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Catalytic ozonation with γ-Al_2O_3 to enhance the degradation of refractory organics in water

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ABSTRACT

Nowadays, heterogeneous catalytic ozonation appears as a promising way to treat industrial wastewaters containing refractory pollutants, which resist to biological treatments. Several oxides and minerals have been used and their behavior is subject to controversy with particularly the role of Lewis acid sites and/or basic sites and the effect of salts. In this study, millimetric mesoporous γ-Al_2O_3 particles suitable for industrial processes were used for enhancing the ozonation efficiency of petrochemical effluents without pH adjustment. A phenol (2,4-dimethylphenol (2,4-DMP)) was first chosen as petrochemical refractory molecule to evaluate the influence of alumina in ozonation. Single ozonation and ozonation in presence of γ-Al_2O_3 led to the disappearance of 2,4-DMP in 25 min and a decrease in pH from 4.5 to 2.5. No adsorption of 2,4-DMP occurred on γ-Al_2O_3. Adding γ-Al_2O_3 in the process resulted in an increase of the 2,4–DMP oxidation level. Indeed, the total organic carbon (TOC) removal was 14% for a single ozonation and 46% for ozonation with γ-Al_2O_3. Similarly, chemical oxygen demand (COD) removal increases from 35 to 75%, respectively. Various oxidized by-products were produced during the degradation of 2,4-DMP, but after 5 h ozonation 90% of organic by-products were acetic acid > formic acid ≫ oxalic acid. Some of the carboxylic acids were adsorbed on γ-Al_2O_3. The use of radical scavengers (tert-butanol) highlighted the involvement of hydroxyl radicals during catalytic ozonation with γ-Al_2O_3 in contrary to single ozonation, which mainly involved direct ozone reaction. γ-Al_2O_3 is an amphoteric solid with Lewis acid $AlOH(H^+)$ sites and basicAl-OH sites. After ozonation the amount of basic sites decreased due to carboxylates adsorption, while the Lewis acid sites remained constant as evidenced by FTIR. Several ozonation runs with γ-Al_2O_3 reported a progressive decrease of its catalytic activity due to the cumulative sorption of carboxylates on the basic sites. After 80 h of ozonation, a calcination at 550 °C allowed to recover allAl-OH basic sites and the initial activity of γ-Al_2O_3. A synthetic petrochemical effluent containing various petrochemicals (phenol, acetic acid, naphtenic acid, pyrene, naphtalene) was then treated with γ-Al_2O_3 with and without NaCl. Sodium ions prevented carboxylates adsorption on γ-Al_2O_3 leading to a higher efficiency of γ-Al_2O_3 in presence of NaCl and allowed to decrease the toxicity of the petrochemical effluent.

1. Introduction

In recent years, many efforts on the advanced oxidation processes (AOPs) development have been done for wastewater treatment especially in industries to treat organic compounds resistant to biological treatments [1]. Among the AOPs, processes based on ozone appear as promising technologies for the removal

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of refractory compounds [2–7]. In aqueous media, O_3 can react directly with organic compounds and/or indirectly when O_3 is decomposed into free radicals, which have higher oxidizing rate than O_3 itself [2–4,8]. Consequently, favoring this second route allows to reach higher levels of toxic pollutant mineralization. The indirect reaction in single ozonation is influenced by the pH of the solution (high pH), the solution composition and the temperature, but it is limited to a certain extend of mineralization [3,8]. In this context, some studies have focused on heterogeneous catalytic ozonation in aqueous media since the early 2000s, due to the enhancement of the production of hydroxyl radicals with materials such as activated carbons, zeolites, oxides (CeO_2, TiO_2, MgO, Al_2O_3, MnO_2, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, ZrO_2,...) and the subsequent ozone economy [4,8–17]. However, all of these materials have never been studied in identical conditions, so it is difficult to compare their efficiency. An excellent review by Nawrocki and Kassprzyk-Hordern in 2010 reported the different materials and conditions used in catalytic ozonation in this last decade [8]. They report that the following order in term of better heterogeneous catalysts appears in certain conditions (ozonation of dinitrobenzene at pH 3): $Fe_2O_3 > Co_3O_4 > MoO_3 > CuO \sim NiO > Al_2O_3 > TiO_2 > Cr_2O_3 \sim MnO_2 \sim O_3$, which seems to follow the basicity strength of the oxides (Mn > Fe > Co > Ni > Cu > Zn) except for MnO_2. However, in some other studies MnO_2 was demonstrated as the more active catalyst, but leaching of some cations have been also observed, as well as for CuO. Some of these oxides need to be supported for industrial processes to avoid fine particles and the leaching of metal has to be avoided. In this review was also highlighted the wide controversy of mechanisms proposed in literature responsible for the increase of ozone activity in the presence of materials and especially the role of Lewis acid sites and/or basic sites, which remained a subject of debate. Catalytic ozonation appears as a highly suitable process for petrochemical wastewater treatments as ozone is especially active for refractory molecules of this industry such as aromatic molecules substituted with electron donor groups as alkyl-benzene (toluene, xylene, ethylbenzene), phenols (alkylphenols) and polyaromatic hydrocarbons (naphtalene, phenantrene, anthracene, ...).

