Chemical Engineering Journal 211–212 (2012) 388–395

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

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 pH_{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.

ARTICLE INFO

Article history:
Received 20 June 2012
Received in revised form 11 September 2012
Accepted 16 September 2012
Available online 5 October 2012

Keywords:
Catalytic ozonation
Methylene blue
Ozone
Surface hydroxyl groups
Surface properties
Zeolite

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 ($Z\text{-}OH_2^+$, Z-OH, $Z\text{-}O^-$) 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 N_2 adsorption at 77 K, X-ray fluorescence, acidimetric–alkalimetric titration, and by NH_3 and 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 (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 (pH_{PZC}) and could be related to the presence of surface hydroxyl groups in the deprotonated form.

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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http://dx.doi.org/10.1016/j.cej.2012.09.069