Experimental study on combination of microbial flocculants with PAC in in-situ remediation of black odorous water and sediment

H Y Cheng, J X Long, Z Liu and A L Yang

School of environmental science and engineering, Xiamen University of Technology, 600 Ligong Road, Xiamen, 361024, China
E-mail: 2012111601@xmut.edu.cn

Abstract. This study, the sediment of black and odorous water body in Xinyang main flood drainage channel of Xiamen City was taken as the research object, and the effect of in-situ remediation of black and odorous water body sediment by microbial flocculant (MBF) and polyaluminium chloride (PAC) in different proportions was studied through laboratory static simulation test. The experimental results show that: (a) The MBF dosage of 20 mg/L has a good effect on the remediation of the sediment in the black-odor river. The removal rates of TP and COD in the overlying water are 86.5% and 87.37% after 15 days of experiments, respectively. The removal efficiency of acid volatile sulfur in sediment (AVS) is not very good, the removal rate is only 27.1%. 100 mg/L PAC is added to remedy the black-odor river sediment, and the overlying water under the same experimental conditions. The removal rate of TP was 51%. (b) The combination of MBF and PAC has a good effect on the remediation of the sediment and overlying water of the black and odorous river in the city. The optimum dosage scheme is PAC with 20 mg/L and microbial flocculant with 10 mg/L. Under this scheme, the removal rates of NH_4^+-N, TP and COD in overlying water were 92.37%, 70.82% and 64.52% respectively after 15 days of restoration experiment. AVS in sediment was reduced by 52.21%, which basically eliminated the black odor in overlying water.

1. Introduction
Nowadays, remediation of black and odorous water body is the most popular problem in water environment treatment. The polluted river sediment is the main source of internal pollution which causes black and odorous water body. There are a lot of nutrients in the sediment, which are easy to cause secondary pollution. Therefore, remediation of polluted sediment is particularly important. In-situ chemical remediation technology can effectively curb the problem of black and odor in polluted sediment, and its treatment effect is fast and secondary pollution is small, so it becomes an ideal treatment method. Polyaluminium chloride (PAC), polyacrylamide (PAM) and other inorganic or synthetic organic macromolecule flocculants are commonly used in advanced sewage treatment. However, it will cause insecurity and secondary pollution to the environment in the process of use[1]. Microbial flocculant is a kind of macromolecule substance produced by microbial cells[2]. Its main components are glycoprotein, mucopolysaccharide, protein, cellulose and deoxyribonucleic acid[3-4], etc. This substance has good flocculation performance[5] and is safe and non-toxic. It has attracted wide attention as a green water treatment agent[6]. However, the large dosage and high price of flocculant limit its wide application in large-scale production and industry.
2. Materials and methods

2.1. Experimental Materials

The bacteria used in the experiment were separated and preserved from activated sludge of sewage treatment plant. The seed culture medium consists of beef extract, peptone and NaCl. The fermentation medium consisted of sucrose, (NH₄)₂SO₄, MgSO₄, CaCl₂, phosphate buffer solution and trace element solution. The inoculation amount of seed liquid was 3% (V/V). After 72 hours of fermentation, 50mL fermentation broth was centrifuged. The supernatant after centrifugation was mixed with absolute ethanol at a ratio of 1:3. The supernatant was centrifuged for 16 hours, 5000r per minute for 15 minutes. The supernatant was poured out and dried to prepare microbial flocculant solution. Polyaluminium chloride (PAC) is prepared from solid polyaluminium chloride. Other concentrations of microbial flocculant and polyaluminium chloride flocculant used in the experiment are obtained by diluting the concentration of PAC.

2.2. Experimental Instruments and Methods

The instruments used in the experiment include: ultraviolet-visible spectrophotometer, electronic analytical balance, oven, digestion instrument, centrifuge, etc. The indexes of overlying water include ammonia nitrogen (NH₄⁺-N), total phosphorus (TP), and biochemical oxygen demand (COD). The methods of detecting these indexes are consulted with relevant literatures [7]. The reason why sludge organic sediment shows black odor is that there are a lot of sulfides in the sediment. The device for measuring AVS is shown in the Figure 1. Principle of AVS determination reaction: adding a certain concentration of hydrochloric acid and blowing with nitrogen to escape sulfide from sediment in the form of H₂S gas, and then absorbed by NaOH solution, colorimetric analysis of the amount of H₂S absorbed by NaOH was carried out.

Figure 1. Sketch of AVS Measuring Reactor.

