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Fabrication of novel oxygen-releasing alginate beads as an efficient oxygen carrier for the enhancement of aerobic bioremediation of 1,4-dioxane contaminated groundwater

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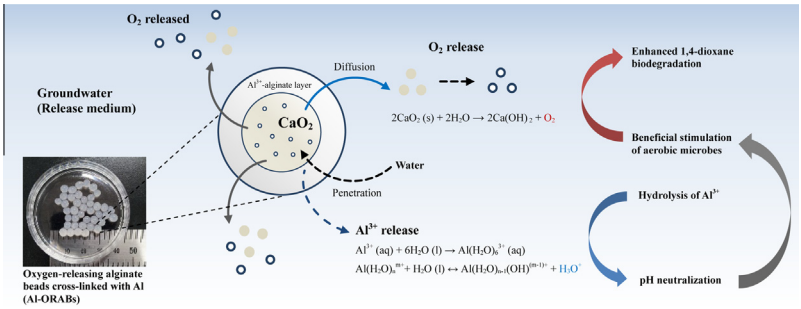
HIGHLIGHTS

- Novel oxygen-releasing alginate beads (ORABs) were newly fabricated.
- The oxygen-releasing properties of ORABs were tested in real groundwater conditions.
- The size and valence of cross-linking ions greatly affected the properties of ORABs.
- A synergistic effect on 1,4-dioxane biodegradation was observed only with ORABs.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxygen-releasing alginate beads (ORABs), a new concept of oxygen-releasing compounds (ORCs) designed to overcome some limitations regarding the fast oxygen release rate and the high pH equilibrium of ORCs, were fabricated to promote the stimulation of aerobic biodegradation in anaerobic groundwater. Slow oxygen-releasing rate and maintenance of constant pH were achieved by changing the parameters (ionic radius and valence) related to the cross-linking ions composing ORABs, and the best results were obtained for ORABs cross-linked with Al (Al-ORABs). Furthermore, the mechanism of the improved aerobic biodegradation using Al-ORABs under oxygen-limiting groundwater conditions was elucidated in batch and column studies with 1,4-dioxane and *Mycobacterium* sp. PH-06 as a model contaminant and aerobic microbes, respectively. Maximum 1,4-dioxane degradations of 99% and 68.1% were achieved when Al-ORABs were applied in batch and column conditions, respectively, whereas 34.3% and 18% of 1,4-dioxane were degraded without Al-ORABs in batch and column conditions, respectively.

1. Introduction

Contamination of groundwater due to hazardous and toxic pollutants is one of the major problems throughout the industrialized world today. Various conventional remediation technologies (e.g., pump and treat, air sparging, bioremediation, chemical oxidation and phytoremediation) have been used to remediate contaminated groundwater (Mackay and Cherry, 1989; Brunsting and McBean, 2014; Li et al., 2010; Liang et al., 2011; Vangronsveld et al., 2009). Among these technologies, bioremediation has emerged as an inexpensive and environmentally friendly remediation strategy (Li et al., 2010). However, the low concentration of dissolved oxygen (DO) in groundwater (below 3 mg/L) could significantly reduce the efficiency of intrinsic bioremediation. Moreover, the negative impacts of severe DO deficiency that frequently arise from

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pollutants or oxygen sinks (i.e., the dissolved iron and others waiting to be oxidized) in groundwater on bioremediation using aerobic microorganisms were reported in several studies (Chapman et al., 1997; Wilson et al., 2002).

To solve the anoxia in groundwater, oxygen-releasing compounds (ORCs), such as CaO_2, MgO_2, or Na_2CO_3, have been applied because they can quickly release oxygen upon contact with water, thereby resulting in a high DO concentration to effectively allow aerobic microbes to flourish and naturally enhance *in-situ* biodegradation (Landmeyer et al., 2001; Kao et al., 2003). In comparison with the mentioned ORCs, calcium peroxide (CaO_2), which exhibits continuous and long-lasting oxygen-releasing properties, has been applied in sites suffering from anoxia, such as soil, groundwater, and lakes to supply oxygen through the following reaction (Kao et al., 2003; Cassidy and Irvine, 1999; Nykänen et al., 2012):

$$2CaO_2 + 2H_2O \rightarrow O_2 + 2Ca(OH)_2 \quad (1)$$

The study of Cassidy and Irvine (1999) reported that a large amount of calcium peroxide could maintain its oxygen-releasing capacity over a period of days to weeks due to its low solubility. However, application of calcium peroxide to the groundwater could exhibit several limitations: generation of insoluble products of $Ca(OH)_2$ and increasing pH levels of surrounding solution (ranging from 10–12), which would exceed the buffering capacity in the immediate area of application and might consequently have negative effects on indigenous microbes (Kao et al., 2003). Therefore, recent studies have used a phosphate buffer, such as K_2HPO_4 or KH_2PO_4 (Yeh et al., 2010), or an organic acid, including citric acid (Lin et al., 2012), to keep the pH in the optimum range of 5–8. However, these pH buffers require additional costs and can affect the rate of oxygen release. Furthermore, the rapid oxygen-releasing rate of calcium peroxide might lead to bubbling off during the early stage of the releasing process caused by exceeding the solubility limit of groundwater. This "bubble off" could reduce the biologically available oxygen. Although those problems are important factors that could reduce the efficiency of field-scale groundwater remediation, they have been largely ignored.

