



Catalytic ozonation for the removal of organic contaminants in water on alumina



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ABSTRACT

This study aims to understand the efficiency and role of adsorption of common water pollutants (volatile organic chemicals (VOCs), pharmaceuticals and carboxylic acids) in the catalytic ozonation process on γ -alumina. In order to understand the catalytic processes occurring, the effects of pH, hydroxyl radical scavengers, humic acids and phosphates on the efficiency of catalytic ozonation on alumina were studied. The results revealed that catalytic ozonation on alumina could substantially enhance the removal of ibuprofen and acetic acid when compared with ozonation alone. However, alumina did not catalyse the removal of VOCs. The adsorption of pollutants plays a key role in the effectiveness of this process. The presence of hydroxyl radical scavengers, phosphates and humic acids had a significant effect on the removal of pollutants on alumina. It is therefore suggested that catalytic ozonation of organic pollutants on alumina proceeds via a radical mechanism that involves reactions of hydroxyl radicals with pollutants adsorbed on the surface of alumina.

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1. Introduction

Heterogeneous catalytic ozonation is one of the oxidation techniques used to improve the efficiency of ozonation process. It has been successfully applied in the degradation of organic compounds such as aromatic hydrocarbons, pharmaceuticals, pesticides, dyes, and organic acids etc. Many materials such as activated carbons [1], Al_2O_3 [2] and TiO_2 [3] were utilised as heterogeneous catalysts. Despite years of research, the mechanisms of catalytic ozonation are largely unknown and there are many controversies in this area [4,5]. Therefore, it is indeed important to understand the process of catalytic ozonation in order to apply this technique on an industrial scale.

Ozonation on alumina oxides has been studied for several years with different types of pollutants. However, there are several, often contradictory, views on the catalytic activity of alumina. Some reports indicate that alumina does not catalyse the decomposition of aqueous ozone [6]. It is important to mention here that lack of ozone decomposition does not indicate the lack of catalytic activity [2]. In contrast, other reports indicated that alumina decomposes aqueous ozone leading to the production of hydroxyl radicals.

The surface hydroxyl groups on alumina were identified as active catalytic sites of ozone decomposition [7–9]. Qi et al. [10] also confirmed that alumina promotes the generation of hydroxyl radicals but the group claimed that surface hydroxyl groups of γ -alumina do not interact with aqueous ozone. It has been recently highlighted by Nawrocki et al. [11] that alkaline impurities present in alumina oxides can play an important role in ozone decomposition and hydroxyl radicals formation. This is because their desorption into the bulk solution results in pH changes of the aqueous solution, which then affect stability of molecular ozone in water. Therefore it is indeed important to monitor pH during the catalytic ozonation process.

The role of adsorption of pollutants on alumina is also not well understood [5]. Some reports suggested that adsorption plays an important role in the catalytic process [7,12,13]. Others indicated that adsorption could have a detrimental effect on the catalytic activity of alumina [14]. Therefore it is important to study catalytic ozonation on alumina in the presence of different types of pollutants with different affinity towards alumina's active surface sites.

This paper aims to understand mechanisms of ozonation on alumina in the presence of different types of pollutants. Among them are: volatile organic chemicals (VOCs), pharmaceuticals and carboxylic acids. VOCs are regulated pollutants that have been detected in drinking water [15]. Chlorinated aromatic compounds

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are highly toxic, widely used and are known to be highly resistant to ozonation [16]. Pharmaceuticals are emerging and still unregulated pollutants. Although they are present in trace quantities in the aquatic environment, long term exposure to these pollutants poses a potential risk to humans and aquatic life. Pharmaceuticals have also been detected in drinking water. Carboxylic acids are refractory to direct ozone attack and are known to be stable ozonation by-products of other organic pollutants [17]. The selection of acetic acid as target pollutant may further help to understand whether catalytic processes on alumina involve a radical mechanism or direct molecular ozone reactions. This is because acetic acid is highly resistant to direct ozone attack. In order to verify the catalytic processes occurring on alumina, the effect of initial pH, pH changes during the process and the effect of hydroxyl radical scavengers, humic acids and phosphates have also been investigated.

2. Experimental

2.1. Materials and reagents

γ -Alumina used in this work was supplied by Alcoa Inc, USA. Ibuprofen, humic acid, VOCs and acetic acid were obtained from Sigma-Aldrich. All chemicals were of analytical grade and were used without further purification.

