Materials and Design 101 (2016) 210–217

Contents lists available at ScienceDirect

Materials and Design

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

Nitrophenols removal from aqueous medium using Fe-nano mesoporous zeolite

Pham-Thi Huong, Byeong-Kyu Lee *, Jitae Kim, Chi-Hyeon Lee

Department of Civil and Environmental Engineering, University of Ulsan, Nam-gu, Ulsan 680-749, Republic of Korea

ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form 28 March 2016
Accepted 7 April 2016
Available online 09 April 2016

Keywords:
Fe-nano zeolite
Economic effect
Nitrophenols
Wastewater
Adsorption
Regeneration

ABSTRACT

In this study, Fe-nano zeolite was applied to the removal of ortho, meta and para-nitrophenols to evaluate its potential applications as an effective adsorbent. Scanning electron microscopy, Fourier-transformed infrared spectroscopy, and gas adsorption analysis were used to compare the advanced properties of Fe-nano zeolite with those of commercial activated carbon (AC). The Fe-nano zeolite with a greatly improved surface area was particularly effective in the removal of the nitrophenols. The maximum adsorption capacity of *m*-, *o*- and *p*-nitrophenol were 168.7, 193.9 and 223.1 mg/g, respectively. These adsorbents were applied to the remediation of wastewater containing high *p*-nitrophenol concentration of 380 mg/L. The results revealed 92.8% removal efficiency of *p*-nitrophenol from wastewater by Fe-nano zeolite, which is much higher than those AC (56.5%). The regeneration characteristics of the *p*-nitrophenol-loaded adsorbent were analyzed. Even after 15 adsorption-desorption cycles, the removal efficiencies of *p*-nitrophenol by Fe-nano zeolite and AC were 78.6 and 57.9%, respectively. The required adsorption cost for the treatment of 1000 kg wastewater containing 380 mg/L of *p*-nitrophenol using Fe-nano zeolite was 67.6% lower than that using AC. Based on these results, Fe-nano zeolite can be used as economic and effective adsorbent for removal of nitrophenols from wastewater.

1. Introduction

Nitrophenols are important chemical intermediates that serve as a precursor for many pharmaceuticals and pesticides [1]. A range of industries, such as the plastics and paper industries use nitrophenols extensively in their products. A significant amount of nitrophenols are commonly present in the effluents of these industries and need to be treated before being discharged into the environment [2–3].

Many methods are used to remove nitrophenols from wastewater stream, including advanced oxidation processes for the removal of organic compounds, chemical oxidation, and adsorption. Among these techniques, adsorption is used widely because it has easy operation and simple design requirements [4–6]. Adsorption processes using biological materials, mineral oxides, and activated carbon (AC), or polymer resins have been attractive for the effective removal of organic compounds from water systems [7–8]. AC is one of the most commonly used adsorbents for the adsorption removal of organic pollutants. On the other hand, the high regeneration and purchase expenses of AC has prompted many attempts to develop low-cost adsorbents to remove toxic organic compounds. Zeolites have been utilized as good adsorbents, molecular sieves, membranes, ion exchangers and catalysts for municipal and industrial pollution control. Many studies have examined the use of zeolites to remove organic pollutants [9–15]. Recently, there has been increasing interest in the synthesis of nano-crystalline zeolites to utilize their favorable properties for environmental treatment [16–19].

The main aim of this study was to evaluate the feasibility of using synthesized Fe-nano zeolite for removing *o*-, *m*- and *p*-nitrophenol from water. A range of adsorption parameters were investigated, including solution pH, reaction time, adsorbent dose, and initial concentration of pollutants. The adsorption-desorption of nitrophenols in wastewater containing a high concentration of 380 mg/L using Fe-nano zeolite and commercial AC were studied.

This study also focused on reducing the adsorption cost for nitrophenol removal in wastewater.

2. Materials and methods

2.1. Material

The commercial activated carbon "Activated Charcoal Norit®; PCode: 101530190" used in this study was purchased from Daejung Chemical and Metals Co. LTD., South Korea. Fe-nano zeolite was prepared by mixing of 0.36 g NaOH and 0.152 g sodium aluminate salt in H_2O and aging it for 3 h at 20 °C with magnetic stirring. After adding 6.8 g of silica sol drop-wise, the resulting mixture was stirred at room temperature for 10 h to produce a homogenous mixture that was then heated for 12 h at 160 °C under autogenous pressure. The solid product was centrifuged and washed with deionized water until its pH reached

* Corresponding author.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

http://dx.doi.org/10.1016/j.matdes.2016.04.020
0264-1275/

4.0. After drying the synthesized nano zeolite, an appropriate amount was immersed in a 0.3 M $Fe(NO_3)_3$ solution to obtain the Fe ion-doped nano zeolite solid. The resulting solid was recovered by filtration, washed with distilled water, dried at 50 °C for 12 h. The physical and chemical properties were characterized and the product was used for the adsorption experiments [20–21].

2.2. Characterization of adsorbent

Scanning electron microscopy (SEM) was performed using a Hitachi S-4700 scanning electron microscope. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. The Fourier transform infrared (FTIR) transmittance spectra in the region 4000–500 cm^{-1} were recorded on a Perkin–Elmer Nicolet Nexus 470 FTIR spectrometer at room temperature. The phase structure of the Fe-nano zeolite was examined by powder X-ray diffraction (XRD, Bruker AXN) using CuKα radiation, 30 kV/15 mA current and a Kβ-filter over the 2θ range of 5–80°.

