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Fabrication of polyacrylonitrile-coated kapok hollow microtubes for adsorption of methyl orange and Cu(II) ions in aqueous solution

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ABSTRACT

Polyacrylonitrile (PAN)-coated kapok hollow microtubes were synthesized using a facile surfactant-assisted method. Cetyltrimethylammonium bromide (CTAB) was employed to assist in polymer deposition and arrangement. The kapok fibers retained its hollow microtube structure after PAN coating. A drastic decrease in water contact angle from 133.43 to 0° was also determined. Generally, thicker and more uniform PAN coating was achieved at higher concentration of CTAB. On the other hand, addition of larger amount of AN resulted in thicker PAN coating. Batch experiments were utilized to investigate the effect of contact time and temperature on the adsorption efficiency of methyl orange dye and Cu(II) from aqueous solution. Isotherm studies revealed that removal of methyl orange and Cu(II) follow the Langmuir isotherm model, with maximum adsorption capacity of 34.72 and 90.09 mg/g, respectively. This suggests that Cu(II) is preferentially adsorbed on the PAN-kapok fibers over methyl orange. Kinetic studies show that the adsorption of methyl orange and Cu(II) on PAN-kapok follow a pseudo-second order kinetic model, indicating chemisorption as the rate-determining step. Based on thermodynamic data, both Cu(II) and methyl orange adsorption is spontaneous and endothermic.

1. Introduction

Water pollution is a rapidly growing concern among developing countries. Stringent environmental regulations have ensured that various contaminants from industrial effluents are removed before its discharge into water bodies. These contaminants include, but are not limited to, heavy metal contaminants, organic matter and harmful microbes. Heavy metal contaminants are not biodegradable, and can persist in an environment for indefinite periods of time. Because of this, even minute amounts of heavy metal pollution can impose health risk if left unchecked due to its tendency to bioaccumulate [1].

Copper (Cu) ions is one of the most commonly used metals with a maximum contaminant level in effluents of 1.3 mg/l from USEPA and 1.0 mg/l from the Philippine Clean Water Act of 1990 [2]. Increase in Cu intake may lead to health problems such as irritation of the central nervous system, mucosal irritation, kidney and liver failure [3]. On the other hand, anionic azo dyes such as methyl orange (MO), with molecular formula $C_{14}H_{14}N_3NaO_3S$, is one of the commonly used dyes in several industries such as cosmetics, foodstuffs, leather, paper and textiles [4]. Exposure to high concentration of MO can cause harmful effects such as cyanosis, diarrhea, increased heart rate, shock and vomiting [5].

Many advanced methods have been employed in order to provide clean water resources, such as solvent extraction, membrane separation, electrochemical operation, adsorption, catalysis and ion exchange [6,7]. Among these, adsorption and ion exchange are the most widely used for the removal of contaminants from solutions due to their flexibility, ease of application and efficiency. In fact, adsorption has been considered as a low cost efficient alternative for the treatment of both organic pollutants and heavy metals in waste water relative to other cleaning technology [8]. Common adsorbents are activated carbon, metal oxides, various polymers, resins and biosorbents [9–11].

Kapok trees are commonly found in tropical countries. They are characterized by their fruits that releases low density fibers when ripe. The fibers exhibit a hollow lumen of about 10–20 μm in diameter, with wall thickness of about 1–2 μm [12,13]. This microtube structure results in higher surface area compared to other plant fibers, which is desirable as template material for various applications [14]. However, kapok fibers are naturally hydrophobic. On the other hand, previous studies on polyacrylonitrile (PAN) fibers

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fabricated by electrospinning reveal that the material is a highly efficient adsorbent for heavy metals [15]. Therefore, deposition of PAN onto hollow microtubular kapok fibers may result in a composite material with superior adsorption capacity.

In general, polymeric materials which have capability to absorb different types of pollutants are candidate materials to deposit on the surface of the kapok microtubes. These include polymers having functional groups which are (1) polar, (2) containing lone pair of electrons and (3) double or triple bonds. Functional groups that have polarity and which contains lone pair of electrons are capable of attracting (1) ionic pollutants (*e.g.*, metal ions) and (2) pollutants with polar functional groups. On the other hand, functional groups with double or triple bonds may have the capability of forming complexes with some metals. Polyacrylonitrile [15–19] has low density, resistant to corrosion, excellent mechanical strength, large elastic modulus, and thermal stability. Polyacrylonitrile has also been recognized as a highly efficient material for the collection, enrichment and subsequent removal of heavy metal ions dissolved in solution. It has nitrile functional group which has (1) lone pair of electrons, (2) strong polarity and (3) carbon–nitrogen triple bonds. The lone pair of electrons and its strong polarity has potential of attracting ionic pollutants (*e.g.*, Cu ions) and pollutants with polar functional group. On the other hand, its triple bonds are capable of forming complexes with metal. PAN is also cheap and widely available.

In this work, kapok fibers were coated with a thin layer of PAN using CTAB as surfactant. The effect of CTAB concentration on the morphology and wetting property of the PAN-kapok fibers were analyzed by scanning electron microscopy (SEM), Fourier Transform-Infrared Spectroscopy (FTIR), and water contact angle measurement. The PAN-kapok fibers were then utilized in the removal of MO and Cu(II) from aqueous solution. Equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm models, while kinetics was determined using the pseudo-first order and pseudo-second order models. Various thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated.