2.2. Ozonation experiments

The ozonation experiments were conducted in a semi-continuous mode at room temperature (20°C) as shown in Fig. S1 (column length, 70 cm; width, 31 mm; catalyst bed height, 5 cm). Aqueous solution (490 mL) spiked with organic pollutants (ibuprofen, 15 mg/L; acetic acid, 15 mg/L; or cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, 0.5 ± 0.1 mg/L) was poured to the column containing 5.0 g of

alumina, and was recirculated at a flow rate of 15 mL/min over the period of 30 min. Ozone was produced from pure oxygen by AZCO HTU-5000GE-120 ozone generator and was continuously bubbled through the column by using a ceramic sparger at a flow rate of 0.1 mL/min (in the case of VOCs ozonation) or 0.5 mL/min (in the case of acetic acid and ibuprofen ozonation). Samples were collected at 5 min intervals and residual ozone was removed by quenching with 0.025 M Na₂SO₃. All the samples were filtered (PTFE 0.45 μ m syringe filter) prior to the analysis.

Possible loss of VOCs due to volatilization was also determined. A saturated solution of VOCs was used in the ozonation experiments and was prepared by directly spiking VOCs to a flask containing 1 L of ultrapure water [18].

Ozonation experiments in the presence of humic acid, tertiary butyl alcohol (TBA), and phosphates were performed as described above by adding 7 mg/L of humic acid or phosphates, or 50 mg/L of TBA to the semi-continuous reactor following the above procedure. It is important to mention here that the humic acid removal experiments in ozonation and the catalytic ozonation processes have been performed without the addition of VOCs and ibuprofen.

For reuse performance experiments, 490 mL solution containing ibuprofen (15 mg/L) was added to a column containing 5 g of the catalyst. After every 30 min a fresh solution of pollutants was introduced in a semi-continuous reactor. The cycle was repeated 12 times.

2.3. Adsorption experiments

The adsorption experiments were performed in the semi-continuous reactor by adding 490 mL of saturated VOCs solution (cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, 0.5 ± 0.1 mg/L) or acetic acid (15 mg/L) or ibuprofen (15 mg/L) solutions to the semi-continuous column containing 5 g of catalyst. The solutions were recirculated for 30 min

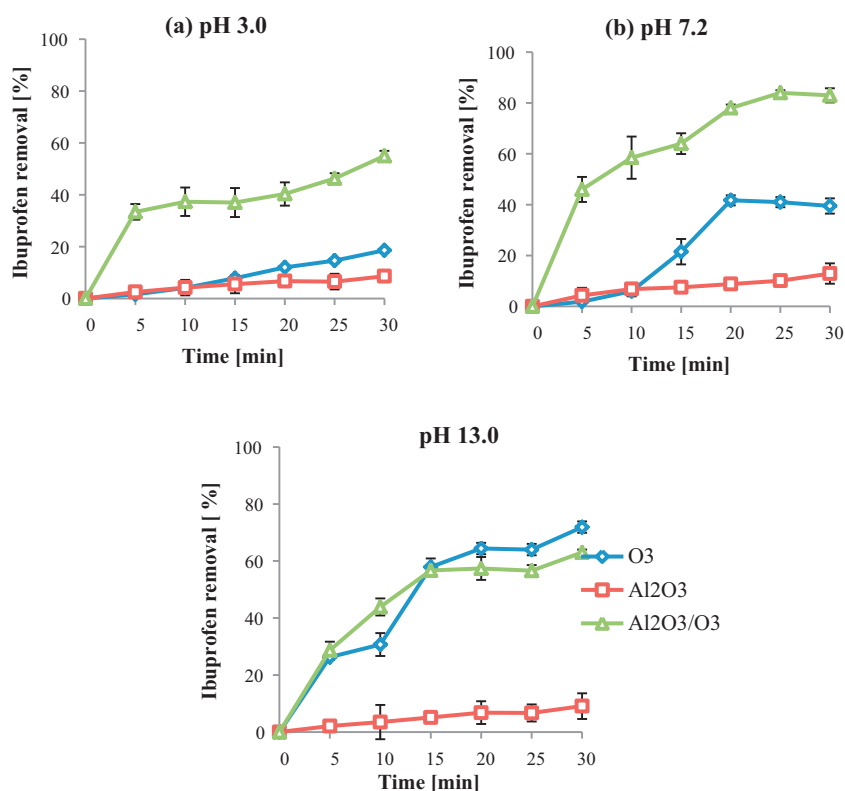


Fig. 1. Removal of ibuprofen by adsorption, ozonation alone and catalytic ozonation ($C_{0(\text{ibu})} = 15 \text{ mg/L}$; $O_3 = 0.5 \text{ mg/min}$; $T = 20^\circ\text{C}$; $\text{pH} = 3.0, 7.2 \text{ and } 13.0$; catalyst dose = 5.0 g; $V = 490 \text{ mL}$).

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