(1. Nitrogen cylinder. 2. Gas flow meter
3-4. Gas cylinder. 5. Flat-bottomed Reaction Bottle. 6. magnetic stirrer. 7-8. Gas absorption bottle)

3. Result and analysis

3.1. Effect of PAC on Sediment Rehabilitation and Overburden Water

The concentration of 100 mg/L polyaluminium chloride (PAC) was added into the bottom mud, the solution of polyaluminium chloride was injected into the bottom mud, distilled water was added into the bottom mud, and placed in a 26-degree thermostatic incubator. The dosage was as follows: blank control test No. 1, 100 mg/L wet mud was added to No. 2, and the measuring days were 1, 3, 5, 7, 9, 12 and 15 days. The change of AVS in the bottom mud was measured, and ammonia nitrogen (NH₄ nitrogen) in the overlying water was also detected. + N, total phosphorus (TP), biochemical oxygen demand (COD) in water. The effects of PVA as a restorative agent on sediment AVS and NH₄⁺-N, TP, COD in overlying water were shown in Figure 2 to Figure 5, respectively.
As shown in Figure 2, when PAC is added to the bottom mud, the removal effect of AVS pollution of the bottom mud is not obvious, but remains at a level. AVS of the bottom mud remains at 14-18 umol/L. Compared with the blank control group, the floatation is smaller and there is a small increase. Polyaluminium chloride will form flocculent layer on the surface of the bottom mud.

While in Figure 3, NH$_4^+$-N in sediment increased to a certain extent, increased slightly in a short time, followed by a downward trend. PAC hydrolyzed on the surface of sediment to form Al$_2$(OH)$_3$ flocculant, and formed a cover layer at the interface of mud and water. From 15 days' observation, it can be found that NH$_4^+$-N in overlying water increased slightly in a short time, but the increase was not obvious.

From Figure 4, the inhibition of PAC on phosphorus was very obvious in the early stage of reaction, especially in the first five days. Compared with the blank reactor, the TP content in the overlying water was significantly reduced and stabilized at the level of 1.5 mg/L. The blank control group had no effect because of the absence of it.

As can be seen in Figure 5, after PAC was injected into sediment, COD in overlying water decreased significantly and remained at a low level, at 18-20 mg/L. The possible reason[9] is that aluminium salts are hydrolyzed to form Al$^{3+}$, and aluminium hydroxide produced by Al$^{3+}$ adsorbs humic acid, humus and other macromolecule organic matter in sediment. Small molecule organic matter will be adsorbed by the adsorption sites in the flocculent layer of aluminium hydroxide when it diffuses to the overlying water, so adding PAC will reduce the COD in overlying water.

3.2. Effect of MBF on Sediment Rehabilitation and Overlying Water
It can be seen from Figure 6 to Figure 9 that MBF has a good effect on the removal of \( \text{NH}_4^+ \)-N, COD and TP remove. Even the removal rate of AVS from sludge is higher, which is similar to the results of relevant researchers [10].

3.3. Effect of PAC and MBF on Sediment Rehabilitation and Overlying Water

In order to reduce dosage and enhance flocculation effect, the flocculation effect of treating secondary effluent by mixing PAC and MBF according to different dosage was investigated.

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Figure 12. Effect of combination of PAC and MBF on COD in overlying water.

Figure 13. Effect of combination of PAC and MBF on NH$_4^+$-N in overlying water.

It can be seen from Figure 10 to Figure 13 that the removal rate of AVS, NH$_4^+$-N, COD and TP can be significantly increased by the combination of microbial flocculant and PAC. The removal rate increases with the increase of PAC and MBF dosage. This is because on the one hand [11], the addition of cations neutralizes the negative charges on the functional groups of microbial flocculants and colloidal particles, which makes it easier to bridge with microbial flocculants. On the other hand, through the adsorption and coagulation of cationic flocculants, colloidal particles can be more effectively adsorbed and netted by microbial flocculants [12]. When PAC dosage was 20 mg/L and MBF dosage was 50 mg/L, COD removal rate and TP removal rate reached 64.52% and 70.82%, respectively. When 20 mg/L PAC was added alone, COD removal rate and TP removal rate were 18.2% and 51%, respectively. When MBF dosage was 50 mg/L, when PAC dosage was more than 20 mg/L, the removal rates of COD and TP did not increase significantly. Therefore, microbial flocculant 50 mg/L and PAC 20 mg/L were selected as the optimal dosage.

4. conclusion

(1) When MBF is used alone to treat overlying water, when the dosage range is 10-20 mg/L, MBF can effectively remove COD and TP from the water, but the excessive dosage will reduce the flocculation efficiency and affect the quality of the effluent. The optimal dosage is 20 mg/L.

(2) When the overlying water is treated by PAC alone, the coagulation effect of AVS is worse than that of MBF alone, and that of TP is the best. MBF has stronger humus removal ability than PAC, but its microbial metabolites removal ability is not strong.

(3) The combination of MBF and PAC can reduce 50% of MBF dosage and 33% of PAC dosage. The optimal dosage is 50 mg/L MBF and mg/L PAC. At this time, COD removal rate reaches 64.52% and TP removal rate reaches 70.82%. Among the components of secondary effluent, the removal of fulvic acid by compound coagulant is the most significant, followed by humic acid.

5. References

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