2. Experimental

2.1. Preparation of polyacrylonitrile-kapok hollow microtubes

Kapok pods were harvested from Rizal, Nueva Ecija, Philippines. The kapok hulls and seeds were removed by hand in order to obtain the hollow fibers. The fibers were then washed three times with diluted ethanol in order to remove impurities. Hexadecyltrimethylammonium bromide (CTAB, 99.0%), potassium peroxodisulfate (KPS, 98.0%), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 99.5%), and acrylonitrile monomer (C_3H_3N) were purchased from Nacalai Tesque. Absolute ethanol (C_2H_6O) was supplied by Wako. All reagents were analytical grade. Deionized water was used throughout the experiment.

In this study, about 30 mg of washed and dried kapok fibers were immersed in 10–40 mg CTAB solution for 1 h. Then, 0.75–3.00 ml of acrylonitrile was injected to the solution and heated to 70 °C for 30 min. 60 mg KPS was then added to the total solution to catalyze the polymerization process. The mixture was stirred for 6 h and then washed with deionized water and ethanol. Finally, the PAN-coated kapok fibers were dried in air.

2.2. Characterization

The surface morphology of the kapok fibers was observed using a scanning electron microscope (SEM, Hitachi SU6600). The presence of PAN on the kapok's surface was evaluated using Fourier Transform Infrared (FT-IR) spectroscopy. Water contact angle was then performed to determine the wetting properties of the PAN-kapok fibers.

2.3. Adsorption experiments

Batch experiments were carried out using 30 mg PAN-kapok fibers in a 20 ml solution of MO and Cu(II) at 25 °C. The effect of contact time (3–1400 min) on the adsorption capacity of PAN-kapok fibers in the removal of Cu(II) and MO was performed. To evaluate the equilibrium data, experiments were performed using 30 mg PAN-kapok fibers in a 20 ml Cu(II) solution with initial concentration range from 40 to 280 mg/l, where the solution was kept for 24 h. For the kinetic study, about 30 mg PAN-kapok fibers and 20 ml solution with initial concentration of 200 mg/l Cu(II) and 160 mg/l MO were agitated under 25 °C at pre-determined time intervals (3–1400 min). To study the thermal effects on PAN-kapok fiber adsorption, the temperature was varied from 298 to 343 K. About 30 mg PAN-kapok fibers was placed in contact with 20 ml of solution for 24 h. The residual concentration of Cu(II) and MO was analyzed using atomic absorption and UV-Vis spectroscopy, respectively.

3. Results and discussions

3.1. Effect of CTAB concentration

Fig. 1 shows the SEM images of kapok fibers after PAN deposition with increasing CTAB concentrations (10–40 mg). It can be clearly seen in Fig. 1a that large agglomerates of PAN particles have sparsely adhered onto the kapok surface when only 10 mg of CTAB was used. The PAN particles are about 4–12 µm in size. The coating was also apparently unstable since it could be easily removed from the fiber surface by weak abrasion. With an increase of CTAB concentration from 10 to 15 mg, a substantial improvement in coating stability and a reduction in PAN particle size to around 2 µm were observed. The PAN layer is noticeably smoother and more even as seen in Fig. 1b. Additionally, the degree of PAN agglomeration visibly decreased throughout the fiber surface. Further increasing the amount of CTAB to 20 mg resulted in a homogeneous coating of PAN onto the kapok surface. No PAN agglomerations can be observed as shown in inset of Fig. 1d. The outer and inner diameters of the kapok fiber composite are about 27.63 and 22.97 µm, respectively. This indicates that the PAN coating is about 0.67 µm in thickness. Addition of 30–40 mg CTAB yielded no significant difference in the morphology and topography of the PAN-kapok fibers. The PAN layer is approximately 0.61 and 0.60 µm for samples with 30 and 40 mg of CTAB, respectively. In all CTAB concentrations experimented, the kapok fibers retained their hollow structure, suggesting no reduction in the kapok surface area. These results strongly indicate that CTAB has a significant contribution in the arrangement of PAN particles across the kapok fiber surface. [20]

Fig. 2 shows the corresponding FTIR spectra of pristine kapok and PAN-kapok composites modified using 10-40 mg of CTAB. Several characteristic bands were observed in the FTIR spectra of pristine kapok fibers and PAN-coated kapok. Notable peaks due to C–H stretching, C–H bending and C–C stretching are observed in both pristine and PAN-coated kapok fibers at 2900, 1200-1400, and 1020 cm^{-1}, respectively. All peaks are common for cellulosic materials [21]. On the other hand, the broad band of pristine kapok at about 3400 cm^{-1} derived from the stretching vibration of O–H in cellulose has become less pronounced after PAN coating in all CTAB concentration experimented. It is known that PAN does not have OH functional groups in its structure.

On the other hand, the FTIR spectra for the PAN-kapok fibers in Fig. 2b–d show prominent peaks of C≡N stretching at around 2250 cm^{-1}, a nitrile functional group that is absent in the pristine

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