



## Role of surface hydroxyl groups of acid-treated natural zeolite on the heterogeneous catalytic ozonation of methylene blue contaminated waters

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### HIGHLIGHTS

- ▶ Acid treatment enhances catalytic ozonation activity of natural zeolite.
- ▶ Acid treatment of natural zeolite decreased the  $\text{pH}_{\text{PZC}}$ .
- ▶ Zeolite acidic nature was elucidated by IR spectroscopy of pyridine adsorption.
- ▶ Brønsted acidity increases significantly on acid-treated zeolite.
- ▶ Brønsted acid sites are claimed to be the main active centres for catalytic ozonation.

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### ABSTRACT

The effect of surface properties of zeolites on the kinetics of heterogeneous catalytic ozonation of organic pollutants is still under discussion. In this work, the influence of hydroxyl groups ( $\text{Z-OH}_2^+$ ,  $\text{Z-OH}$ ,  $\text{Z-O}^-$ ) of acid-treated natural zeolite on the catalytic ozonation of methylene blue (MB) contaminated waters is analysed. A Chilean natural zeolite was acid-treated using HCl (2.44 M). Acid-treated zeolite was chemically and physically characterised by  $\text{N}_2$  adsorption at 77 K, X-ray fluorescence, acidimetric–alkalimetric titration, and by  $\text{NH}_3$  and  $\text{CO}_2$  temperature-programmed desorption methods. Fourier transform infrared spectroscopy of pyridine adsorption was used to elucidate the nature and strength of acidic sites resulting from the acid treatment of natural zeolite. Experimental results obtained here are kinetically modelled using a set of two homogeneous and three heterogeneous surface reactions. Moreover, the quantitative effects of single ozonation, adsorption and coupled treatment on MB removal rate, together with the effect of pH and the presence of radical scavengers are analysed. Brønsted acid sites in the form of proton-donating OH groups ( $\text{Z-OH}$ ) of acid-treated zeolite are claimed here to play an important role on the catalytic ozonation of MB in water, acting as active sites for the adsorption of reacting species. The higher catalytic activity is observed at pH above the pH of point of zero charge ( $\text{pH}_{\text{PZC}}$ ) and could be related to the presence of surface hydroxyl groups in the deprotonated form.

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### 1. Introduction

Heterogeneous ozonation has attracted significant research in the last decade. A novel ozonation method combining adsorptive ozonation process using high silica zeolite adsorbents for drinking water treatment has been developed [1–6]. This adsorptive ozonation process is based on the enhanced adsorption of the targeted compounds, and ozone adsorption. As a result, selective decomposition of the target compounds was achieved, and the ozone requirement was minimised [7,8]. Making use of the possibility that adsorption property of high silica zeolites can be controlled

by the pore size and Si/Al ratio, organics and ozone were concentrated in micropores and the reaction rates were drastically enhanced [7]. Moreover, it has been shown that high silica zeolites are stable against dissolved ozone [8].

Recently, an interesting advanced oxidation process based on the combination of natural zeolites and ozone within a single unit operation has been reported in the literature for colorant removal from effluents of textile and paper industries [9,10]. In this integrated treatment, ozonation reactions in the presence of natural zeolite, comprises a combination of reactions in homogeneous and heterogeneous phase; where zeolite surface plays a fundamental role in the reaction mechanism, reducing the inhibitory effect of radical scavengers. Surface hydroxyl groups of natural zeolite were claimed to play an important role in aqueous ozone decomposition,

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leading to an increase in organic pollutant removal rates [11,12]. While the application of ozone together with natural zeolites seems to be attractive, experimental evidences have shown that using acid-treated natural zeolite increases organic removal rate [12].

Zeolites are known to exhibit both acidic and basic sites on their surfaces that can participate in surface chemistry [13,14]. Acidic sites, such as acidic OH groups (Brønsted acid centres), “true” Lewis sites (aluminium-containing extra-framework species) and cations as well as basic sites (such as basic oxygen atoms or alkaline metal clusters) are encountered in zeolites and are known to be of paramount importance in acid–base catalysis on zeolites [13].

