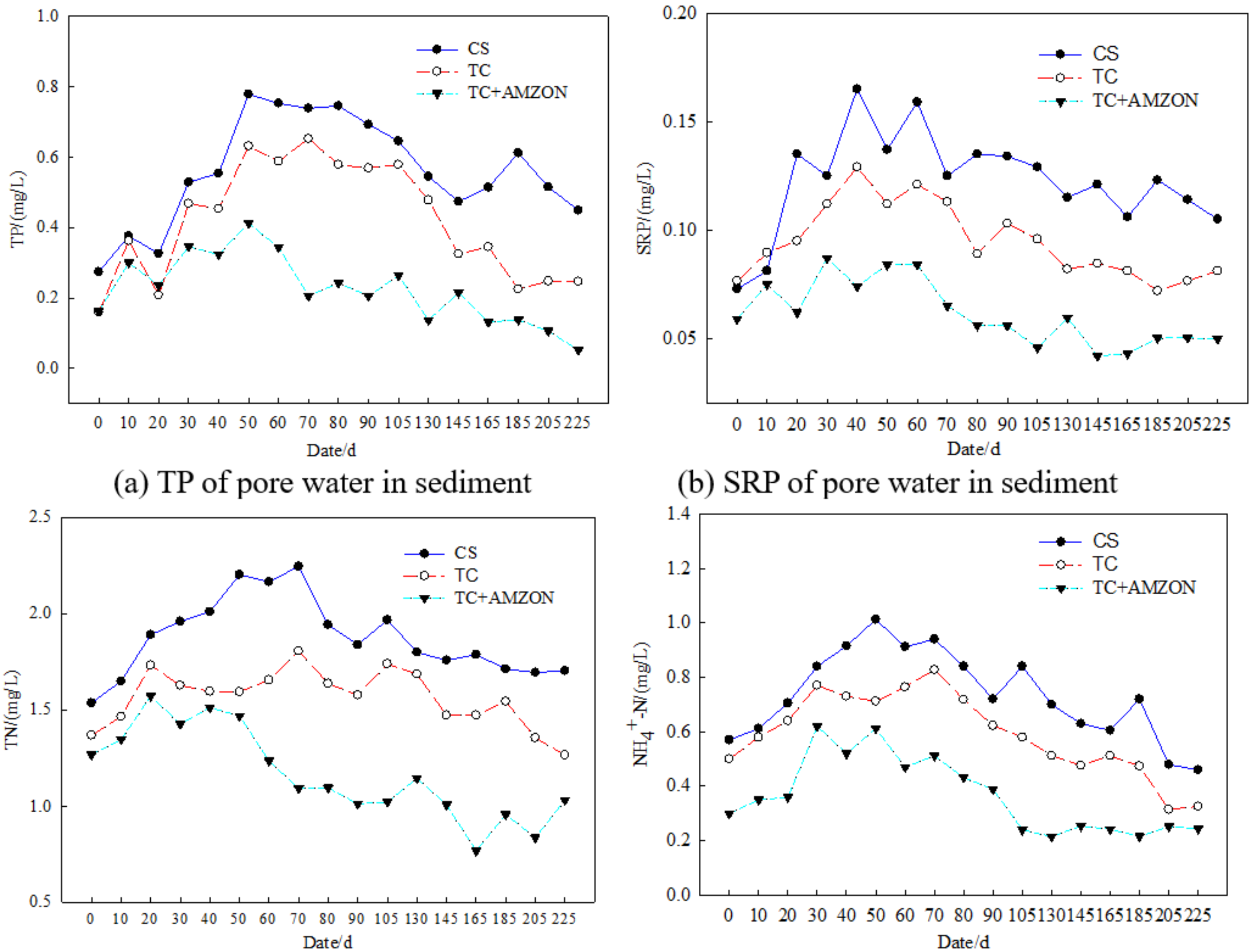


Figure 2

Test process Figures

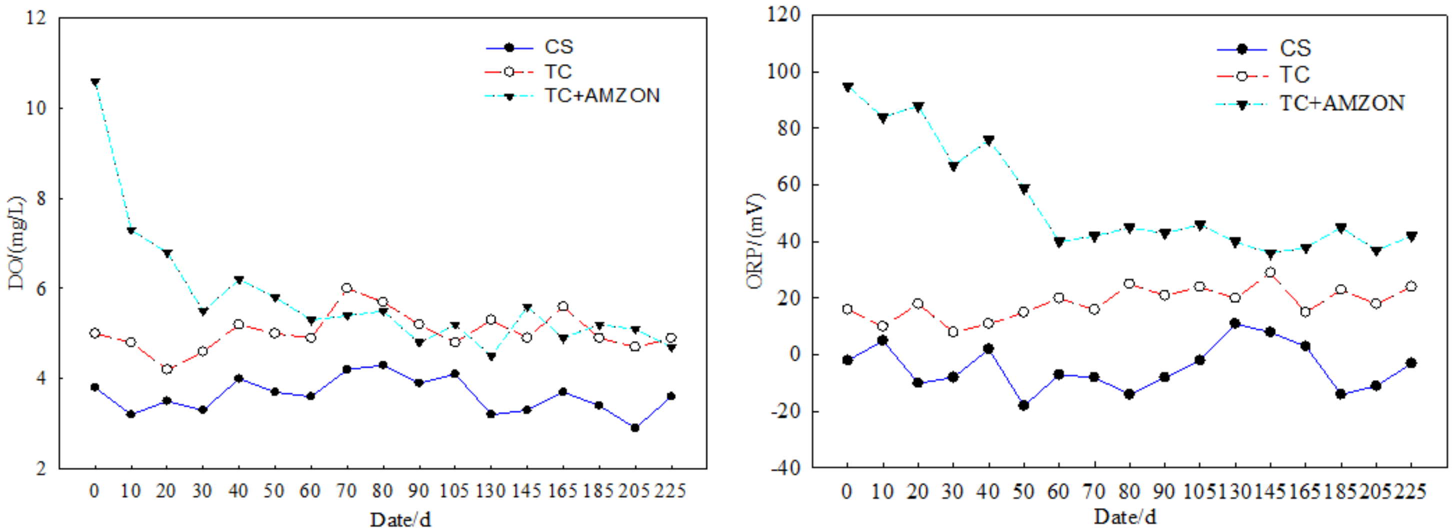


(a) TP of pore water in sediment (b) SRP of pore water in sediment

