Effects of simulated in-situ electrokinetic remediation on physicochemical properties and phosphorus migration of sediments

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Abstract. The effect of simulated in-situ electrokinetic remediation (EKR) on phosphorus release from contaminated sediments was investigated. The effects of different anode materials (iron, aluminum, graphite and stainless steel) on the physicochemical properties and phosphorus migration were compared. The results showed that aluminum anode had the best inhibition effect on phosphorus release from sediments, and the highest inhibition rate of phosphorus release was 78.20% compared with non EKR, but the sustainability was poor, and the performance of iron anode is generally stable. The phosphorus in the sediments generally shows the migration trend from cathode to anode. After EKR, the Oxidation-Reduction Potential (ORP) of the sediment decreased with the increase of normalized distance from anode. The anaerobic environment of the sediment on iron anode was the most serious, and the lowest was -616mV. The ORP of the sediment from the anode area to the middle area of other electrodes was effectively improved. The pH of the sediment increases gradually from anode to cathode, and is characterized by acidification in the anode area and alkalization in the cathode area. Iron and stainless steel electrodes have more acidic areas, showing better electrolysis efficiency.

1. Introduction

Sediment is an important part of the aquatic ecosystem. Due to the long-term development and utilization of various chemical elements by human activities, the original biogeochemical cycle of these elements has been broken, and various pollutants enter the water through different channels, leading to the serious deterioration of the aquatic environment, and most pollutants are accumulated in the sediments[1]. Sediment can not only contain a variety of pollutants in the water, but also be released into the overlying water under appropriate environmental conditions to pollute the water again[2]. Therefore, research on sediment remediation technology is the key link to solve the aquatic pollution problem, whether it is urban black and odorous water or lake eutrophication.
Electrochemical remediation technology is to realize the electron transfer by constructing a chemical battery to generate the corresponding electrode reaction, thereby completing the oxidation or reduction of the pollutants[3]. According to the different principles of chemical batteries, it can be divided into EKR with the external electric field and galvanic cell remediation with spontaneous reaction. Among them, EKR mainly relies on various electrodynamic processes (electromigration, electroosmotic flow, electrophoresis etc.) under the direct current (DC) electric field to move pollutants to both ends of the electrode to achieve the degradation of pollutants[4]. At present, EKR is mostly used in the field of soil remediation, and the research on sediment remediation is still in its infancy. Secondly, in terms of the types of pollutants, many scholars have focused on the field of organic pollutants and heavy metals[5-6], but less on nutrients[7]. In this study, the effects of four anode materials (iron, aluminum, graphite and stainless steel) on the release of phosphorus from sediments to overlying water were investigated by simulating in-situ EKR. The changes in physical and chemical properties of sediments and the migration of phosphorus were analyzed. The results provide basic data for in-situ EKR of sediment.

2. Materials and methods

2.1. Experimental sediment collections and preparation

Sediment used in the experiment was collected from Qixing Wharf, Huixian Karst National Wetland Park, Guilin, Guangxi (N 30°5′31″, E 110°11′52″). The Qixing Wharf is a gathering point for local residents and tourists. Therefore, the lake is facing a severe environmental crisis, particularly eutrophication caused by large domestic sewage and non-point source pollution.

After removing large rocks and weed, the fresh sediment was screened through an 8-mesh sieve, sealed and frozen for storage. The initial sediment pH was 7.03, the ORP was -349mV, the moisture content was 73.40%, and the TP (Total Phosphorus) concentration was 3106mg/kg.

2.2. Experimental setup configurations and experimental design

Figure 1(a) shows the schematic diagram of the setup used for EKR experiments. The experimental setup is constructed by a Perspex chamber (20 cm×5 cm×20 cm), two cylindrical electrodes (5 cm×φ1cm) with electrode gaps of 15 cm, two copper wire conductors are used to connect the power supply to the electrodes, and a 30 V DC power supply to form 1 V/cm voltage gradient.

A total of 5 experimental setup were designed, one of which was the control check (CK), to assess the influence of 4 anode materials (iron, aluminum, graphite and stainless steel) on the remediation effect (the cathode material is stainless steel), the experimental design parameters are shown in Table 1. The experimental setup was equipped with 5cm of sediment, 10cm of overlying water (RO pure water). After standing for 12h, the setup was started to operate after the sediment-water interface was stabilized. The duration of the experiments was 5 days and TP content in the overlying water was monitored daily. The sediment samples were collected with a medicine spoon after the end of EKR operation. The locations of sampling site are shown in figure 1(b). All experiments were carried out at room temperature (25°C).
2.3. Chemical analyses
The overlying water TP concentration was measured by Lianhua multi-parameter water quality tester [5B-3B(V8), China]. The pH of sediments was measured by E-301F electrode and ORP was measured by 501 composite electrode (PHS-3E, China). The TP concentration within sediment was determined by SMT (The Standards, Measurements and Testing Programme) method[8]. Recorded current changes through DC power supply during EKR process.

