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Abaca/polyester nonwoven fabric functionalization for metal ion adsorbent synthesis via electron beam-induced emulsion grafting

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HIGHLIGHTS

- An amine type adsorbent from abaca/polyester nonwoven fabric was synthesized.
- Pre-irradiation method was used in grafting glycidyl methacrylate on nonwoven fabric.
- Radiation-induced grafting was performed with monomer in emulsion state.
- The calculated adsorption capacity for Cu^{2+} is four times higher than Ni^{2+} ions.
- Grafted adsorbent can remove Cu^{2+} faster than a chemically similar commercial resin.

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ABSTRACT

A metal ion adsorbent was developed from a nonwoven fabric trunk material composed of both natural and synthetic polymers. A pre-irradiation technique was used for emulsion grafting of glycidyl methacrylate (GMA) onto an electron beam irradiated abaca/polyester nonwoven fabric (APNWF). The dependence of degree of grafting (*Dg*), calculated from the weight of APNWF before and after grafting, on absorbed dose, reaction time and monomer concentration were evaluated. After 50 kGy irradiation with 2 MeV electron beam and subsequent 3 h reaction with an emulsion consisting of 5% GMA and 0.5% polyoxyethylene sorbitan monolaurate (Tween 20) surfactant in deionized water at 40 °C, a grafted APNWF with a *Dg* greater than 150% was obtained. The GMA-grafted APNWF was further modified by reaction with ethylenediamine (EDA) in isopropyl alcohol at 60 °C to introduce amine functional groups. After a 3 h reaction with 50% EDA, an amine group density of 2.7 mmole/gram adsorbent was achieved based from elemental analysis. Batch adsorption experiments were performed using Cu^{2+} and Ni^{2+} ions in aqueous solutions with initial pH of 5 at 30 °C. Results show that the adsorption capacity of the grafted adsorbent for Cu^{2+} is four times higher than Ni^{2+} ions.

1. Introduction

Radiation-induced grafting is widely used for expanding the utilization of synthetic and natural polymeric materials. This was achieved by modifying the original polymers through introduction of graft chains from different types of monomers. Vinylic monomers were successfully grafted onto synthetic materials like polyethylene (PE) fibers (Seko et al., 2007), PE nonwoven fabric (Ueki et al., 2011) and PE/polypropylene (PP) nonwoven fabric (Ma et al., 2011; Kavakli et al., 2007), and materials composed of natural polymers such as nonwoven cotton fabric (Sekine et al., 2010), cotton–cellulose (Takacs et al., 2005) and water hyacinth fibers (Madrid et al., 2013). Some of these grafted polymer chains contain functional groups which are responsible for the new properties of the polymer material while other grafted polymers serve as precursors for introduction of other functional groups after post-grafting reactions. Properties that can be imparted to both synthetic and natural polymers using this method include improved hydrophilicity/hydrophobicity, sorption activity, permselectivity, flame retardancy and improved electrochemical properties to mention a few. Among these, improving the sorption activity, particularly for metal ions, has been an active field of research over the past years.

The attention given by the world on environmental problems due to input of heavy metal ions to different bodies of water has been increasing. This heightened awareness is driven by the different diseases caused by these metal pollutants. High level of

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exposure to copper may lead to weakness, anorexia, and damage to gastrointestinal tract (Theophanides and Anastassopoulou, 2002). At high concentrations, nickel is known to be toxic to plants and animals and at very high levels of exposure, nickel salts are known to be carcinogenic (Smith-Sivertsen et al., 1997). Hence, water treatment is necessary for water systems containing high amounts of these metals. Although there are several methods for heavy metal removal from polluted or waste waters, adsorption is considered as one of the most effective and popular process.

Adsorbents synthesized from natural polymers have several advantages over their synthetic counterparts. Natural polymers are renewable and abundant in nature, unlike synthetic polymers which are mostly petroleum based. Furthermore, it has been found that cellulosic polymers can be grafted with high efficiency using the method of emulsion polymerization (Ueki et al., 2011; Sekine et al., 2010). This method uses water instead of organic solvents as primary component of the monomer mixture which contributes to the green chemistry of the process (Seko et al., 2007). Also, high degree of grafting can be achieved even at low dose, making it an economical alternative over the traditional grafting techniques.

This work aims at the synthesis of an amine type adsorbent from an abaca/polyester nonwoven fabric. Abaca (*Musa textilis),* more popularly known as Manila hemp, is a primary product of some farming regions in the Philippines. The adsorbent is developed by using pre-irradiation technique followed by emulsion grafting of GMA with subsequent ring opening reaction of the epoxy groups with ethylenediamine. The effects of pH, initial concentration and time of contact on the adsorption of Cu^{2+} and Ni^{2+} from prepared aqueous solutions by the amine type adsorbent were studied. The performance of the synthesized adsorbent was compared with a commercial resin.