(c) TN of pore water in sediment (d) NH_4^+-N of pore water in sediment

Figure 3

N and P of pore water in sediment



(a) DO of pore water in sediment (b) ORP of pore water in sediment

Figure 4

DO and ORP of pore water in sediment

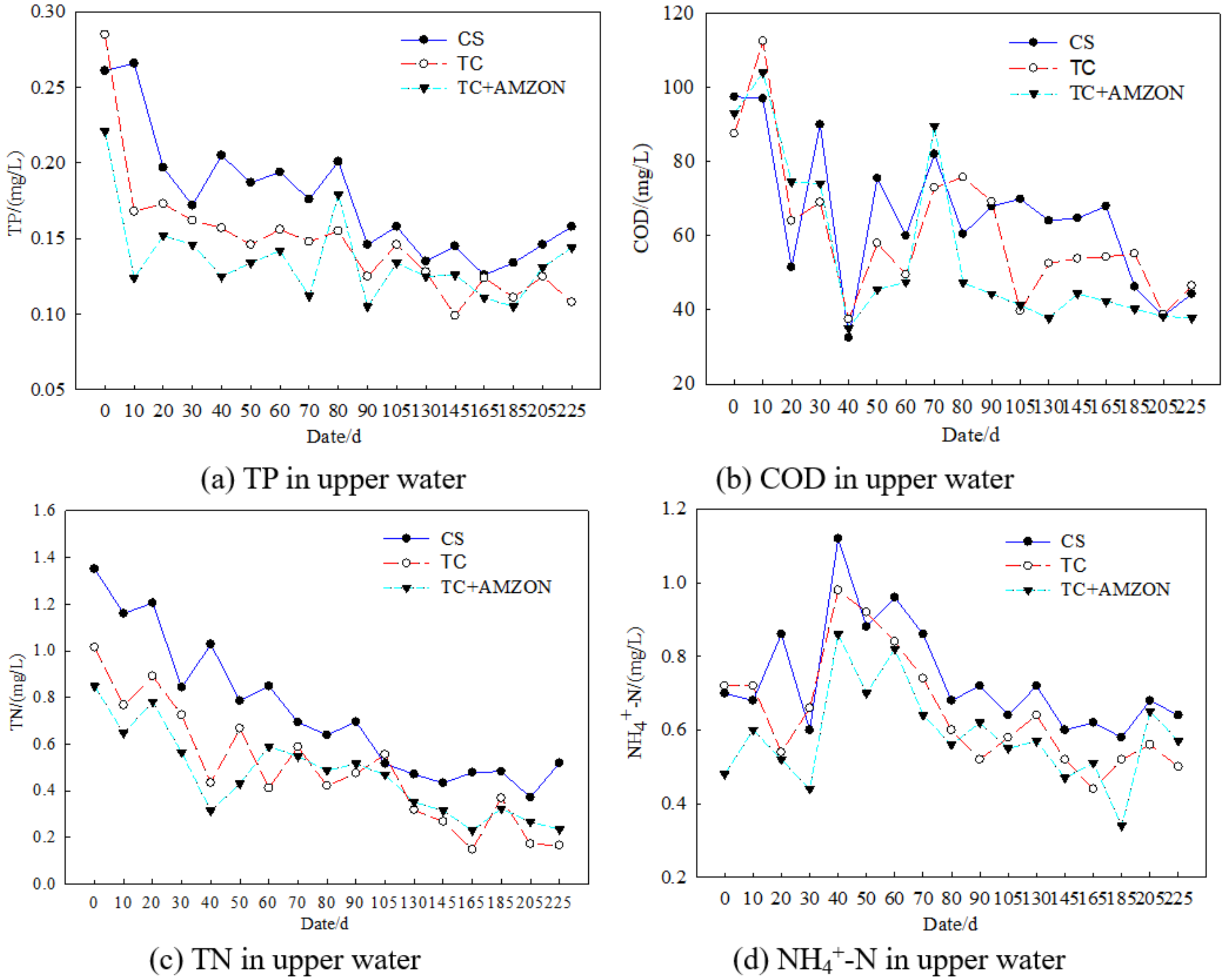


Figure 5

N, P and COD in upper water

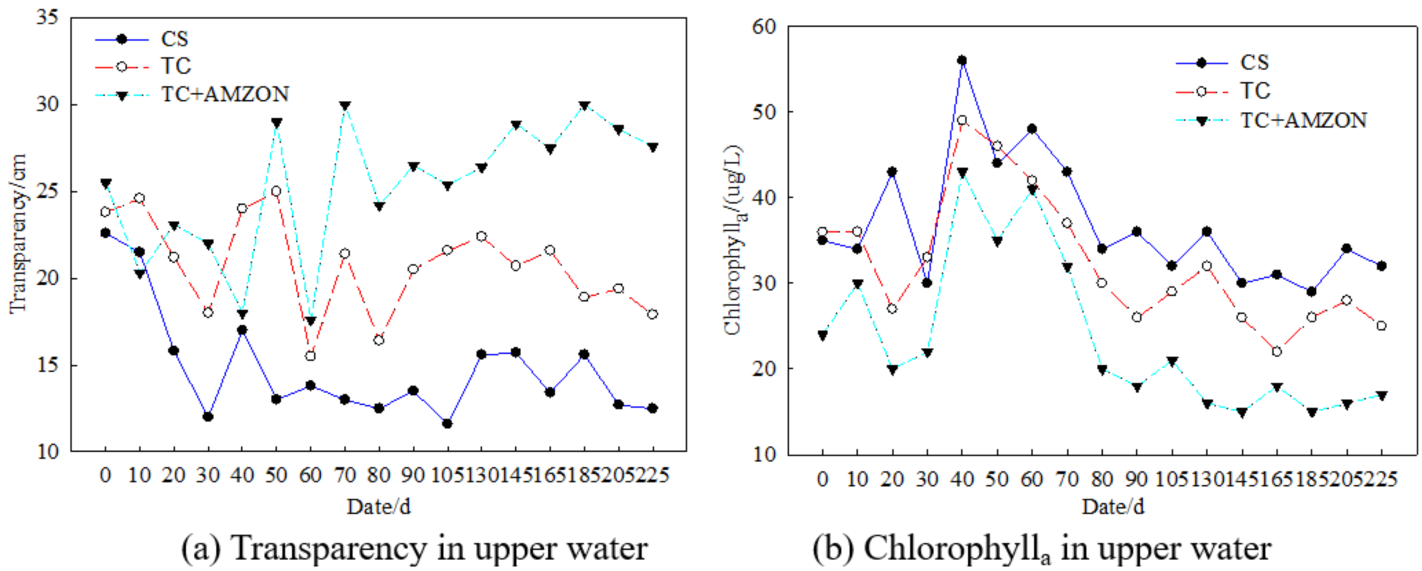


Figure 6

Transparency and chlorophyll$_a$ in upper water