Journal of Water Process Engineering 12 (2016) 47–51

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Cobalt-exchanged natural zeolite catalysts for catalytic oxidation of phenolic contaminants in aqueous solutions

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 25 May 2016
Accepted 29 May 2016

Keywords:
Cobalt exchanged zeolite
Phenol removal
Zero-order kinetics
Advanced oxidation

ABSTRACT

Indonesia (IZ) and Australia (AZ) natural zeolites were employed to prepare cobalt exchanged catalysts. Characterization tests of scanning electron microscopy (SEM), X-ray diffraction (XRD) and Brunaeuer-Emmet-Teller (BET) were used for performing sample analyses. The efficiencies of phenol removal on the catalysts were evaluated by the catalytic oxidation of phenol with sulfate radicals. Cobalt-exchanged catalysts showed higher phenol removal efficiencies than adsorption, Oxone self-oxidation and unmodified zeolites. The reactions were observed to be more efficiently described by the zero-order kinetics, while the respective Co/IZ and Co/AZ activation energies were 44.1 and 59.5. This study provides a novel application of low-cost natural zeolites for environmental remediation.

1. Introduction

Many organic compound that possess toxicity for environment and living organisms are usually found in industrial and residential wastewaters [1]. Therefore, the wastewaters have to be treated before being discharged in the environment. Toxic organics treatment efficiency of the conventional wastewater treatment technology has been proven to be limited. Advanced oxidation processes (AOPs) have been noted as one of the technologies that show promise as effective processes to completely degrade organic substances in aqueous media. Mineralization of organic contaminants as CO_2 and H_2O due to production of high-reactivity oxidizing agents like hydroxyls is the driving factor for AOPs [2,3].

Application of environmental remedies or absorbents is often driven by nature of molecular sieve, sorption, catalysis, higher cation exchange capacity and other physicochemical characteristics. Commonly occurring economic materials such as natural zeolites have been largely used for these purposes [4–6]. Conversely, the use of catalysts based on natural zeolites for oxidizing organic contaminant has not been thoroughly researched.

Many investigations showed Co^{2+}/peroxymonosulfate as an effective route for sulfate radical production and oxidation of various toxic organics [7]. However, secondary pollution may be caused by the high toxicity heavy metal ions. Consequently, metal oxide catalysts, such as Co_3O_4 [8] and supported Co [9–12], have been proposed as alternative materials. Recently, α-MnO_2 and Mn_3O_4 have also been reported to be effective for phenol degradation [10,13].

The possibility of secondary pollution can be reduced by preventing leaching of metal through the use of zeolites. In a previous study by the authors, it was observed that chlorophenol and phenol were decomposed by ZSM-5 [14] and SBA-15 and Co-exchanged synthetic zeolites through Oxone/PMS. This is further elaborated in the following reaction equations [14,15]

$$S\text{-}Co^{2+} + HSO_5^- \rightarrow S\text{-}Co^{3+} + SO_4^{\bullet -} + OH^- \text{ (slow)} \quad (1)$$

$$SO_4^{\bullet -} + C_6H_5OH \rightarrow SO_4^{2-} + C_6H_5O^{\bullet} + H^+ \text{ (fast)} \quad (2)$$

This study has been conducted to prepare Co catalysts that are based on low-cost Indonesian and Australian natural zeolites. Their physicochemical and morphological properties were characterized and reaction kinetics and catalytic activities were studied.

2. Experimental work

2.1. Material synthesis

Indonesia natural zeolite (IZ) and Australia natural zeolite (AZ) samples were crushed into particle sizes of 40–60 μm. A conventional ion-exchanging process was followed by the loading of Cobalt ions in natural zeolite samples. IZ (9 g) and a 250 mL diluted aqueous solution of 0.03 M cobaltous nitrate were mixed under vigorous stirring in a refluxing flask. When the dispersion of IZ was

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http://dx.doi.org/10.1016/j.jwpe.2016.05.012
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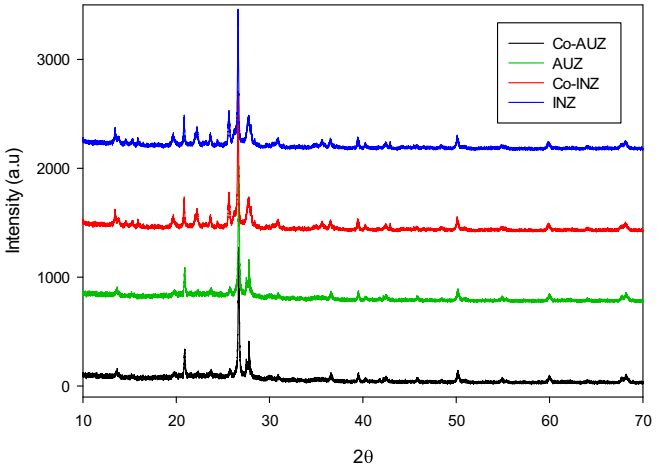

Fig. 1. Spectral patterns for natural zeolite and Co-exchanged zeolite XRD data.