It was previously shown that the catalytic activity of activated carbons in ozonation decreased after several runs by the loss of their basic sites and no regeneration was possible [5–7]. Inorganic catalysts should be preferred. Zeolites and oxides in ozonation for wastewater treatment provide many advantages: no chemicals to add, simplicity of use and high pollutant removal efficiency [15]. Concerning the zeolites in ozonation process for organic compounds removal, it seems that the reaction mechanisms are zeolite structures dependent [18]. Some studies revealed the adsorption capacity of pollutant and/or ozone into the micropores of zeolites, especially in ZSM-5 structure type, which does not confer any radical pathway but serve as reservoir of ozone and adsorbents of organic compounds [19–21]. Besides, it was also demonstrated that zeolites could catalyze ozone decomposition and enhance the generation of hydroxyl radicals ($HO^\bullet$) [11]. Indeed, it was recently reported that basic zeolites as LTA zeolite can enhance radicals generation by combining two pathways: the production of hydroxide ions during the cation-exchange of Na-zeolite with the protons of the solution and by the interaction of ozone with some hydroxyl groups present as defects in the material [18]. However, a decrease of the LTA catalytic activity was observed for a second run of phenol compounds ozonation due in part to the irreversibility of the cation-exchange [18]. Other porous materials especially γ-Al_2O_3 have been identified to generate free radicals from the interaction between their hydroxyl groups and ozone [20,22,23]. A study suggested that γ-Al_2O_3 combined to O_3 allowed an enhancement of $HO^\bullet$ radical via ${}^\bullet O_2^-$ and/or ${}^\bullet O_3^-$ radicals, resulting in a faster carboxylic acids removal than single ozonation [22]. Recently, Ikhlaq et al. [20] confirmed this hypothesis and pointed out also that $HO^\bullet$ radicals can combine with themselves to produce H_2O_2, depending on the pH of the solution. This was demonstrated after pH adjustment for pH higher than pH = 6.2. Another catalytic reaction mechanism with aluminum oxides was also proposed due to the ir capacity to adsorb ozone and to decompose it into free radicals by interacting with the hydroxyl groups of the materials [16,24]. Moreover, the catalytic effect of γ-Al_2O_3 was preserved after several ozonation runs, indicating no poisoning of the active sites for ozone decomposition [16]. However, the increase of the pollutant removal efficiency by heterogeneous ozonation with γ-Al_2O_3 was also attributed to the adsorption of ozonation by-products. On the one hand, pharmaceutical pollutant removal experiments were performed by alternating single ozonation and catalytic ozonation with γ-Al_2O_3 in order to observe the by-products adsorption capacity of γ-Al_2O_3. The authors explain that carboxylates could be adsorbed onto γ-Al_2O_3 when the solution pH is lower than the pH_{PZC} of the material [2]. On the other hand, 2,4-dimethylphenol (2,4-DMP) removal was performed by single ozonation in order to generate oxidized by-products and, then γ-Al_2O_3 was added to examine its adsorption ability [17]. These experiments clearly evidenced no adsorption of the oxidized by-products generated after 35 min of single ozonation, but an adsorption of the by-products generated after 3 h of single ozonation. Consequently, it appears that reaction mechanisms in aluminum oxides/ozone processes are by-products dependent and are still unclear, especially concerning γ-Al_2O_3 material. The adsorption of oxidized by-products and the role of Lewis acid sites and basic sites of γ-Al_2O_3 are subject to large controversy.

In the present study, a commercial γ-Al_2O_3 with millimetric particles, suitable for industrial ozonation processes, was investigated for 2,4-DMP degradation in the presence of ozone, without adding any chemical, so without pH adjustment. Substituted phenols, such as 2,4-DMP are highly toxic compounds and are typical pollutants found in petrochemical wastewater [25,26]. The kinetics of pollutant degradation was followed, as well as the formation of the oxidized by-products by chromatography, by total organic carbon (TOC) and chemical oxygen demand (COD) measurements. Adsorption isotherms of 2,4-DMP and of the final oxidized by-products (carboxylic acids) on γ-Al_2O_3 were performed to clarify the adsorption capacity of γ-Al_2O_3. FTIR studies were performed to examine the acid and basic sites of the material before and after ozonation. The reusability of γ-Al_2O_3 was investigated by performing several ozonation runs of the pollutant. γ-Al_2O_3 was also used in the ozonation of a complex synthetic petrochemical effluent (phenol, acetic acid, naphtenic acid, pyrene, naphtalene) to confirm the observations obtained with 2,4-DMP. Toxicity tests were performed to evaluate the efficiency of γ-Al_2O_3 in ozonation.

2. Experimental procedure

2.1. Materials

Acetonitrile (ACN) and water (H_2O) for high performance liquid chromatography (HPLC) analyzes are HPLC grade (Sigma Aldrich). γ-Al_2O_3 was purchased from Alpha Degussa. All other chemicals are high grade commercially available from Sigma Aldrich: 2,4-dimethylphenol (2,4-DMP) (98%), acetic acid, formic acid, oxalic acid, phenol, pyrene, naphtalene and *tert*-butanol (*t*-BuOH). Naphtenic acid was purchased from Fluka. 2,4-DMP and carboxylic acids solutions were prepared using Millipore Milli-Q water.

2.2. Inorganic materials characterization

X-ray diffraction (XRD) pattern of the material was performed using a Bruker D8 Advance diffractometer with a Bragg-Brentano

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