Table 1 Experimental design of EKR

| Number | Anode materials | Electrode gap/cm | Voltage gradient/(V·cm⁻¹) | Time/d |
|--------|----------------|------------------|---------------------------|--------|
| EK-0   | -              | -                | -                         | 5      |
| EK-1   | Iron           | 15               | 1                         | 5      |
| EK-2   | Aluminium      | 15               | 1                         | 5      |
| EK-3   | Graphite       | 15               | 1                         | 5      |
| EK-4   | Stainless steel| 15               | 1                         | 5      |

3. Results and discussion

3.1. Changes of TP concentration in overlying water during EKR
It can be seen from figure 2 that TP concentration in the overlying water of Ek-0 increases with time, and reaches the peak value on the second day, increasing by about 66%, and then the growth trend slows down. This is because with the continuous anaerobic of the sedimentary environment, Fe³⁺ is easy to be reduced to Fe²⁺, which promotes the release of phosphorus adsorbed by Fe(OH)₃ or other Fe-P[9], and anaerobic will accelerate the reduction of SO₄²⁻, and the generated H₂S will combine with Fe²⁺, It also promotes the release of NaOH-P (phosphorus that can be extracted by NaOH)[10]. Under the EKR of different electrode materials, the TP concentration in the overlying water of each device showed a trend of first increasing and then decreasing. EK-1 and EK-4 gradually inhibited the release of phosphorus in sediments from the second day, and the inhibitory effect of EK-4 was better and stable. Both EK-2 and EK-3 hindered the release of phosphorus from the first day. However, the effect of EK-3 is very small, and the inhibitory effect of EK-2 is the best among the four materials.

The electrolytic reaction of water occurs during the EKR of graphite and stainless steel anodes. The oxygen generated by the anode effectively inhibits the anaerobic environment of the sediment, which significantly weakens the release of phosphorus from the sediment overlying water. The release of phosphorus in EK-3 is higher than that of EK-0 in 3-5 days. This is because the collected sediment samples originally contained a large amount of algae, and the rapid growth of algae absorbed the phosphorus in the overlying water. Figure 3 shows the apparent changes of sediment during the EKR process. It can be seen from figure 3 that there are significantly more algae in EK-0 than in other groups. In the first two days, the phosphorus release from the sediment of EK-1 was even higher than that of Ek-0, and then decreased rapidly, because iron lost two electrons at the anode to form Fe²⁺. Fe²⁺ had strong reducibility and was easy to combine with the electron acceptor, which made the ORP of sediment very low and promoted the release of phosphorus. However, with the formation of Fe³⁺ and the increase of water pH, Fe³⁺ hydrolyzed to form Fe(OH)₃ colloid. The TP concentration of overlying water is greatly reduced by flocculation.

Aluminum as anode will have the following electrolytic reaction:

\[
2Al-6e^-+3H_2O=Al_2O_3+6H^+ \quad \text{(formed film reaction)}
\]

\[
Al_2O_3+6H^+= Al^{3+}+3H_2O \quad \text{(dissolution film reaction)}
\]

At the initial stage of electrolysis, due to the hydrolysis of Al³⁺, the generated Al(OH)₃ has a good flocculation effect, reducing the TP concentration of overlying water. At the same time, the formed film reaction of aluminum is divided into two steps, the first is the electrolysis reaction of water at the anode (i.e. Releasing O₂), and the second is the oxidation reaction of Al, which also makes the sediment does not release phosphorus due to the low ORP. Therefore, Ek-2 always maintains a relatively...
low TP concentration in the overlying water. However, as Al₂O₃ is a dense oxide film, it will constantly hinder the electrolytic reaction, and its sustainability remains to be further explored.