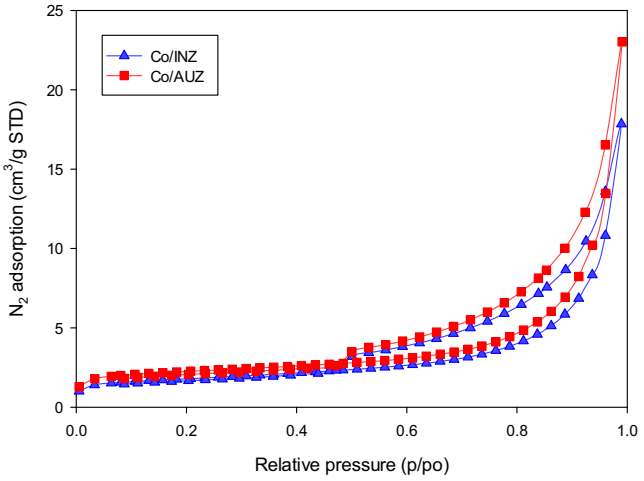

Fig. 3. N_2 adsorption isotherms of Co/IZ and Co/AZ.

completed, the temperature was increased to 80 °C and the mixture was left to stir for 5 h before filtering and washing with distilled water for several times to remove remaining nitrate ions. Maximum ion-exchange was ensured by repeating the process thrice, which was then followed by drying at 75 °C and 2 h calcination of the samples at 550 °C. The sample was denoted as Co/IZ. The same procedure was also implemented for Cobalt exchanged AZ, and the sample was denoted as Co/AZ.

2.2. Characterization of catalyst

Micromeritics Tristars-II 3020 was used for performing the N_2 absorption analysis to measure the pore sizes and surface areas of Co/IZ and Co/AZ samples after degassing the samples at 200 °C for 24 h. BJH and BET techniques were used to calculate the pore size distribution and surface areas, respectively. Bruker D8 diffractometer with electron beam of filtered Cu-Kα (λ = 1.54178 Å), current 30 mA accelerating voltage 4 kV and 10°–80° of 2θ scan was used Scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) Zeiss Neon 40 EsB was used for determining the chemical composition and morphological characteristics.

2.3. Study of phenol oxidation kinetics

Phenol solutions (25 ppm) were oxidized in a reactor of 500 mL capacity by catalysts to study the chemical kinetics and sulfate radicals were oxidized by peroxymonosulfate (Oxone, DuPont's triple salt: $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, Sigma-Aldrich). A filtering film of 0.45 μm and syringe were used to respectively withdraw and filter 0.5 mL of the reaction solution following each time interval. High performance liquid chromatography (HPLC) containing UV detector of λ = 270 nm. Mobile phase of high-purity water and CH_3CN at a respective proportion of 70% and 30% was contained in the C-18 column employed while the analyzer used for determining the total organic carbon or TOC of selected specimens was Shimadzu TOC-5000 CE.

3. Discussion/analysis of experiment results

3.1. Characterization of catalysts

Samples XRD spectra, both before and after ion-exchange with Co^{2+}, have been shown in Fig. 1. These correspond to their respective zeolite patterns. It can be observed that the ion-exchange of zeolite with cobalt did not affect the crystal structure (position and intensity) of natural zeolite, which can be concluded from the XRD pattern obtained in the 2 theta range of 10°–70°.

Fig. 2 shows the SEM micrographs of Co/IZ and Co/AZ catalysts. Both Co/IZ and Co/AZ presented an irregular shape with average sizes of 2 μm and 5 μm, respectively. From the SEM images, it can also be seen that there was no agglomeration of particles after ion-exchange with Co^{2+}.

Specific surface areas (S_{BET}) and distribution of pore sizes were identified by characterization of the catalyst specimens based upon the N_2 adsorption. The N_2 adsorption/desorption isotherm of cobalt-exchange zeolite catalysts has been shown in Fig. 3. As seen in Table 1, the S_{BET} of Co/AZ (8.2 m^2/g) and pore radius (170 Å) are greater than of Co/IZ. However, both cobalt-exchanged zeolite cat-

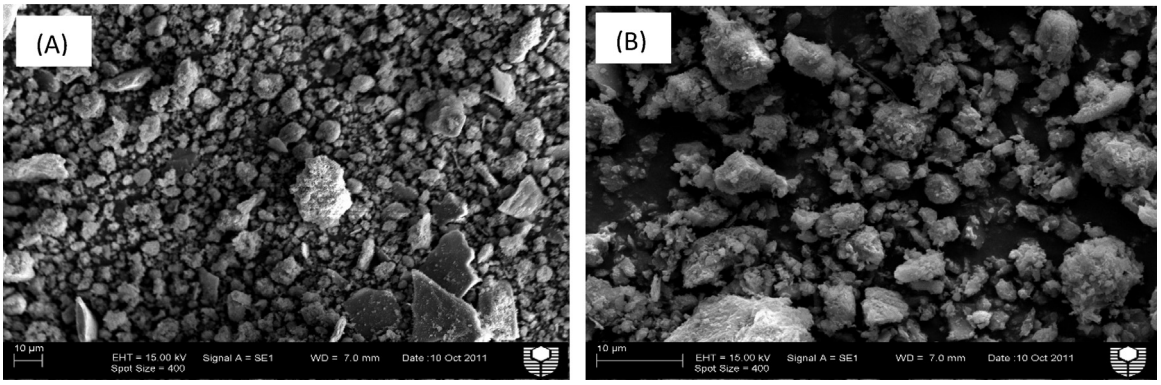

Fig. 2. SEM micrographs for natural zeolite: (a) Co/IZ and (b) Co/AZ.