2.3. Adsorption experiments

The adsorption experiments were carried out by agitating 0.5 g of adsorbent in 100 mL of an *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol solution at concentrations ranging from 10 to 500 mg/L and solution pHs ($2.0 \le pH \le 10$) with a mechanical shaker rotating at 150 rpm. The solution pH of the reaction mixture was measured using a pH meter (Orion 5 Star). The adsorption effect of the solution pH was analyzed by adjusting the pH of the *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol solutions using 0.1 M HCl and 0.1 M NaOH solutions. After the adsorption experiments, the samples were removed and filtered using Whatman 45 filter paper. The *o*-, *m*- and *p*-nitrophenol concentrations in the supernatant liquid were analyzed by monitoring the absorbance at 350, 330 and 315 nm, respectively, using a UV–Vis spectrophotometer (Model UV 2100).

The Langmuir and Freundlich adsorption isotherms were used to analyze the equilibrium adsorption. The amount of nitrophenols adsorbed per unit mass of adsorbent at equilibrium was obtained using the following Eq.(1):

$$Q_e = (C_o - C_e) \times V/W \quad (1)$$

where V is the volume of the solution (L), C_o the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), and W is the mass of the adsorbent (g).

After adding either the Fe-nano zeolite or AC to the wastewater, the nitrophenol-loaded adsorbents were washed with distilled water before being treated with 100 mL of 30% C_2H_5OH for a contact time of 180 min at room temperature 20 ± 1°°C. The percentage desorption was calculated using the following Eq. (2):

$$\%\ \text{Desorption} = [(C_e - C_d)/C_e]) \times 100 \quad (2)$$

where C_d (mg/L) represents the final nitrophenol concentration identified in the desorption medium. After desorption, the Fe-nano zeolite and AC were washed with distilled water and reused for another adsorption cycle.

3. Results and discussion

3.1. Morphology analysis of Fe-nano zeolite and AC

SEM is an extremely useful tool for examining the surface morphology and physical state of an adsorbent surface. Fig. 1A and B showed the differences in surface morphology of AC and Fe-nano zeolite, respectively. The surface morphology of AC consisted mainly of multilayers with a number of pores (Fig. 1A). On the other hand, a SEM image of the synthesized Fe-nano zeolite with particles was composed of very small nanocrystals (Fig. 1B).

3.2. The surface area (BET)

Table 1 presents the results of BET analysis of the Fe-nano zeolite and AC. The specific surface areas of the Fe-nano zeolite and AC were 987.8 and 640.6 m^2/g, respectively. Generally, an increase in specific surface area would lead to a better adsorption performance for the adsorbent.

On the other hand, the pore size of Fe-nano zeolite and AC were 2.9 and 1.2 nm, respectively. An increase in surface area and pore size of Fe-nano zeolite also facilitates the adsorption process, as the large nitrophenol molecules can bind to the adsorption site more easily, resulting in an improved adsorption capacity of the nitrophenols compared to AC.

3.3. FTIR analysis

Fourier transform infrared (FTIR) spectroscopy is used to investigate the functional groups present in the Fe-nano zeolite and AC (Fig. 2A andB). The characteristics of Fe-nano zeolite (Fig. 2A), which consists of Fe ions was reflected by the peaks at 480–560 cm^{-1} [22]. A strong peak around 1000 cm^{-1} represented the Si—O stretch. The small peaks around 1650 cm^{-1} are linked to the adsorbed water in the nano zeolite. The broad band range from 3320 to 3600 cm^{-1} was assigned to the O—H stretching vibrations of the hydrogen-bonded molecules. The broad stretch in this wavenumber range was attributed to the loosely-bound water molecules hydrogen-bonded to Si—OH groups in the nest defects due to Al vacancies in the zeolite structure [23]. Fig. 2B presents the FTIR spectra of AC. A wide band in the range, 3200–3450 cm^{-1}, was assigned to the stretching peak of hydroxyl groups

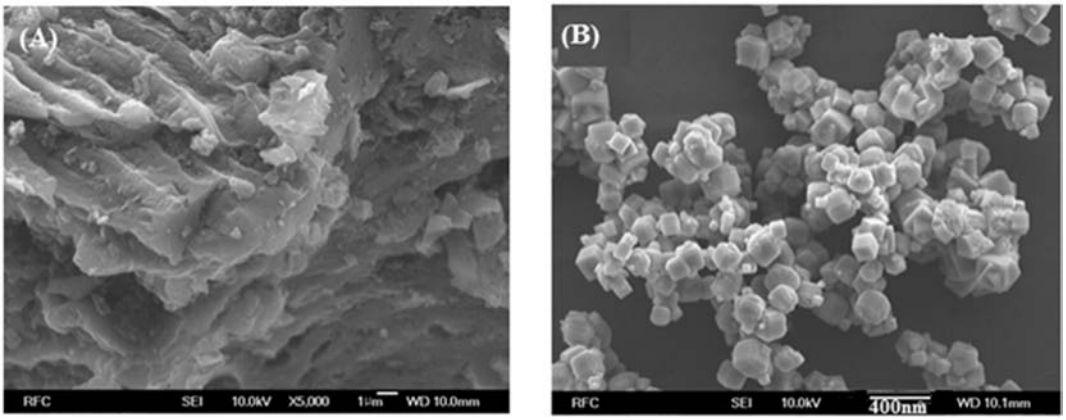

Fig. 1. Scanning electron microscopy of: (A): AC; (B): Fe-nano zeolite.