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Palladium-Zeolite nanofiber as an effective recyclable catalyst membrane for water treatment

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ABSTRACT

Zeolite is an exciting natural material due to its unique capability of ammonium nitrogen (NH_3–N) adsorption in water. In this study, multifunctional hybrid composites of zeolite/palladium (Ze/Pd) on polymer nanofiber membranes were fabricated and explored for sustainable contaminant removal. SEM and XRD demonstrated that zeolite and palladium nanoparticles were uniformly distributed and deposited on the nanofibers. NH_3–N recovery rate was increased from 23 to 92% when palladium coated zeolite was embedded on the nanofiber. Multifunctional nanofibers of Ze/Pd membranes were able to adsorb NH_3–N on the zeolites placed on the surface of fibers and palladium catalysts were capable of selective oxidation of NH_3–N to N_2 gas. The cycling of NH_3–N adsorption-oxidation, high flux, hydrophilicity, and flexibility of the membrane makes it a strong candidate for water treatment.

1. Introduction

Nitrogen is an essential nutrient element for living organisms. However, discharge of nitrogen containing wastewater into the environment without removal of the contaminants can be harmful to ecosystems (Li et al., 2011). Excessive nitrogen (Especially ammonia nitrogen, NH_3–N) can be toxic to human and aquatic life. Also, excessive nitrogen can cause eutrophication in rivers and marine waters. In wastewater treatment plants (WWTPs), NH_3–N is traditionally removed by nitrification-denitrification by activated sludge (AS) with biological nitrogen removal (BNR) (Kurama et al., 2010; Kurniawan et al., 2006). In AS with BNR systems, anoxic (or anaerobic) and aerobic reactors are utilized to remove NH_3–N mainly due to lower cost and fewer byproducts formed compared to other chemical approaches. For example, chloramines are formed during chlorination to remove NH_3–N in water treatment plants (WTPs) as shown in Equation (1).

$$NH_3 + HOCl \rightarrow NCl_3 + H_2O \quad (1)$$

However, efficiency of AS systems using either aerobic or anaerobic bacteria is sensitive to various environmental changes, especially during cold weather (Morgan-Sagastume and Allen, 2003). In addition, chlorine supplied for removal of NH_3–N reacts with humic or fulvic acids, which produces trihalomethane (THM), a well-known carcinogen (Liang and Singer, 2003). Recently adsorbents such as activated carbon or zeolite have attracted great interest due to its simplicity of operation, less byproducts, and robustness to operation environment. Particularly zeolite, had been actively explored in WTPs and WWTPs due to high adsorbance capacity for ammonia in aqueous environments (Hedström and Amofah, 2008; Weatherley and Miladinovic, 2004; Xie et al., 2014; Yan et al., 2013). NH_3–N attached to zeolite can be chemically or biologically recycled by NaCl, NaOH, and microorganisms. However, wide use of zeolite is hindered by high processing cost, complicated recycle processes, and the disposal challenges of chemicals or microorganisms used to recycle zeolite (Doula, 2009; Faghihian and Kabiri-Tadi, 2010; Kumar et al., 2006). Also, pulverized zeolite particles used during the water treatment process are difficult to harvest from water, which limits the minimum size of zeolite and reduces the surface area for NH_3–N adsorption.

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In this study, zeolite micro-particles were embedded on electrospun nanofibers to enhance the efficiency of zeolite particles by increasing the active surface area. Metal catalysts were coated on the nanofiber mat to perform the zeolite recycle process, which can replace the conventional chemical process. The electrospinning technique was utilized to fabricate a membrane with high surface area, porosity, and provide a substrate for the uniform distribution of zeolite particles (zeolite membrane). Catalyst metal nanoparticles were synthesized on the surface of the nanofibers to recycle zeolite by an in-situ chemical reduction process (Electroless Plating, EP). The NH_3–N removal process applied in the fabrication of zeolite/palladium membrane (Ze/Pd membrane) consisted of the following steps.

Step 1: Adsorption of NH_3–N on the nanofiber membrane containing zeolite.
Step 2: Oxidation of NH_3–N in the presence of a catalyst vis ($4NH_3 + 3O_2 \xrightarrow{catalyst} 2N_2 + 6H_2O$).

2. Material and methods

2.1. Material

Poly-acrylonitrile-co-methyl acrylate (PAN-co-MA) with a molecular weight (MW) = 100,000(Scientific Polymer Products), natural zeolite (<10 μm powder, 0.6 K_2O: 4.0 Na_2O: 1 Al_2O_3: 2.0 ∀ 0.1 SiO_2: × H_2O, Sigma Aldrich), palladium acetylacetonate ($Pd(acac)_2$, 99%, Sigma Aldrich), and dimethylformamide (DMF, Anachemia) were utilized to fabricate the membranes. The EP solution for coating the membranes consist of palladium chloride ($PdCl_2$, 99.9%, Alfa Aesar), ethylenediaminetetraacetic acid disodium salt (EDTA·2Na, 99.0+%, Alfa Aesar), ammonium hydroxide (NH_4OH, 28%, Sigma-Aldrich), and monohydrate hydrazine ($N_2H_4H_2O$, 64–65%, Sigma-Aldrich).

