



Hydrolysis of oxidized polyacrylonitrile nanofibrous webs and selective adsorption of harmful heavy metal ions



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ABSTRACT

Polyacrylonitrile (PAN) nanofibrous webs were prepared by electrospinning, and then stabilized by a heat treatment. Through these processes, oxidized PAN (oxy-PAN) nanofibers were obtained. After the stabilization, the residual nitrile groups on the surface were hydrolyzed using a high concentration NaOH solution; consequently, hydrolyzed oxy-PAN (H-PAN) nanofibrous webs were prepared. Attenuated total reflection infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) were used to confirm the chemical conversion on the surface of the H-PAN nanofibrous webs. Also, the initial pH and contact time were varied to examine the adsorption behavior against heavy metal ions. The adsorption amounts on the heavy metal ions of the H-PAN nanofibrous webs were evaluated by an inductively coupled plasma atomic emission spectrometer (ICP-AES), and they depended on the initial pH and contact time. The maximum adsorption amounts of Pb²⁺ and Cd²⁺ were 116.2 mg/g and 85.7 mg/g, respectively. Lastly, the adsorption rate of the H-PAN nanofibers followed the pseudo-second order.

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1. Introduction

The industrial development of the current era raises the problem of significant water pollution. In particular, harmful heavy metal ions such as lead, copper, cadmium, and mercury have been a major factor of water pollution [1]. These heavy metal ions can cause a variety of harmful influences to humans, e.g., kidney damage, muscle paralysis, and cardiovascular problems. [2]; therefore, many research studies have been conducted to remove heavy metal ions from wastewater. For instance, adsorption, ion exchange, separation, and precipitation methods have been developed to remove heavy metal ions. Among these methods, the adsorption method is commonly used to remove heavy metal ions because of its high effectiveness and eco-friendly properties [1,3].

Recently, nanotechnology and various nanostructured materials have been used in the removal of heavy metal ions. On account of a nanostructure with a high specific surface area, a number of studies related to nanoadsorbents which include nanobeads, nanocomposites, magnetic nanoadsorbents, and nanofibrous webs, have

been conducted [4–6]. Among the nanoadsorbents, the nanofibrous webs have unique advantages such as a high specific surface area and a high porosity; these strong points could cause the high adsorption capability of the adsorbent. In general, the nanofibrous webs can be easily fabricated using electrospinning with various polymers [7].

Polyacrylonitrile (PAN) is one of the polymeric materials that is widely applied to adsorbents for the removal of heavy metal ions, since chelating groups can be introduced using simple chemical methods. The nitrile groups in the PAN molecules are converted to carboxylic acid and amide groups by a hydrolysis reaction [8]; however, the dimensional shape of electrospun PAN nanofibrous webs cannot be kept under severe hydrolysis conditions, although they have a high surface area due to the nano-scaled diameter. To overcome this problem with respect to dimensional stabilization, an appropriate pre-treatment process is needed.

In this study, PAN nanofibrous webs were stabilized by a thermal treatment in the temperature range of 200 °C–300 °C under an air atmosphere [9]. During the thermal treatment, the PAN nanofibers underwent significant chemical and physical changes such as cyclization, dehydrogenation, oxidation, and crosslinking [10]; therefore, the oxidized PAN (oxy-PAN) nanofibrous webs showed improved chemical and thermal stabilities, whereby the webs

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could maintain their fibrous shape even in high concentrated alkaline solutions or under high temperatures.

Here, the PAN nanofibrous webs were first fabricated by electrospinning and then stabilized by the heat treatment. In the next step, the oxidized PAN webs were hydrolyzed at a high concentration of a NaOH solution to provide a highly effective adsorption for heavy metal ions. The resultant PAN webs with a high adsorption capability were achieved through the chemical conversion of the nitrile groups on the surface of the nanofibrous webs. Attenuated total reflection infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) were used to confirm the chemical conversion on the surface of the hydrolyzed product of the oxidized PAN (H-PAN). Also, the dimensional stability of the H-PAN was observed by field emission scanning electron microscopy (FE-SEM). The adsorption amounts against the various heavy metal ions were evaluated by an inductively coupled plasma atomic emission spectrometer (ICP-AES).

2. Experimental

2.1. Materials

PAN copolymer (91.4% acrylonitrile and 8.6% methylacrylate, $M_w = 50,000$ g/mol) was supplied by Taekwang Industrial Co. (South Korea). N, N-dimethylformamide (DMF, 99.5%) was purchased from Daejung Co. (South Korea). Sodium hydroxide (NaOH, 5 N) was purchased from Samchun Co. (South Korea). All of the agents were used without further purification. Salts containing heavy metal cations such as $\text{Co}(\text{ClO}_4)_2$, $\text{Ni}(\text{ClO}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$, $\text{Li}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, CsClO_4 , and $\text{Pb}(\text{ClO}_4)_2$ were obtained from Alfa Aesar (UK).

