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Application of ozone micro-nano-bubbles to groundwater remediation

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HIGHLIGHTS

- This paper presents the high efficiency of gas supply and mass transfer in water using MNBs.
- The ozone MNBs technique was applied for in situ groundwater remediation of an organics-contaminated site.
- Ozone MNBs show considerable advantages in contaminant cleanup and time efficiency.
- Ozone MNBs potentially represent an innovative technology for in situ remediation of organics-contaminated groundwater.

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ABSTRACT

Ozone is widely used for water treatment because of its strong oxidation ability. However, the efficiency of ozone in groundwater remediation is limited because of its relatively low solubility and rapid decomposition in the aqueous phase. Methods for increasing the stability of ozone within the subsurface are drawing increasing attention. Micro-nano-bubbles (MNBs), with diameters ranging from tens of nanometres to tens of micrometres, present rapid mass transfer rates, persist for a relatively long time in water, and transport with groundwater flow, which significantly improve gas concentration and provide a continuous gas supply. Therefore, MNBs show a considerable potential for application in groundwater remediation. In this study, the characteristics of ozone MNBs were examined, including their size distribution, bubble quantity, and zeta potential. The mass transfer rate of ozone MNBs was experimentally investigated. Ozone MNBs were then used to treat organics-contaminated water, and they showed remarkable cleanup efficiency. Column tests were also conducted to study the efficiency of ozone MNBs for organics-contaminated groundwater remediation. Based on the laboratory tests, field monitoring was conducted on a trichloroethylene (TCE)-contaminated site. The results showed that ozone MNBs can greatly improve remediation efficiency and represent an innovative technology for in situ remediation of organics-contaminated groundwater.

1. Introduction

Soil and groundwater contamination are major environmental problems; thus, numerous technologies have been developed to remediate such contaminants [1]. In situ chemical oxidation is one method commonly used to remediate polluted sites. Oxidants such as Fenton's reagent, peroxydisulfate, and permanganate show remarkable efficiency in the oxidation of organic contaminants and are generally used for site remediation [2]. However, the efficiency of the Fenton process is strongly dependent on the pH [3]. A considerable amount of oxygen is formed during the Fenton process, which may cause the blockage of pore channels and can limit the area affected by Fenton's reagent [2]. Peroxydisulfate tends to be relatively stable at ambient temperatures (~20 °C) and must be activated to be used in site remediation [4]. A large amount of sulfate is produced as a by-product [5], however, which results in secondary contamination. In situ chemical oxidation with permanganate produces MnO_2, which also may result in pore plugging and can lower the remediation efficiency [6].

Ozone is widely used for oxidation of pharmaceuticals in drinking water [7,8]. Because of its strong oxidation ability, ozone also has high potential in the treatment of wastewater [9,10]. Hydrogen peroxide can be used to accelerate the oxidation of contaminants by ozone [11,12]. However, the efficiency of ozone oxidation is limited by the rapid decomposition rate of dissolved ozone in water, which is much faster than that in the gas phase. Methods used to prolong

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the reactivity of aqueous-phase ozone are thus urgently needed, and some stabilisers have been used to increase the stability of ozone in groundwater [13].

Micro-nano-bubbles (MNBs) are tiny bubbles with diameters ranging from tens of nanometres to several tens of micrometres [14,15]. Owing to their small diameter, MNBs present high internal pressures and rapid mass transfer rates, which can significantly improve gas solubility. Compared with normal bubbles, MNBs have lower rising velocity in the liquid phase. Nano-bubbles can persist in water for long periods [16,17]. Those with radii of 150–200 nm have been shown to remain stable for two weeks [18], and clusters of nano-bubbles could further increase their stability [19]. Owing to their long existence in water, MNBs can migrate with the water flow and provide continuous gas supply for the dissolution phase. In our previous work, the properties and mass transfer efficiency of MNBs were studied [20–22]. One remarkable proven characteristic of MNBs is that their large specific surface area leads to a considerable capacity for pollutant adsorption on the bubble surface [23]. In recent years, the potential application of MNBs in environmental engineering has become a research focus [24–27]. Such studies include the use of MNBs in surface water treatment owing to their special characteristics of large specific surface area, negatively charged surface, and high mass transfer efficiency [28–30]. Although the MNB technique has remarkable advantages in environmental cleanup, its application to groundwater remediation has not been systematically investigated thus far [20–22].

The purpose of this study is to investigate the feasibility and efficiency of applying ozone MNBs to groundwater remediation. The physic-chemical characteristics of ozone MNBs, such as the size distribution and zeta potential, were studied experimentally, and the mass transfer behaviour was investigated by model tests. The remediation efficiency for contaminated water and groundwater was examined under laboratory conditions using methyl orange as a representative organic contaminant. A field test on a trichloroethylene (TCE)-contaminated site was also conducted to study the efficiency of in situ remediation by ozone MNBs.