To overcome the above-mentioned problems associated with the pH increase and the fast release kinetics, in this study, the encapsulation of calcium peroxide within alginate beads was newly proposed with a type of cross-linking ion as a variable to further improve the groundwater remediating performance. Alginate is a natural linear copolymer consisting of α-L-guluronic acid (G) and β-D-mannuronic acid (M). Alginate bead formation has been reported to be generally achieved by a gelling process between alginate and cross-linking ions (i.e., calcium and barium), and these alginate beads have a long history of use in many applications which fall into three broad categories: (i) biosorbent (Pandey et al., 2003; Papageorgiou et al., 2006; Mata et al., 2009), (ii) controlled release technology (CRT) (Anal and Stevens, 2005; Finotelli et al., 2010; Song et al., 2012), and (iii) encapsulation technique (Kim et al., 2010; Bezbaruah et al., 2011; Durante et al., 2012).

The objectives of this study were to fabricate the calcium peroxide-encapsulated alginate beads, named oxygen-releasing alginate beads (ORABs), to investigate the effects of various cross-linking ions (Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, and Al^{3+}) on the oxygen-releasing properties of ORABs, such as the efficiency, rate, and final pH equilibrium, and finally to estimate the performance of ORABs as an oxygen carrier for aerobic microbes (*Mycrobacterium* sp. PH-06) in both the batch and column scales to achieve enhanced 1,4-dioxane biodegradation. Herein, 1,4-dioxane, which is a probable human carcinogen and is found in groundwater, was chosen as the model contaminant (Zenker et al., 2003).

2. Methods

2.1. Materials

Sodium alginate, calcium chloride ($CaCl_2{\cdot}2H_2O$, >99%), ferric chloride ($FeCl_3{\cdot}6H_2O$, >99%), aluminium chloride ($AlCl_3{\cdot}6H_2O$, >99%), copper chloride ($CuCl_2{\cdot}2H_2O$, >99%), zinc chloride ($ZnCl_2$, >99%), calcium peroxide (CaO_2, >99%), and 1,4-dioxane were supplied by Sigma–Aldrich. All chemical reagents were of analytical grade and used without further purification. Ultrapure water obtained from a water purification system (Millipore, France) with a specific resistivity of >18 MΩ cm was used in all trials. Deoxygenated, deionized (DO/DI) water was prepared by purging with high-purity N_2 for 1 h.

2.2. Preparation of oxygen-releasing alginate beads (ORABs)

The preparation of oxygen-releasing alginate beads was performed according to a previous study with small modifications (Hackel et al., 1975). Briefly, calcium peroxide was added to a homogenous solution of sodium alginate in water (2% w/v) and mixed. This suspension was dropped into each stirred solution containing $CaCl_2$, $CuCl_2$, $ZnCl_2$, $FeCl_3$, and $AlCl_3$, each at a concentration of 50 mM, by a peristaltic pump (Masterflex L/S model 7519-25, Cole-Parmer Instrument Company) at a speed of 0.2 ml/min. The spherical beads were obtained and allowed to harden for 1–2 h at room temperature and then finally washed with distilled water several times. Thereafter, these alginate beads cross-linked with Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, and Al^{3+} were denoted as Ca-ORABs, Cu-ORABs, Zn-ORABs, Fe-ORABs, and Al-ORABs, respectively.

In this study, ORABs were maintained and applied in the swollen state. Note that a small amount of leftover CaO_2 (non-encapsulated) was present in the alginate solution due to aggregation caused by the reaction between CaO_2 and alginate. On average, approximately 0.013 g of CaO_2 was incorporated into 50 beads through all of the experimental sets in our study. ORABs obtained were characterized using scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX, JEOL JSM-7401F) after air-drying.

2.3. Evaluation of the oxygen-releasing properties of ORABs

Herein, natural groundwater collected from rural areas in Korea was used throughout all of the experiments to mimic the environmental conditions.

The oxygen-releasing properties of ORABs were investigated using custom-made 100 mL glass reactors which have an additional hole for insertion of a probe. Fifty ORABs made from different cross-linking ions and a corresponding amount of CaO_2 powder (0.013 g) were added into each glass reactor, and groundwater was then filled without headspace into the reactors. DO and pH probes were inserted through the top and the right side of batch reactor, respectively. The pH and DO of groundwater in the batch reactor were measured via an automatic data collection system composed of a computer (Samsung Co., Korea) connected to a pH meter (Orion model 720A, Thermo Scientific) and a dissolved oxygen meters (Orion 3 Star Portable DO meter, Thermo Fisher Scientific). The time interval of the data acquisition was once every 2 h for one week. The reactor was maintained as a closed system during the entire experimental process.

2.4. Batch and column studies on 1,4-dioxane biodegradation using ORABs and aerobic microbes

To evaluate the effects of ORABs on the 1,4-dioxane degrading activity of microbes, an effective 1,4-dioxane degrading bacterial