Evaluation of the Slow Release Oxygen Properties and pH Control Ability of Oxygen Slow-releasing Materials

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Abstract. In this study, an oxygen slow-releasing materials (OSRM) was developed by simple one-step synthesis. The composition of OSRM included calcium peroxide, bentonite or carclazyte, cement, potassium dihydrogen phosphate (KH₂PO₄) and ammonium sulphate((NH₄)₂SO₄). The OSRM was natural and non-toxic. The slow release oxygen properties and pH control ability of OSRM were evaluated. Results showed that the oxygen concentration increased and kept stable in a week after the addition of OSRM. The OSRM added with KH₂PO₄ and (NH₄)₂SO₄ was better than The OSRM doped with carclazyte in controlling the pH approaching to neutralization. Besides, The OSRM doped with carclazyte instead of bentonite led to the oxygen release slowly. In stimulated sediment environment, the pH value in water was stable at about 7.6 after 4 g/L of OSRM added. This phenomenon may be due to functional groups with buffer capacity occurred in sediment.

1. Introduction

The content of dissolved oxygen in water is an important parameter to measure the quality of water environment, which can also indicate the impact of human activities on sediments and water [1]. For example, the eutrophication of lakes and rivers and the ability of microorganisms to degrade pollutants are often related to the level of dissolved oxygen [2].

Nowadays the aeration technology mainly includes mechanical aeration technology and chemical aeration technology. Compared with chemical oxygenation technology, mechanical aeration technology such as artificial aeration [3] is rarely used in some water bodies due to high energy consumption and low oxygenation effect. In addition, aeration is only suitable for wastewater treatment and small river channel restoration at present, and it is not convenient for large-scale aeration for lake restoration. Compared with mechanical aeration, chemical oxygenation technology mainly supply DO in water body in a simple but efficient way such as adding oxygen release materials, which could not only release O₂ to stimulate aerobic respiration of indigenous microorganisms, but also reduce the generation of anaerobic metabolites. Besides, after the addition of oxygen slow-releasing materials (OSRM) into the water body, a layer of aerobic film is formed at the sediment-water interface, which can effectively prevent the release of pollutants from the bottom mud to the overlying water body, especially the release of phosphorus in the bottom mud [4]. Therefore, OSRM is now used in different kinds of water environment restoration project such as lake restoration [5] ~ [6] and groundwater remediation [7] ~ [9].

The performance of OSRM on water restoration is affected by numerous factors, such as the compatibility of the OSRM with the environment [10] ~ [11], the internality of the OSRM [12], and its...
effective oxygen-releasing characteristics [13]–[14]. Traditionally, single solid peroxides such as CaO₂ are generally mixed with cement as OSRM to release oxygen upon reaction with water as in equation (1).

\[ \text{CaO}_2 + \text{H}_2\text{O} \rightarrow 0.5\text{O}_2 + \text{Ca(OH)}_2 \]  

(1)

Although OSRM can effectively increase DO concentration, a large proportion of oxygen escapes inevitably before entering the sediment environment, resulting in low oxygen utilization efficiency. Besides, Calcium hydroxide produced from CaO₂ released hydroxyl ion, causing high pH problem in water.

In order to minimize the unnecessary OSRM consumption and overcome the high pH problem, different oxygen slow-releasing materials (OSRM) have been developed to slow down the oxygen release properties [15]. Zhang et al. synthesized an oxygen releasing material from CaO₂, bentonite and two kinds of butters [16]. The results of evaluating performance properties of OSRM revealed that oxygen was released slowly by oxygen releasing material and the DO concentration was maintained at over 5 mg/L for a long period. Li et al. also synthesized an oxygen releasing material doped with humic acid sodium and zeolite in water restoration and found that OSRM could slow down the oxygen properties but the DO concentration was too low at 1.32 mg/L [17]. Besides, an oxygen slow-releasing material (OSRM) consisted of calcium peroxide (CaO2), stearic acid (SA) and quartz sand exhibited higher oxygen-releasing capacity, and more effective pH control due to the change SA content [18]. Otherwise, oxygen releasing alginate beads (ORABs) was synthesized by using calcium peroxide (CaO2) embedded sodium alginate is proposed to overcome the limitations regarding fast oxygen release rate and high pH induced by OSRM application [19]. However, in all of the researches above, the high pH is still big problem.

In this study, an oxygen slow-releasing material (OSRM) was synthesized. This OSRM was a mixed materials composed of calcium peroxide as oxygen applying agent, bentonite or carclazyte as slow-release-formulation, cement as binder, potassium dihydrogen phosphate (KH₂PO₄) and ammonium sulfate ((NH₄)₂SO₄) as butters. Besides, OSRM was evaluated on the release ability of oxygen and regulation of pH through the comparison and a stimulated sediment environment was set to research the influence of bottom mud on overcoming the high pH problem caused by OSRM.