![Figure 2](image1.png)

**Figure 2** Changes of TP concentration in overlying water during EKR

![Figure 3](image2.png)

**Figure 3** Apparent changes of sediments and overlying water during EKR

### 3.2. Current variations during EKR

Figure 4 shows the changes of current during the EKR. It can be seen from figure 4 that with the extension of EKR time, the current of the four electrode materials gradually decreases, and finally tends to be stable. However, in the initial 12h, the current will increase slightly. This is because the pore water is electrolysis, and the H⁺ and OH⁻ in the solution change more, which promotes the movement of electrons, H⁺ promotes the desorption of metal ions in the sediment, increases the number of mobile ions in the system, and increases the current. With the extension of time, the adsorbed metal ions and OH⁻ form precipitation, blocking the pores of the sediment and increasing the resistance of the sediment. In addition, the accumulation of electrode polarization and concentration polarization will also affect the efficiency of electrode reaction, resulting in the reduction of current. The current drop of EK-2 was the most dramatic. It dropped by 70% in the first 2 days, and then stabilized. Because the hydrolysis of Al³⁺ occurs in the initial stage of EKR, and then with the continuous formation of Al₂O₃ (dense oxide film), it hinders the flow of current and the progress of oxidation reaction, causing the current to drop sharply.
3.3. Changes in ORP in sediment after EKR
As showing in figure 5, ORP of EK-3 and EK-4 near the anode area is significantly increased, because as inert electrodes, the electrode reaction of the two electrodes at the anode is that OH\(^{-}\) loses electrons to generate O\(_2\), effectively providing electron acceptors for the sediment. EK-1 and EK-2 use active electrodes, which are caused by anode corrosion reaction. Fe loses two electrons to form Fe\(^{2+}\). Fe\(^{2+}\) has strong reducibility and it is easy to combine with electron acceptors, which makes the ORP of sediment very low. The first step of formed film reaction of aluminum electrode is the electrolysis of water in the anode. Therefore, aluminum electrode also has the effect of improving ORP of sediment. In general, the EKR under the four electrode materials will show a trend that the farther away from the anode, the lower the ORP of the sediment.

![Figure 4 Changes of current during EKR](image)

![Figure 5 Changes of ORP in sediments after EKR](image)

3.4. Changes of pH in sediment after EKR
Figure 6 shows that the pH of sediment increases gradually from anode to cathode in EKR, and has the characteristics of anodic acidification and cathodic alkalization. Due to the use of micro current in EKR and the buffer property of the sediment, the phenomenon of acid-base is not serious, and the pH value fluctuates in the range of 6 ~ 9. It can be seen that the neutral front of EK-1 and EK-4 migrates further than that of EK-2 and EK-3, that is, iron and stainless steel anode present more acidic area. Generally speaking, effective ionic mobility of H\(^{+}\) is about 1.8 times that of OH\(^{-}\), which makes the acid front occupy most of the area[11]. Therefore, it can be considered that the electrolysis efficiency of iron and stainless steel anode is better than that of graphite and aluminum in this experiment. In addition, the pH
value of the sediment in the anode area of EK-2 is neutral, which may be due to the formation of Al₂O₃ hindering the electrolysis reaction and reducing the formation of H⁺.

3.5. Phosphorus migrations in sediment after EKR

It can be seen from figure 7 that the TP concentration in the sediment near the cathode area is significantly reduced because H⁺ in the cathode is reduced to H₂ and ORP is very low, forming a strong anaerobic environment. Under this condition, microorganisms mineralized the organic phosphorus in the sediments into inorganic phosphate, which moved to the anode under the action of electromigration. Therefore, the concentration of TP in the sediments gradually increased from cathode to anode. The TP concentration of EK-2 in the sediment of the anode area was significantly higher than that of the other three groups. According to the previous analysis of the TP concentration of overlying water, EK-2 fixed more TP, so more phosphorus from the cathode area was accumulated in the sediment of the anode area. Compared with EK-0, the TP concentration of EK-1, EK-3 and EK-4 did not increase significantly, which may be due to the adsorption of migrating phosphorus on the electrode column.

4. Conclusion

1) Simulation experiments show that in situ EKR can control the release of phosphorus from sediments. Aluminum anode showed the best control effect in the remediation, and the inhibition rate of phosphorus
release was up to 78.20%. However, its remediation sustainability still needs further study. Stainless steel anode showed moderate performance in the EKR, which is a very suitable electrode material.

2) The current first increases and then decreases, and finally tends to be stable in the EKR. The current of aluminum anode decreases most acutely because of the coating of Al₂O₃ produced by electrolysis.

3) After EKR, ORP of the sediment decreased with the increase of normalized distance from anode, and the iron anode produced reductive Fe²⁺ by electrolysis, which led to the most serious anaerobic environment. The pH of the sediment increases with the increase of normalized distance from anode, and the iron and stainless steel anodes have more acidic area, showing better electrolysis efficiency.

4) After EKR, the phosphorus in the sediment tended to migrate from cathode to anode. The TP concentration of aluminum in the anode area is much higher than that of other electrodes, which may be that aluminum has a more fixation effect on the phosphorus released in the cathode area during electrolysis.

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