Heterogeneous catalytic ozonation of benzothiazole aqueous solution promoted by volcanic sand

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Abstract

This paper presents experimental results on the catalytic effect of volcanic sands on benzothiazole ozonation. Experiments were assessed at laboratory scale, in a differential circular flow reactor composed of a volcanic sand fixed bed column of 19 cm³ and a 1 dm³ storage tank, operated in batch mode at 20 °C and pH 2–7. Experimental results show that ozone self-decomposition is enhanced by the presence of volcanic sand at all pH. At pH > pHPEC, the increase in aqueous ozone decay could be related to ozone interaction with strong Lewis acid on metal oxide surface sites of the volcanic sand. Ozone self-decomposition reactions occurring on the volcanic sand are less affected by the presence of radical scavengers. Benzothiazole removal by ozonation is also enhanced by the presence of volcanic sand. Moreover, the inhibitory effect of free radical scavengers is also impaired by volcanic sand, suggesting that strong Lewis acid surface sites play a key role on the reaction mechanism.

Keywords: Benzothiazole; Catalytic ozonation; Ozone; Volcanic sand

1. Introduction

Benzothiazoles are organic compounds posing environmental concern, when released into watercourses. These contaminants are frequently present in wastewater from rubber related applications, and could be found in surface and underground water bodies, in soils, and estuarine sediments, causing significant environmental impact [1,2]. Benzothiazoles inhibit micro-organisms activity in conventional biological wastewater treatment systems and most of them are not readily biodegradable [3,4]. Moreover, these compounds can be adsorbed into cell membranes, leading to bioaccumulation and biomagnification [3,5].

Advanced oxidation processes, such as, H₂O₂/UV, photoassisted Fenton, and ozone have been used to oxidise benzothiazole compounds [6–8]. However, the presence of radical scavengers such as carbonates, bicarbonates, and natural organic matter, normally present in water reduce BT removal efficiency in such homogeneous processes, due to the inhibition of radical chain reactions [8].

Recently, ozone combined with activated carbon has been used to oxidise benzothiazole compounds [9–11]. Such heterogeneous treatment has been shown to reduce the inhibition effect produced by radical scavengers. Both homogeneous and heterogeneous reactions are present in combined ozonation/activated carbon, where chemical surface properties play an important role in the reaction mechanism. The generation of secondary radicals from ozone decomposition is promoted by the high electron density of carbon basal planes in activated carbon with basic characteristic, the presence of oxygenated surface groups, and mineral matter, specially iron hydr(oxides) on activated carbon surface, thus increasing benzothiazole removal rate [10,11]. However, the high cost of activated carbon impairs its application at industrial scale, and alternative catalysts should be found.

In this respect, low cost natural solid minerals, such as sand, soils, zeolites, alumina oxide, and goethite, have been recently used in the heterogeneous ozonation of toxic organic pollutants [12–19].

Within this context, this article presents experimental results on benzothiazole (BT) degradation by catalytic heterogeneous ozonation using volcanic sand. Results on ozone self-decomposition in the presence of volcanic sand are also presented here. In particular, the effect of radical scavengers, volcanic sand dosage, and pH were assessed. A full understand-
ing of this aspect is required in order to design a cost-effective treatment technology, based on catalytic ozonation promoted by volcanic sand.

2. Experimental methods

2.1. Experimental system

Experiments were carried out at 20 °C, in a differential circular flow reactor composed of a volcanic sand fixed bed column (19 cm³) and a 1 dm³ storage tank, operated in batch mode. Liquid recirculation using a pump at 1 dm³ min⁻¹ and mechanical stirring at 240 rpm provided mixing. Ozone was produced from dry pure oxygen using an AZCOZON ozone generator rated at 5 g O₃ h⁻¹, and pH was adjusted to 2 and 7 using phosphoric acid or potassium phosphate buffer. Typically, O₂/O₃ gas mixture (120 dm³ h⁻¹) was fed into the reactor containing 1 dm³ benzothiazole-free aqueous solution, for about 30 min until dissolved ozone saturation was reached. Then, a set amount of 7 mM benzothiazole stock solution was injected into the reactor and liquid recirculation over the fixed bed column charged with the volcanic sand was started. Samples were quickly drawn into cylinders containing Na₂SO₃ solution in order to stop ozonation reactions for BT detection, or into syringes containing 2 cm³ Indigo solution for aqueous ozone determination. In the case of adsorption experiments, ozone was not supplied into the system. When only O₃ treatment was applied, volcanic sand was not used.

2.2. Materials and analytical methods

Volcanic sand was used in this study, collected from the Chillán volcano, Bio-Bío region (Chile). Volcanic sand was sieved and then washed with de-ionised water, oven-dried at 105 °C for 24 h, and stored in a dessicator until its use. Volcanic sand was characterised using standard techniques, as follows: macroscopic pellets 0.84–1.0 mm mean diameter, ash content 99.7% (on dry weight basis), and bulk density 2.5 g cm⁻³. Results obtained by nitrogen adsorption isotherms showed that the volcanic sand used in this study is a non-porous material. Data on surface elements as detected by X-ray fluorescence are listed in Table 1. The pH value required by the volcanic sand to give zero net surface charge (pHPZC) was 6.8, following procedures described by Stumm and Morgan [20].

BT was provided by Fluka (96% purity). Terti-butyl alcohol (t-BuOH) and acetic acid (HAc) (Merck, >99% purity) were used here as radical scavengers, since both react very rapidly with hydroxyl radicals (k⁻OH,t-BuOH = 5 × 10⁸ M⁻¹ s⁻¹, k⁻OH,HAc = 1.7 × 10⁷ M⁻¹ s⁻¹) but very slowly with ozone (k₀₂,t-BuOH = 0.03 M⁻¹ s⁻¹, k₀₂,HAc = < 3 × 10⁻⁵ M⁻¹ s⁻¹) [21–23]. All solutions were prepared with ultrapure water obtained from an EASYpure® II RF system. Ozone concentrations in gas and liquid phases were monitored by UV spectrophotometry (Bausch & Lomb TU-1810 S), using flow cells at 253.7 nm and 258 nm, respectively. Data were registered on-line as a function of time and processed using UV Win 5.0 software. When BT was present, ozone gas was continuously bubbled through the liquid storage tank; dissolved ozone concentration was measured by the Indigo method [24]. BT and oxidation by-products were determined by high-pressure liquid chromatography (HPLC) (Merck-Hitachi, L7100) [8].

3. Results and discussion

3.1. Ozone decomposition in aqueous solution

3.1.1. Effect of radical scavengers on aqueous ozone decomposition in the presence of volcanic sand

The influence of radical scavengers on the ozone decay rate, in the presence and absence of volcanic sand, was assessed using acetic acid at acid (Fig. 1) and basic pH (Fig. 2), respectively. Ozone self-decomposition in the presence of glass wool was also evaluated. Glass wool was used instead of volcanic sand to assess possible ozone self-decomposition in the absence of volcanic sand. Acetic acid (HAc) features a pKₐ = 4.75 and is well known as hydroxyl radical scavenger inhibiting the radical chain mechanism (k⁻OH,HAc = 1.7 × 10⁷ M⁻¹ s⁻¹) [21], but reacts slowly with ozone (k₀₂,HAc = < 3 × 10⁻⁵ M⁻¹ s⁻¹) [22]. At basic pH, acetic acid is dissociated forming acetate ions (Ac⁻). Acetate

![Fig. 1](image-url)