2. Materials and method

2.1. Preparation of OSRM

An oxygen slow-releasing material (OSRM) was prepared as follows. A certain percentage of calcium peroxide (CaO₂), cement, bentonite or carclazyte, potassium dihydrogen phosphate (KH₂PO₄) and ammonium sulfate ((NH₄)₂SO₄) were put in a 100 mL beaker and stirred for 5-10 min. After that, a certain amount of water was added into mixture and stirred for 5-10 min. Finally, a number of cubes with a diameter of 2cm were produced by forming mixture into a mould and was placed in a ventilated and air-dried place and for 24h. The composition of different kinds of OSRCs was shown in the Table 1.

2.2. Evaluation of the oxygen-releasing properties of OSRM

An oxygen release experiment was performed in a sealed conical flask (total volume: 500 mL). Another sealed conical flask with 1cm thick layer of mud was used to test the influence of sediment.

To simulate the low level of dissolved oxygen (DO) in common water, 0.3 g /L of Na₂SO₃ was added to both sampling to maintain the DO concentration below 0.1 mg/L. the pH of water was adjusted to neutral. The oxygen concentration was measured using a DO meter (JPBJ-608, China). The pH was measured using a pH meter (PHSJ4F, China). The testing time is not more than one week. The dosage of OSRM was about 4g/L for ORSM -A, ORSM-B, ORSM-B, ORSM-C and ORSM-D. The dosage of OSRM was about 2g/L for ORSM -E, ORSM-F and ORSM-G.
Table 1. The composition of different kinds of OSRM

| Content (g/4gORSM) | A   | B   | C   | D   | E   | F   | G   |
|-------------------|-----|-----|-----|-----|-----|-----|-----|
| CaO₂              | 1   | 1   | 1   | 1   | 2   | 2   | 2   |
| Cement            | 0.5 | 0.5 | 0.5 | 0.5 | 1   | 1   | 0.5 |
| Bentonite         | 0.5 | 0.5 | 0.5 | 0.5 | 1   | 0   | 0   |
| Carclazyte        | 0   | 0   | 0   | 0   | 0   | 1.5 | 1.5 |
| KH₂PO₄            | 2   | 0.5 | 0.25| 0.125| 0 | 0 | 0 |
| (NH₄)₂SO₄         | 0   | 1.5 | 1.75| 1.875| 0 | 0 | 0 |

3. Result and discussion

3.1. The Evaluation of oxygen-releasing properties and pH control ability for OSRM

The dissolved oxygen concentrations and pH changes of the OSRM with different content buffer chemicals were shown in Fig.1 (a). In the first day, oxygen concentrations increased obviously and then become stable between 5.5 mg/L and 7.2 mg/L. Wherein, the dissolved oxygen concentrations released by OSRM-B, OSRM-C and OSRM-D are similar and more stable.

The pH changes were shown in Fig.1 (b). The highest pH value was observed for OSRM-A. The addition of ammonium sulfate was benefit for the pH control and also helped the concentration of O₂ maintain at about 6.5 mg/L. So the addition of KH₂PO₄ and (NH₄)₂SO₄ as buffer chemicals could control the pH to stable at neutralization.

Figure 1. The effects of KH₂PO₄ and (NH₄)₂SO₄ content of OSRM on DO concentration (a) and pH (b)

3.2. The Effects of doped carclazyte and bentonite on release of oxygen and regulation of pH

The effect of doped carclazyte and bentonite on pH in water and oxygen concentration was shown in Fig.2. When the content of carclazyte or bentonite was 1 g, oxygen concentrations increased obviously in the first day. Then oxygen concentrations were about 5.5 mg/L and 4.62 mg/L for OSRM-E and SRM-F, respectively. The doped carclazyte lead to the oxygen release slowly and lower pH value. However, when the increase of carclazyte contented from 0.5 to 1 g, the material was too loose to stability. Moreover, the pH value is the highest for OSRM-G.
The effects of carclazyte and bentonite content of OSRM on DO concentration (a) and pH (b)

3.3. The Effects of simulated sediment environment on release of oxygen and pH control

In simulated sediment environment, the pH value in water (Fig. 3(a)) maintained at about 7.6 by the addition of SRM-A in the whole 6 days, which may be due to functional groups with buffer capacity occurred in sediment. Comparably, the pH value in water increased sharply in the first day without sediment, then stable at about 10.0. The concentration of O2 (Fig. 3(b)) rose sharply in the first day and then decreased slowly. The concentration of O2 was similar, which maintained between 4.5 mg/L and 6.5 mg/L.

The Effects of simulated sediment environment on DO concentration (a) and pH(b)

4. Conclusions

In this study, slow release oxygen materials were developed. The slow release oxygen properties and pH control ability of oxygen slow-releasing material were evaluated. Oxygen concentration was increased and kept stable in a week. The addition of KH2PO4 and (NH4)2SO4 as buffer chemicals may control the pH to become stable at neutralization. The doped carclazyte instead of bentonite led to the oxygen release slowly and lower pH value. In simulated sediment environment, the pH value in water stable at about 7.6, which may be due to functional groups with buffer capacity occurred in sediment.

In the future, the effect of oxygen release materials on pollutants such as nitrogen and phosphorus release from sediment should be further studied.
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