Unfortunately, there is a lack of information on the influence of zeolite surface sites on the heterogeneous catalytic ozonation of organic pollutants. This work aims to unveil some of these issues. In this study, surface charge ( $\sigma$ ), surface acidity equilibrium constants ( $K_{a_1}^{\text{int}}$  and  $K_{a_2}^{\text{int}}$ ), and the pH of point of zero charge ( $\text{pH}_{\text{PZC}}$ ) are determined using an acidimetric–alkalimetric titration method [15]. Additionally, the acidic or basic character of the acid-treated zeolite is established using the temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) and carbon dioxide ( $\text{CO}_2$ -TPD), respectively. Moreover, Fourier transform infrared spectroscopy (FTIR) of pyridine adsorption is used to elucidate the nature and strength of acidic sites resulting from the acid treatment of natural zeolite. Finally, a kinetic model is proposed, with view to scaling up and process design and the effects of operational parameters (i.e. pH, the presence of radical scavengers, material dosage) on organic removal rate in such system are analysed. Methylene blue (MB) is used here as a model organic compound because it is representative of a series of cationic dye pollutants of environmental relevance.

## 2. Material and methods

### 2.1. Materials

Natural zeolite (NZ) was purchased from the Chilean mining company “Minera Formas” and was used in this study as a parent material. This zeolite is composed of clinoptilolite (53%), mordenite (40%), and quartz (7%). XRF analysis reported in previous publication revealed that the Chilean natural zeolite is composed of  $\text{SiO}_2$  (75.0%) and  $\text{Al}_2\text{O}_3$  (14.9%) followed by  $\text{CaO}$  (4.4%),  $\text{Fe}_2\text{O}_3$  (2.0%),  $\text{Na}_2\text{O}$  (1.5%),  $\text{MgO}$  (1.0%),  $\text{K}_2\text{O}$  (0.7%) and  $\text{TiO}_2$  (0.4%) [12]. Before being chemical modified, NZ was crushed and sieved into a mean particle size in the range 0.60–0.85 mm. Then, it was washed with de-ionised water, oven-dried at 378 K for 24 h, and stored in a desiccator until the modification treatment was conducted. MB (99% purity) was supplied from Scharlau Chemie (Sentmenat, Spain). A stock solution of MB ( $31 \times 10^{-3}$  M) was used in all the experiments and was prepared using ultrapure water ( $\geq 18.0$  M $\Omega$  cm) obtained from an EASY pure<sup>®</sup> RF II system (Barnstead|Thermolyne Corp., Dubuque, USA). All chemicals applied in analyses were reagent grade obtained from Merck (Darmstadt, Germany) and were used without further purification. An ozone generator equipped with a corona discharge reactor (AZCO Industries, Vancouver, BC, Canada) was used for ozone generation. Dry pure oxygen was passed through the ozone generator, and a variable ozone generation rate was featured, with a maximum around 5 g  $\text{O}_3$   $\text{h}^{-1}$ .

### 2.2. Chemical modification of natural zeolite

NZ was modified in a Soxhlet extraction apparatus for 6 h, using HCl (2.44 M) with a ratio of 0.3 g NZ per  $\text{cm}^3$  of acid solution. After the acid treatment, samples were washed with de-ionised water and dried in an oven at 378 K for 24 h. Dried samples were stored in a desiccator until use. Acid-treated zeolite was named (AZ).