2.2. Analyses

The ATR-IR spectra were obtained using an ALPHA spectrometer (Bruker, Germany) with diamond ATR module and a maximum analysis thickness of 2 μm . The ATR-IR was used to analyze the chemical structure change of the PAN samples. The surface morphologies of the PAN nanofibrous samples were studied using an FE-SEM (JSM-7000F, Japan). The chemical groups on the PAN samples were analyzed using XPS (MultiLab 2000, USA). An ICP-AES (OPTMA 7300 DV, USA) was used to measure the concentrations of lead ions (Pb^{2+}), cadmium ions (Cd^{2+}), lithium ions (Li^{2+}), cobalt ions (Co^{2+}), cesium ions (Cs^{2+}), nickel ions (Ni^{2+}), and copper ions (Cu^{2+}) in the aqueous solution.

2.3. Electrospinning of PAN nanofibrous webs

The electrospinning equipment is composed of a syringe pump, a high voltage power supply (CPS-40K03VIT, Chungpa EMT, South Korea), and a collector. The PAN solutions were prepared by dissolving the PAN powder in DMF with stirring at 50 °C for 12 h. The solutions were placed in the syringe with a stainless steel needle (0.559 mm diameter) that was connected to a positive high voltage power supply. A voltage of 17 kV was applied to the tip of the needle, and the distance from the tip to the collector is 12 cm. The flow rate of the PAN solution was fixed at 0.7 mL/h, and then the electrospun PAN nanofibrous webs were dried to remove the residual solvent at room temperature for 24 h.

2.4. Preparation of oxidized PAN (oxy-PAN) nanofibrous webs

The oxidized PAN (oxy-PAN) nanofibrous webs were prepared by oxidizing the PAN nanofibrous webs. The oxidation was performed using a furnace (MF-30S, JEIO tech Co. LTD, Japan) at 230 °C

with a heating rate of 10 °C/min under an air condition. The PAN nanofibrous webs were then prepared under 230 °C for 10–120 min to provide the crosslinking of the PAN samples.

2.5. Hydrolysis of the oxy-PAN nanofibrous webs

The hydrolysis of the oxy-PAN nanofibrous webs was immersed in 5 N of the NaOH solution at 50 °C. To examine the effect of the hydrolysis on the surface structure of the webs and the conversion of the nitrile groups, the hydrolysis time was varied from 5 h to 20 h. And then the hydrolyzed oxy-PAN (H-PAN) nanofibrous webs were washed with a distilled water/ethanol mixture and dried in a vacuum oven at 100 °C for 24 h.

2.6. Evaluation of adsorption capacity

The H-PAN nanofibrous web samples were placed in a vial containing a 13 mL solution with heavy metal ions. The initial concentration of the heavy metal ions was 100 ppm that was held at 30 °C. To evaluate the adsorption capacity of the heavy metal ions, the H-PAN nanofibrous webs were immersed in various metal ion solutions over 1 h. To investigate the effect of the pH, the pH of the heavy metal ion solutions was adjusted from 1.0 to 8.0 with 0.1 N of NaOH and 0.1 M of HCl. The amount of the adsorbed heavy metal ions was calculated as follows:

$$q(\text{mg/g}) = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the heavy metal ion solution (mg/L), respectively. V is the volume of the testing solution (L) and M is the weight of the heavy metal adsorbent (g) [1].

3. Results and discussion

3.1. Structural investigation of H-PAN nanofibrous webs

Fig. 1 shows the change of the chemical structure during the preparation of the H-PAN nanofibrous webs by heat treatment and hydrolysis. The first step is an oxidation of the PAN nanofibrous webs by the heat treatment. This process was accompanied by the chemical reactions of cyclization, oxidation, and crosslinking [11]. The cyclization and crosslinking structures were attributed to the nitrile groups. As a result, the oxy-PAN nanofibrous webs showed an improved chemical resistance, heat resistance, and mechanical properties. After the first step, the residual nitrile groups on the surface of the oxy-PAN nanofibrous webs were subsequently hydrolyzed in the high concentration of the NaOH solution. Through the hydrolysis reaction, the nitrile groups were converted to amide and carboxyl groups.

Fig. 2 represents the ATR-IR spectra of the PAN, oxy-PAN, and H-PAN nanofibrous webs, respectively. As shown in Fig. 2(a), the typical bands of the nitrile (2243 cm^{-1}), carbonyl (1732 cm^{-1}), and ether (1203 cm^{-1} and 1032 cm^{-1}) groups were observed. The absorption peaks of the carbonyl and ether groups were assigned due to the methyl acrylate comonomer [6,12]. The absorption peaks of the oxy-PAN appeared at 1608 cm^{-1} and 783 cm^{-1} , corresponding to the -C=N- and -C=C-H- bonds, respectively, as shown in Fig. 2(b). Also, the peak of the nitrile group was slightly decreased, when compared with that of the original PAN nanofibrous webs. On account of the oxidation process, the nitrile groups were partially converted to the -C=N- and -C=C-H bonds [13]. Fig. 2(c) shows the change in the chemical structure of the oxy-PAN after the hydrolysis. The new strong peaks were observed at 3292 cm^{-1} and

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