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Combating hypoxia/anoxia at sediment-water interfaces: A preliminary study of oxygen nanobubble modified clay materials

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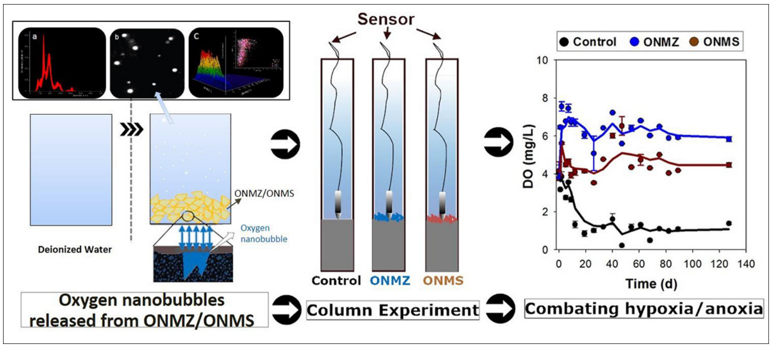
HIGHLIGHTS

- Oxygen nanobubble is a potentially promising technique to mitigate hypoxia/anoxia.
- Oxygen nanobubble modified zeolite can effectively deliver oxygen to bottom water.
- The oxygen-locking surface sediment layer is crucial in reducing sediment anoxia.
- Oxygen-locking sediment layer can switch the anoxia sediment from P source to sink.

GRAPHICAL ABSTRACT



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ABSTRACT

Combating hypoxia/anoxia is an increasingly common need for restoring natural waters suffering from eutrophication. Oxygen nanobubble modified natural particles were investigated for mitigating hypoxia/anoxia at the sediment-water interface (SWI) in a simulated column experiment. By adding oxygen nanobubble modified zeolites (ONMZ) and local soils (ONMS), the oxygen nanobubble concentrations (10^5–10^7 particles/mL) were several orders of magnitude higher in the water than the original water solution (10^4 particles/mL) within 24 h. In the column experiment, an oxygen-locking surface sediment layer was formed after capping with ONMZ and ONMS particles. The synergy of diffusion of oxygen nanobubbles and retention of oxygen in this layer contributes to both the increase of DO and reversal of hypoxic conditions. The overlying water had significantly higher dissolved oxygen (DO) values (4–7.5 mg/L) over the experimental period of 127 days in ONMZ and ONMS compared with the control systems (around 1 mg/L). Moreover, the oxidation-reduction potential (ORP) was reversed from −200 mV to 180–210 mV and maintained positive values for 89 days in ONMZ systems. In the control systems, ORP was consistently negative and decreased from −200 mV to −350 mV. The total phosphorus (TP) flux from sediment to water across the SWI was negative in the ONMZ and ONMS treated systems, but positive in the control system, indicating the sediment could be switched from TP source to sink. The oxygen-locking capping layer was crucial in preventing oxygen consumption caused by the reduced substances released from the anoxic sediment. The study outlines a potentially promising technology for mitigating sediment anoxia and controlling nutrient release from sediments, which could contribute significantly to addressing eutrophication and ecological restoration.

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1. Introduction

Hypoxia/anoxia is a global threat to aquatic ecosystems, often inducing "dead zones" at the sediment-water interface (SWI) (Diaz and Rosenberg, 2008; Feist et al., 2016; Stramma et al., 2008). In the dead zones, sediment release rates may be accelerated for many constituents, including phosphorus, nitrogen, iron, manganese, methyl-mercury and hydrogen sulfide (Beutel et al., 2008; De Vittor et al., 2016; Gantzer et al., 2009; Testa and Kemp, 2012; Zhu et al., 2013). Among the released substances, phosphorus and nitrogen can lead to eutrophication, which is often associated with harmful algal blooms (Funkey et al., 2014). Moreover, the hypoxic/anoxic condition can be exacerbated by the additional oxygen demand from the mineralization of dead algal biomass (Diaz and Rosenberg, 2008; Testa and Kemp, 2012). Thus, mitigation of hypoxia/anoxia at the SWI is crucial for both water quality improvement and eutrophication control.

Current efforts designed to replenish benthic dissolved oxygen (DO) and remove the anoxic environment are often based on the directly injecting either air (aeration) (Henares et al., 2015), or oxygen gas (oxygenation) (Bierlein et al., 2017) sometimes using oxygen-supersaturated water (Forth et al., 2015) into the hypoxic region near the SWI. Although these techniques have been reported to be effective to some extent, they are still limited by high cost and efficiency at large scale (Bormans et al., 2016). Additionally, gas or water pumped into the SWI region may disturb the settled sediment and induce internal releases of nutrients and other contaminants to the water column, as well as potentially leading to additional oxygen consumption and increase hypoxia (Bierlein et al., 2017). The pump system also needs to be continuously operated to maintain the oxygen supply to the SWI, otherwise DO may be rapidly consumed, leading to return of anoxia (Bryant et al., 2010). In the Baltic Sea, where hypoxic waters have expanded in area from 5000 to >60,000 km^2 in the last century (Carstensen et al., 2014), enhanced ventilation of deep waters through additional input of oxygenated surface water has been suggested (Conley et al., 2009). However, this method will require >30 years to take effect and may cause a drastic change in stratification and alteration of the biodiversity (Funkey et al., 2014). Ventilation by pumping oxygen-rich water downward to alleviate hypoxia in the Baltic Sea is estimated to require >100 pump stations (0.6 MW each) at a cost of around 20,000 million Euros (Stigebrandt and Gustafsson, 2007). Therefore, developing a more cost-effective and sustainable technique for hypoxia/anoxia mitigation in bottom waters and at the SWI is vitally important.