2. Methods and materials

2.1. Experimental facilities

2.1.1. Micro-nano-bubble generator

The MNBs used in this research were produced by a spiral liquid flow-type [31] MNB generator (Eco-20, Taikohgiken Ltd., Nishi-ku, Kumamoto, Japan). Water was pumped into the generator, and a maelstrom-like cavity was formed by the high-speed rotation of the liquid flow. Gas was injected into the generator and was reduced to MNBs by the centrifugation effect. The MNB size is affected by the injection rates of water and gas. During the generation of MNBs, a generator was placed inside the water, and a pipe was used to inject gas. In this research, the flow rates of ozone and water were 4 L/min and 270 L/min, respectively.

2.1.2. Millimetre-bubble generation facility

A millimetre-bubble generation facility was used to generate millimetre bubbles for ozone mass transfer tests and treatment efficiency tests. Ozone was generated by the ozone generator and was injected into the water by the air compressor through a pipe having a diameter of 7 mm. A gas flow meter was used to control the flow rate of the ozone.

2.1.3. Ozone generators

Two ozone generators were used in this research. Both are based on the corona discharge method, and oxygen was transformed into ozone by high-voltage discharge. In this study, the output rate of gas was 4 L/min. The generator (RQ-30, Ruiqing Ltd., Jinan, Shandong, China) which was used to produce ozone for all laboratory tests including size distribution, gas mass transfer, and treatment of methyl orange; the supplied ozone had a concentration of approximately 50 mg/L. As a result, the mass percentages of ozone and oxygen in the supplied gas were 3.5% and 96.5%, respectively. A second generator (S4-R02, Ecodesign Inc., Ogawa, Saitama, Japan), which was used to produce ozone in the field tests, supplied ozone with a concentration of approximately 100 mg/L. The mass percentages of ozone and oxygen in the generated gas were 6.8% and 93.2%, respectively.

2.1.4. Size distribution analyser

The size distribution and number of the ozone MNBs were measured by a nanoparticle tracking analyser (NanoSight LM-10, Malvern Instruments Ltd., Malvern, Worcestershire, UK). For nanoparticles in liquids, the rate of Brownian motion was not affected by the particle density and was related only to the viscosity and temperature. MNBs in liquid were illuminated by a laser, and the analyser used a charge-coupled device to capture the MNB movement. The nanoparticle size was calculated according to the rate of nanoparticle movement by using the Stokes–Einstein equation. The measurement range for the size distribution was from 10 to 1000 nm, and the measurement range for the number of MNBs was 10^6–10^9 bubbles per mL.

2.1.5. Zeta potential analyser

The zeta potential of ozone MNBs in solution was measured by using a zeta potential analyser (Delsa-nano C, Beckman Coulter Inc., Brea, California, US). The interfacial charge characteristics of the ozone MNBs were measured by calculating the electrophoretic mobility. The measurement range of the zeta potential was from −200 mV to +200 mV.

2.1.6. Dissolved ozone monitor

The concentration of dissolved ozone in water was measured by a dissolved ozone monitor (Q45H/64, Analytical Technology Inc., Collegeville, Pennsylvania, US). The monitor used a polarographic membrane sensor to accurately determine the concentration of the dissolved ozone. The display range of the monitor was 0–20.00 mg/L, and the accuracy was ±0.1 mg/L.

2.1.7. UV spectrophotometer

The concentration of methyl orange was measured by UV spectrophotometry (DR5000, Hach, Loveland, Colorado, US). Based on the Beer-Lambert law, at a wavelength of 462 nm, the intensity of light absorbed by the methyl orange solution was measured to determine the concentration of methyl orange.

2.1.8. Gas chromatograph

The concentration of TCE was measured by a gas chromatograph (GC-310C, SRI Instruments, Torrance, California, US). Samples were heated in a water bath, and the TCE in the headspace was measured to determine the TCE concentration in the samples. Each of the groundwater samples was measured at least twice, and the deviation was less than 0.005 mg/L.

2.2. Setup of laboratory tests

2.2.1. Size distribution and zeta potential analysis tests

A Perspex tank with internal dimensions of 0.8 m (length) × 0.2 m (height) × 0.2 m (width) was used to perform the experiments. The MNB generator was placed inside 20 L of deionised water to generate ozone MNBs under 20 °C. Ozone MNBs were generated for 30 min, and water samples were then taken to measure the MNB size distribution and quantity over time