Modification of alginate-modified natural zeolite for the degradation of 4-nitrophenol using H₂O₂ and microwaves

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Abstract. 4-Nitrophenol is used as a precursor or an intermediate in the explosive, pesticide, herbicide, and dye and pharmaceutical industries, and causes environmental pollution. One of the solutions for removing 4-nitrophenol is the degradation of dyes using H₂O₂, catalysts, and microwave assistance. In this study, alginate-modified zeolite was used as the catalyst. In addition, the effects of microwave power and degradation time were reported. Alginate-modified zeolite was characterized by UV–visible and Fourier transform infrared spectroscopy. The degradation of 4-nitrophenol (1.0 × 10⁻⁴ M) was observed in 120 s with 0.1 g of alginate-modified zeolite, 2.15 × 10⁻⁴ M of H₂O₂, and a microwave power of 800 W. The degradation of nitrophenol followed a first-order reaction with a k value of 8.95 × 10⁻³ min⁻¹.

Keywords: natural zeolite-alginate, degradation, 4-nitrofenol, microwave

1. Introduction

4-Nitrophenol is used as a precursor or an intermediate for manufacturing explosives, insecticides, pesticides, herbicides, fungicides, and dyes and pharmaceuticals [1–3]. It is obtained by the incomplete combustion of fossil fuels via nitration [4]. 4-Nitrophenol adversely affects the environment, causing headaches, nausea, kidney damage, and skin, eye, and liver irritation [1], similar to mutagenic and carcinogenic compounds [5] and phenol compounds and their derivatives. As a result, the US Environmental Protection Agency has designated mono-, di-, and poly-nitrophenol waste as toxic materials [6].

Several methods, including biological methods, adsorption, extraction, sonolysis, and reduction, have been reported for the removal of 4-nitrophenol [7–11]. However, these methods exhibit disadvantages, including incomplete waste removal limited only because of material absorption, high-energy requirements, and toxic compound production.

In recent years, advanced oxidation processes (AOPs), particularly catalytic wet hydrogen peroxide oxidation (CWPO), have been reported to be suitable for treating wastewater at room temperature and pressure. The CWPO process produces hydroxyl radicals (HO·), which can oxidize various pollutants into small nontoxic molecules such as CO₂ and H₂[12]. AOPs using H₂O₂ as the oxidizing agent with microwave assistance are environmentally friendly [13]. H₂O₂ is a thermal initiator, which can evenly spread the converted heat energy formed by the microwaves, thereby increasing the reaction rate [14–15].

Several heterogeneous catalysts such as zeolites serve as support materials, where their structures, pores, and interlayers can be modified, and have been used in AOPs [16]. Zeolites are catalysts that contain uniform micropores and exhibit high hydrothermal stability [17]. However, zeolites have long,
narrow pore channels; hence, they limit the diffusion of reactants and products during catalysis [18]. To modify natural zeolites, alginate can be used as an environmentally friendly material.

Alginate is a natural polymer that exhibits good water solubility. Furthermore, it can easily form gels by the addition of divalent cations such as Ca²⁺ [19]. Algicates, which belong to the polysaccharide family, are cell-wall constituents of brown seaweed, which produce carboxylate groups by extraction [20]. Alginate is composed of 1,4-linked β-D-mannuronic acid (M) connected to α-L-guluronic acid (G) residues [21]. Calcium alginate exhibits nontoxicity, biodegradability, nonimmunogenicity, water solubility, and thermal irreversibility as the immobilization material of catalyst material [22].

In this study, the degradation of 4-nitrophenol was examined using alginate-modified natural zeolites by utilizing AOPs and H₂O as the oxidation agent with microwave assistance. In addition, the effects of microwave power and degradation time were examined, as well as degradation kinetics.

2. Experimental

2.1. Materials and methods

Natural zeolite was purchased from CV Transindo Citra Utama (Bandung, Indonesia). NaOH, HCl, NaCl, and 30% H₂O, were purchased from Merck (Germany). AgNO₃ was purchased from Sigma Aldrich, and 4-nitrophenol was purchased from PT Antam. Sodium alginate was purchased from Himedia Laboratories Pvt. Ltd. (Mumbai, India). Double-distilled water was purchased from PT Ikapharmindo Putramas.

2.2. Activation of natural zeolite

Natural zeolite was activated by washing in water at 70 °C and stirring for 1 h, and the result was precipitated overnight. The precipitate was dried at 150 °C for 4 h. In addition, natural zeolite was chemically activated by the addition of 0.05 M of NaOH and 0.05 M of HCl. The zeolite cation was uniformed by the addition of 1 M of NaCl. The mixture was stirred at 70 °C for 6 h and precipitated for 12 h. The precipitate was dried at 105 °C and then calcined at 300 °C for 2 h. The chloride ions of zeolite were removed by washing in aquabides. Finally, zeolite was treated with AgNO₃ to confirm chloride-free zeolite. Activated zeolite was characterized by Fourier transform infrared (FTIR) spectroscopy.