### 2.3. Textural and bulk chemical characteristics

Acid-treated zeolite was physical and chemically characterised. Specific surface area and pore volume were obtained by nitrogen adsorption at 77 K, using a Micromeritics Gemini 2370 sorptometer (Norcross, GA, USA). For these assays, 0.2 g of sample was used, previously outgassed at 623 K for 3 h under nitrogen flow. Specific surface area ( $S_{\text{N}_2}$ ) was calculated from the nitrogen adsorption data, using BET equation. Micropore ( $V_{\text{micro}}$ ) and mesopore ( $V_{\text{meso}}$ ) volumes were calculated by applying the Dubinin–Radushkevich relation to the  $\text{N}_2$  adsorption data, as described elsewhere [11]. Bulk chemical composition was determined by X-ray fluorescence (XRF) as described in previous publication [11]. The changes in natural zeolite framework due to acid treatment with HCl were early described by Barrer and Makki [16]. They suggest that natural zeolite underwent structural changes, involving aluminium expulsion in a soluble form and its replacement by a nest of four hydroxyl groups, as shown the schematic representation given in Scheme 1 [13,16]. Results of XRF analysis showed the changes on natural zeolite composition. After the chemical treatment, modified zeolite is mainly composed of  $\text{SiO}_2$  (83%) and  $\text{Al}_2\text{O}_3$  (11.7%) followed by  $\text{Fe}_2\text{O}_3$  (2.0%),  $\text{CaO}$  (1.5%),  $\text{K}_2\text{O}$  (0.6%),  $\text{Na}_2\text{O}$  (0.4%),  $\text{MgO}$  (0.4%) and  $\text{TiO}_2$  (0.4%). As it can be seen, acid treatment not only reduced the aluminium content (Si/Al ratio was raised from 5.0 to 7.1) but also decreased the amount of compensating cations (Na, K, Mg, Ca) in the zeolite framework. These changes could be responsible of the observed increase in surface area. After acid treatment, BET surface area of natural zeolite was increased from 205  $\text{m}^2$   $\text{g}^{-1}$  to 344  $\text{m}^2$   $\text{g}^{-1}$ .

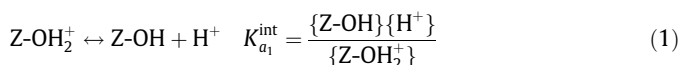
### 2.4. Acidic and basic surface site characterisation

#### 2.4.1. Acidimetric–alkalimetric titration method

HCl, NaOH and NaCl were the acid, base, and electrolyte, respectively, used in the titration. For each sample fifteen vials of 30  $\text{cm}^3$  capacity were used. They were filled with 20  $\text{cm}^3$  of NaCl 0.001 M solution, and 200 mg of samples were weighed and placed into each bottle. Different amounts of HCl (0.1 M) and NaOH (0.1 M) were added to each bottle: seven bottles for acid, seven bottles for base, and one without acid or base. Volumes of acid or base in the range from 0.040 to 1.5  $\text{cm}^3$  were added. The equilibrium pH was measured after 48 h shaking at  $293 \pm 0.1$  K. Surface charge ( $\sigma$ ), surface acidity equilibrium constants ( $K_{a_1}^{\text{int}}$  and  $K_{a_2}^{\text{int}}$ ) and the pH of point of zero charge ( $\text{pH}_{\text{PZC}}$ ), were determined applying the procedure described elsewhere [10]. Fig. 1 shows the surface charge density ( $\sigma$ ) of acid-treated zeolite sample as a function of pH. Table 1 summarises key textural and chemical characteristics of acid-treated zeolite sample.

Acid-treated zeolite presents a heterogeneous surface and its surface charge changes as a function of pH. The reduction on the aluminium content after acid treatment of natural zeolite decreases the charge density of anion framework of the natural zeolite. Thus, the  $\text{pH}_{\text{PZC}}$  of natural zeolite was reduced from 8.7 to 2.9 after acid treatment. Hence, hydroxyl groups on acid-treated zeolite are subjected to less intense interaction with the framework, facilitating the deprotonation, i.e., enhancing the acidity strength.

Surface hydroxyl groups present on zeolites are known to act as Brønsted acid sites or basic sites [15]. At  $\text{pH} < \text{pH}_{\text{PZC}}$ , an excess of protons at the surface hydroxyl groups (positive charge) occurs:



Whereas a proton deficit (negative charge) appears at the surface hydroxyl groups when  $\text{pH} > \text{pH}_{\text{PZC}}$ :