2.2. Fabrication of PAN-Ze/Pd membrane

Nanofiber mats were fabricated by the electrospinning process (Ko and Wan, 2014; He et al., 2014). Electrospinning solutions were prepared by sonication of the $Pd(acac)_2$ (1.0 wt% to PAN-co-MA) and zeolite (0, 0.1, 0.3, 0.5 and 1.0 g zeolite/g PAN-co-MA) in DMF. PAN-co-MA of 10 wt% concentration to solution was then added to the prepared $Pd(acac)_2$/DMF mixture. Vials containing solutions were then sealed and stirred in 90 °C oil-bath to dissolve the polymers. As depicted schematically in Fig. 1(step 1), the spinning solution was electrospun into nanofiber webs using an electrospinning apparatus (Kato Tech, Japan) with applied voltage of 16–18 kV at the spinneret. The spinning solutions were fed through a gauge 18 syringe needle. The high voltage power supply was clipped to a syringe needle tip and the cathode was connected to a metal collector. During electrospinning, the distance between spinneret to target was 15 cm apart and the flow rate of the spinning solution was 0.1 ml/min. The electrospun fibers were collected on aluminum foil wrapped around the metal drum target at a rotating speed of approximately 100 rpm. The collected nanofiber membrane was dried in an oven at 100 °C for 24 h before post processing. The dried electrospun nanofibers were then heat treated at 250 °C in argon with the ramp rate of 1 °C/min.

2.3. Electroless plating of palladium metal on the nanofiber membrane

The fabricated nanofiber mats containing zeolite were coated with Pd catalyst nanoparticles by EP (Fig. 1(step 2)). The composition of EP solutions and reductant, N_2H_4 are provided in Table 1. $PdCl_2$ was the source of palladium and NH_4OH was used to keep the pH between 11 and 12. The plating solution was kept at room temperature during the process.

The electrospun membrane was immersed in a mixture consisting of 16 ml of EP solution and 2 ml of (N_2H_4) H_2O for 2 h for palladium growth. After the plating process, the Pd deposited mat was carefully removed from the plating bath and rinsed with deionized water. The resulting PAN-Ze/Pd membrane was dried in an oven at 100 °C for 24 h and stored in a desiccator for later use.

2.4. Adsorption of zeolite and oxidation by the catalyst

In order to verify the reusability of the Ze/Pd membrane, the adsorption and oxidation test of Ze/Pd membranes were carried out as illustrated in Table 2 and Fig. 2.

Experiments on the adsorption of NH_3–N were carried out with batch (Table 2 (A)) and continuous circulation (Table 2 (B))

Table 1
Composition of EP solutions and reductant.

No.	Components	Amount
1	$PdCl_2$	4.0 g/L
2	EDTA·2Na	67.2 g/L
3	NH_4OH	400 ml/L
4	$(N_2H_4)H_2O$	0.63 M
Plating temperature		20-25 °C
Time for plating		1 h
Plating pH		11–12

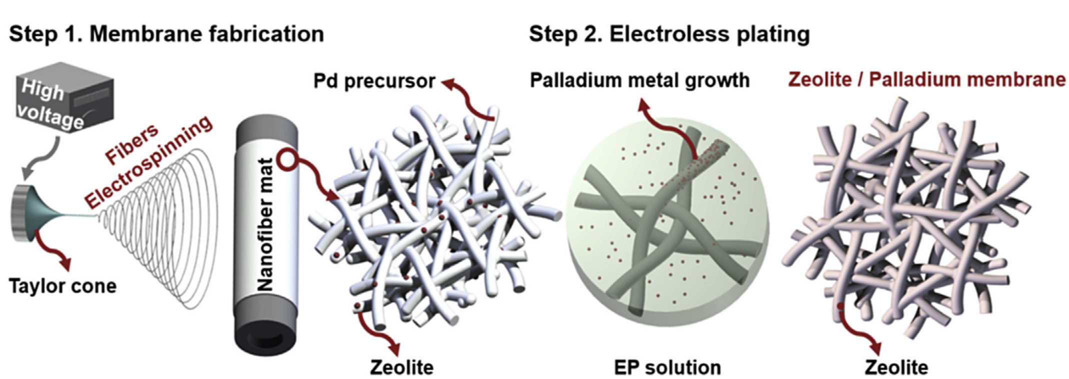

Fig. 1. Schematic diagram of the electrospinning process (step 1) and electroless plating (step 2).