2. Experimental

2.1. Materials and reagents

Abaca-polyester nonwoven fabric (APNWF) was supplied by Philippine Textile Research Institute. The glycidyl methacrylate (GMA, $>95.0\%$) monomer was obtained from Tokyo Chemical Industry Co., while ethylenediamine (EDA, $>99.0\%$), polyoxyethylene sorbitan monolaurate (Tween 20), $Ni(CH_3COO)_2 \cdot 4H_2O$ ($>98.0\%$), $CuSO_4 \cdot 5H_2O$ ($>99.5\%$), ultrapure nitric acid, and the copper and nickel standard solutions (1000 ppm) for quantitative tests were purchased from Kanto Chemical Co., Inc. The isopropanol (IPA, $>99.7\%$) used in functionalization was acquired from Chameleon Reagent. Reagent grade methanol was used in all washing steps.

2.2. Irradiation of nonwoven fabrics

The APNWF was cut into 3 cm $\times$ 3 cm square pieces which were placed in polyethylene bags. The air inside the polyethylene bags was displaced with nitrogen gas. The samples were then irradiated at dry ice temperature with electron beam of 2 MeV energy and 3 mA current up to doses of 50, 100 and 200 kGy. The dose of electron beam was evaluated from the response of cellulose triacetate dosimeter (CTA).

2.3. Grafting of GMA onto APNWF and amination process

The irradiated APNWF samples were placed in a glass ampoule which is immediately evacuated of air using a vacuum line. Afterwards, a previously deaerated emulsion composed of GMA and Tween 20 in deionized water was drawn into the glass ampoule. The emulsion grafting was carried out by keeping the glass ampoule in a thermostated water bath at 40 °C for 1–4 h. After grafting, the grafted APNWF pieces were washed repeatedly with methanol, to remove the remaining non-reacted GMA, and dried in vacuo. The amount of GMA grafted onto APNWF was expressed in terms of degree of grafting (*Dg*) and was calculated using the equation: $Dg\,(\%)=(Wg-Wo)/Wo \times 100$, where *Wg* corresponds to the weight of APNWF after grafting and *Wo* is the initial weight of APNWF. Five parallel samples were grafted and *Dg* value was reported as an average.

GMA-grafted APNWF was reacted with EDA to introduce amine functional groups. A solution of EDA in IPA was added to a glass ampoule containing the sample. The reaction was performed for 15–180 min in a thermostated water bath at 60 °C. After the reaction time, the aminated APNWF was removed from the solution and washed thoroughly with methanol. After drying in vacuo, the amine group density was determined using two methods. One is gravimetrically, using the equation: amine group density (mmole/gram-adsorbent)$=[(Wf-Wg)/Wf] \times (1000/MW)$, where *Wg* and *Wf* are the weights of GMA-grafted APNWF before and after amination and *MW* is the molecular weight of EDA. The other method is based on the nitrogen content of aminated APNWF which was determined using an elemental analyzer.

2.4. Batch adsorption

The Cu^{2+} and Ni^{2+} ion solutions were prepared by dissolving cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$) in deionized water. The initial concentration ranged from 10 to 1000 ppm. A weighed amount of the aminated GMA grafted APNWF was added to a 50 mL solution of the metal ion. The batch adsorption studies were conducted in a continuously stirring batch process for 20 h at room temperature with the stirring rate kept at 300 rpm. The metal ion concentrations were measured before and after adsorption. The metal ion uptake by the synthesized adsorbent was calculated by the equation: amount adsorbed (mg metal ion/gram-adsorbent)$=(Co-Cf) \times V/W$, where *Co* and *Cf* are the initial and final concentration (ppm) of the metal ion in the aqueous phase, *V* is the volume of the solution (mL) and *W* the mass of the aminated GMA-grafted APNWF.

2.5. Effect of contact time on Cu^{2+} and Ni^{2+} ion uptake

Approximately 0.2 g of aminated GMA-grafted APNWF was mixed with 100 mL of 7 ppm solution of the metal ion with initial pH of 5. The solution was stirred in a 30 °C thermostated water bath. At appropriate time intervals, the stirring is stopped and 0.2 mL supernatant solution was obtained. The supernatant solutions were filtered with 0.2 μm filter disk and analyzed for residual ion concentration. The amount of adsorbed Cu^{2+} and Ni^{2+} was expressed in terms of percentage removal which was calculated by the equation: percentage removal$=(Co-Ct)/Co \times 100$, where *Co* is the initial ion concentration and *Ct* is the ion concentration of the solution at time t.

2.6. Analysis

The infrared spectra of APNWF, grafted samples and aminated APNWF were examined by a Perkin Elmer Spectrum One FTIR spectrophotometer in attenuated total reflectance (ATR) mode. The samples were scanned in the range 600–4000 cm^{-1} with a resolution of 4 cm^{-1}.

Metal ion concentrations before and after adsorption were determined using a Perkin Elmer Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) Optima 4300 DV. Samples were made 0.1 M in HNO_3 prior to analysis. The wavelengths