Oxygen nanobubbles have attracted increasing attention in recent years due to the characteristics of high gas solubility and long lifetime of oxygen in the liquid (Ebina et al., 2013; Peng et al., 2015). As opposed to oxygen gas (Cavalli et al., 2009), nano-scale oxygen bubbles could slowly diffuse oxygen into the surrounding water phase and last >70 days when diameter is <200 nm (Ebina et al., 2013). The oxygen nanobubble technique has already been widely used in medicine (Cai et al., 2015), physiology (Ebina et al., 2013) and water treatment (Agarwal et al., 2011). However, a cost-effective method to deliver the oxygen nanobubbles into the SWI for hypoxia/anoxia mitigation remains a bottleneck. It was recently reported that oxygen nanobubbles can be generated and will persist at solid particle-water interfaces (i.e., surface nanobubbles) (Pan et al., 2016; Wang et al., 2016; Yang et al., 2013). The presence of oxygen nanobubbles has been proven and quantified at the rough and irregular surfaces of clay particles (Pan et al., 2016). It is a means to increase total oxygen content in a suspension by adding clay particles loaded with oxygen nanobubbles (Pan and Yang, 2012; Pan et al., 2011). Sedimentation of a carrier loaded with oxygen nanobubbles due to the gravity effect provides a mechanism to alter the hypoxia/anoxia near the SWI but has not been investigated systematically.

Many geo-engineering methods, such as adding phosphorus-adsorbing materials, have been demonstrated to significantly contribute to remediating eutrophication control and contributing to lake restoration (Huser et al., 2016; Noyma et al., 2016; Spears et al., 2014; Waajen et al., 2016). However, the sinking materials cover the sediment and their effect on redox potential at the SWI may be temporary (Pan et al., 2012). Additionally, most of the adsorbing materials, e.g., metal salts and Phoslock®, are synthesized artificially and may have potential side-effects on the environment. Natural sediments entering lakes through weathering and runoff, have high microporous surface area (Pan et al., 2013). These natural particles can potentially act as oxygen nanobubble carriers to deliver oxygen to the SWI. However, no previous study has applied such technology and there is little knowledge about the effects of oxygen nanobubbles on the oxygen conditions, redox potential and nutrient fluxes at the SWI.

The objective of this study is to investigate for the first time the efficacy and sustainability of a surface oxygen nanobubble technique for mitigating hypoxia/anoxia and its effect on nutrient fluxes across the SWI. Local soil and natural zeolite were selected as the oxygen nanobubble carriers in the experiment. After oxygen nanobubble modified zeolite (ONMZ) or oxygen nanobubble modified soils (ONMS) were applied in simulated eutrophic water-sediment systems in the laboratory columns, oxygen levels in the overlying water and redox potential at the SWI were monitored. Nutrient concentrations, including total phosphorus (TP), total nitrogen (TN), ammonium (NH_4^+-N), nitrate (NO_3^--N), and nitrite (NO_2^--N), were measured in the overlying water and nutrient fluxes across the SWI were calculated.

2. Materials and methods

2.1. Preparation of oxygen nanobubble modified materials

Natural zeolite and local soil were selected as the carrier materials to investigate the effect of surface oxygen nanobubble technology on hypoxia/anoxia mitigation at the SWI. Zeolite with particle size of 1–2 mm was purchased from Yongjia Natural Minerals Ltd., Hebei, China. Local soil from Lake Ngaroto, Waikato, New Zealand, was sieved through a mesh sieve to remove particles >380 μm. Ngaroto is the largest peat lake in the Waikato region, with a surface area of about 108 ha, maximum depth of 4 m and average depth of c. 2 m. Land in the catchment of this lake is mostly used for pastoral grazing. The lake is hypertrophic and has major cyanobacteria harmful algal blooms throughout summer. The specific surface area and micropore size of the natural zeolite and local soil were determined by the Brunauer–Emmett–Teller (BET) method with a Micromeritics ASAP-2020 apparatus (Micromeritics Inc., USA) (Zhang et al., 2014).

The zeolite and soil, were washed with deionized water and dried for 10 h at 90 °C. The preparation of oxygen nanobubble modified zeolite (ONMZ) and soil (ONMS) followed a modified method based on exposure to oxygen supersaturating ambient conditions (Pan et al., 2016). Briefly, the materials (zeolite or soil) were placed into a pressure-resistant and airtight container. A vacuum was created to hold pressure to −0.08 to −0.1 MPa for 2 h to remove gas from the micropores of zeolite and soil. Thereafter, pure O_2 (99.99%) was pumped into the container and held at a pressure of 0.12 to 0.15 MPa for 4 h to load the O_2. The oxygen nanobubble loading process, including the creation of the vacuum, was repeated three times to achieve supersaturation of O_2 in the particle micropores.

2.2. Nanobubble analysis

Prior to the column experiment, the release potential of oxygen nanobubbles into water from the modified solid particles was tested via a flask experiment. Twenty grams of the oxygen nanobubble modified zeolite or soil was put into 250 mL flasks with 200 mL deionized water and sealed by gas-permeable sealing film (0.3 μm). Controls consisted of flasks of 250 mL filled with 200 mL of deionized water. Each control and treatment flask experiment was conducted in