2.3. Modification of natural zeolites with alginate

Alginate was synthesized by dissolving solid sodium alginate with the desired mass into 100 mL of water and stirring for 12 h, yielding a viscous yellow solution [23]. Zeolite was modified using alginate by mixing zeolite with the desired mass and a sodium alginate solution for 2 h, followed by overnight precipitation. The precipitate was dried at 40 °C for ~12 h. The alginate-modified natural zeolite was characterized by FTIR spectroscopy.

2.4. Degradation of 4-nitrophenol using alginate-modified natural zeolite

First, 0.1 g of zeolite-alginate was mixed with 2.15 × 10⁻⁴ M of H₂O, followed by vortexing for 5 min. Next, 10⁻¹ M of 4-nitrophenol was incorporated into the zeolite and H₂O mixtures, followed by vortexing for 5 min. The mixture was subjected to a microwave power of 800 W for 120 s. The mixture was characterized by UV–visible spectroscopy.

2.5. Characterization

UV–visible spectra (Shimadzu 2600) were recorded to obtain the maximum wavelength of the alginate-modified natural zeolite and to examine the degradation activity of 4-nitrophenol. FTIR spectra were recorded on a Perkin-Elmer system for functional group identification.

3. Results and discussion

FTIR spectra were recorded to identify the functional groups in alginate-modified natural zeolites. After activation, significant changes were not observed for natural zeolite and Na-modified zeolite (figure 1a). FTIR spectra revealed an increased intensity for the peak at 421 cm⁻¹, indicative of the presence of the Na–O group in activated zeolite. The intensity increase indicated the presence of a considerable amount of Na–O in the zeolite pores. In other words, the activation of zeolite using NaCl
Figure 1. FTIR spectra of (a) natural zeolite and (b) alginate-modified zeolite

Figure 2. UV–visible absorption spectra of (a) alginate and (b) degradation of 4-nitrophenol in 120 s.

was successfully carried out. Chloride ions were removed; hence, NaCl is not formed again. The presence of chloride ions was confirmed by the addition of AgNO₃. The mixture did not form any AgCl precipitate. Hence, zeolites are free of chloride ions. The FTIR spectrum of alginate-modified natural zeolites is shown in figure 1b). Different peaks were observed for Na-modified zeolite and alginate-modified natural zeolite. C–H and C–N stretching peaks were observed at 2901 and 1387 cm⁻¹, respectively, with a predominance of the C–H groups in the alginates, indicative of the successful modification of zeolite by alginate.

The UV–visible absorption spectrum of alginate is shown in figure 2a. Alginate formation was confirmed at a maximum wavelength of 274 nm. UV–visible absorbance as a function of time for the degradation of 4-nitrophenol is shown in figure 2b. The decrease in the absorbance at maximum wavelengths of 318 and 405 nm can be used to estimate the percentage degradation of 4-nitrophenol. After degradation, the peaks almost disappeared at the maximum wavelengths of 318 and 405 nm, as confirmed by dissociation of the p-nitrophenoxide ion [24]. With increasing degradation time, the absorbance value decreased, and a considerable amount of 4-nitrophenol was degraded. From this study, 4-nitrophenol was first converted into smaller non-light-absorbing compounds, which were
subsequently converted into CO$_2$ and H$_2$O [24]. Na zeolite-alginate degraded $1.0 \times 10^{-4}$ M of 4-nitrophenol in 120 s with 0.1 g of alginate-modified natural zeolite, an H$_2$O concentration of $2.15 \times 10^{-4}$ M, and a microwave power of 800 W.

The relationship between percentage degradation and microwave power is shown in figure 3a. A microwave power of 800 W gave the highest percentage degradation of 4-nitrophenol of 70.30%. Microwave energy causes the rotating molecules that trigger the H$_2$O$_2$ activity to produce OH radicals. It can form alginate radicals, which degrade 4-nitrophenol. The kinetics model for the degradation of 4-nitrophenol using alginate-modified natural zeolite was examined by plotting 4-nitrophenol concentrations as a function of time (figure 3b). The degradation of 4-nitrophenol followed a first-order reaction with a k value of $8.95 \times 10^{-2}$ min$^{-1}$.

4. Conclusions

In this study, alginate-modified natural zeolites as the catalyst were used for the degradation of 4-nitrophenol by utilizing advanced oxidation processes and H$_2$O$_2$ as the oxidation agent with microwave assistance. Modification with alginate leads to the high activity of zeolites. A microwave power of 800 W led to the degradation of 70.30% of 4-nitrophenol in 2 min. The results indicated that the degradation rate of 4-nitrophenol is affected by microwave power. The degradation of 4-nitrophenol followed a first-order reaction with a k value of $8.95 \times 10^{-2}$ min$^{-1}$.

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