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Fabrication of kapok paper-zinc oxide-polyaniline hybrid nanocomposite for methyl orange removal

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ABSTRACT

In this study, hydrophilic kapok papers (KP) with grammage of 60 g m^{-2} were synthesized by treating naturally hydrophobic kapok fibers with chloroform and sodium chlorite. A hybrid nanocomposite consisting of zinc oxide (ZnO) and polyaniline (PANI) was successively deposited on the hand-made paper. SEM images show nano-size PANI and ZnO particles. XRD results revealed amorphous structure of the PANI with presence of peaks correlating to ZnO. FT-IR showed the change on kapok fibers upon chemical treatment and confirmed the presence of PANI on the synthesized paper. The KP-ZnO-PANI nanocomposite was further applied to test the photocatalytic removal of methyl orange (MO) from aqueous solution under UV irradiation. Results showed that the hybrid nanocomposite could be employed as an adsorbent of MO dye and was 10% more efficient when irradiated under UV light.

1. Introduction

Exponential population growth elicits rapid industrialization which imparts a role in water pollution proliferation. Industries such as those in the food and textile division contribute to the dissemination of pollutants mainly in the form of effluents. These effluents contain organic and synthetic dyes that are toxic to aquatic creatures and humans even at very low concentrations, i.e. 1 ppm [1]. Some of the adverse effects of these dyes include skin diseases, kidney dysfunction, throat swelling, and neurological problems. Some are even carcinogenic. There are already numerous ways of purifying water such as coagulation [2,3], electrofiltration [4], membrane separation process [5], electro-oxidation [6], ion exchange [7], reverse osmosis [8], and adsorption [9–11]. Among these techniques, adsorption has been proven as one of the most preferred method to treat waste water due to its easy handling, high efficiency, reusability, and availability of different adsorbents [9–11].

Polyaniline (PANI) is one of the conducting polymers with promising applications due to its high conductivity, simple synthesis, good environmental stability, and large variety of applications [12–16]. Additionally, PANI is a material with good hole conductivity. PANI is already an established adsorbent of synthetic and organic dyes in aqueous solution, such as methyl orange [17,18], methylene blue [11,19], malachite green [20], reactive orange 16 [21], congo red [22], eosin yellow [23], naphthol blue black [23], brilliant green [24], crystal violet [10], amido black 10B [25], etc.

Adsorption using suspended nanoparticles is a common and efficient process of removing contaminants in an aqueous solution. However, the subsequent removal of the nanoparticles dispersed in the liquid solution is impractical and burdensome. Additionally, if the nanoparticles were not fully filtered from the water, it can be another source of pollutant. Therefore, it is of best interest that the nanoparticles be attached to a support [26]. Paper could be a great substrate for nanoparticles for this application because of its flexibility. Furthermore, paper substrates are cheap and made up of biological material which, in turn have a better biodegradability compared to synthetic materials, such as polyethylene, PVC, nylon, etc. In this study, we will synthesize our own paper support by utilizing kapok fibers.

Kapok, *Ceiba pentandra* (L.) Gaertn., is a tropical tree widely found in tropical countries, such as the Philippines and other parts of South East Asia. The fruit of kapok is cultivated for its cotton-like fluff that is mainly used for stuffing of pillows, mattresses, and upholstery. It is also used as filling for life preservers and floatation devices due to its natural buoyancy and hydrophobicity [27]. The hydrophobic property of kapok fibers (KF) comes from its high lignin content. KF is mainly composed of 64% cellulose, 13% lignin, and 23% is composed of a combination of hemicelluloses, pectin, and wax that coats the individual fibers

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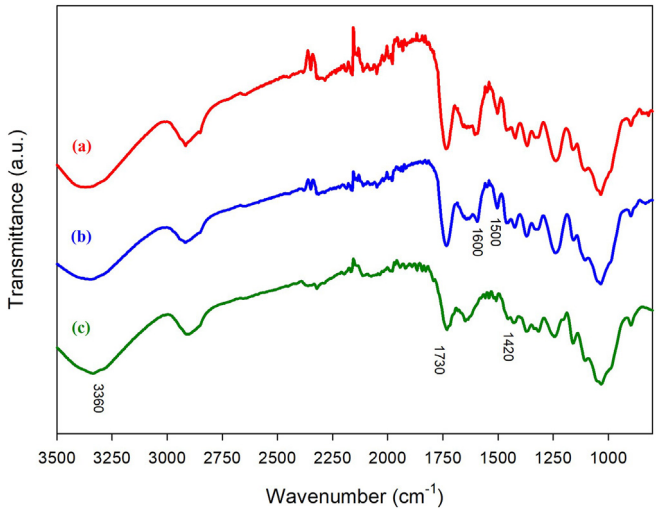

Fig. 1. (Color online) FT-IR spectra of (a) raw kapok fiber, (b) chloroform-treated kapok fiber, and (c) chloroform and sodium chlorite-treated kapok fiber made into kapok paper. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compared to cotton which is at least 90% cellulose [28]. Nevertheless, by chemical treatment of KF, it is still a good potential one pulp source for papermaking [29].

Photocatalytic decomposition of organic dyes present in contaminated water and their conversion into harmless component have been broadly investigated. Photocatalysis using metal oxide materials such as ZnO [30,31], titanium oxide (TiO_2) [32], zirconia (ZrO_2) [19], tin oxide (SnO_2) [33], copper oxide (CuO) [34], etc. have been extensively used to degrade non-biodegradable organic dyes by photocatalytic routes. Among the different metal oxides, zinc oxide (ZnO) is an important oxide semiconductor photocatalyst with a mechanism of photocatalysis similar to TiO_2 [35,36]. ZnO is more advantageous due to its low cost, wider band gap (3.37 eV), large binding energy (60 meV), many active sites, high surface reactivity, and environmentally stable [37,38]. Additionally, this large band gap is suitable for the collection of high energy photons. However, since ZnO cannot utilize a large part of solar energy with the exception of ultraviolet (UV) radiation, hybrid components with ZnO are being explored [39]. ZnO can be combined with polymeric and organic nanoparticles (e.g. polyaniline, polypyrrole, polythiophene, etc), leading to photocatalytic enhancement [20].

In the present study, high value adding was performed on kapok fibers by engineering it to be a photocatalytic dye adsorbent. It has been established that naturally occurring hydrophobic KF can be altered to make it a potential pulp source for paper. By coating the kapok fiber papers with ZnO and PANI, a KF-ZnO-PANI hybrid nanocomposite was produced. Its adsorption and degradation of methyl orange (MO) dye under dark and UV irradiation conditions was then investigated.

2. Methodology

2.1. Materials

The kapok fibers were harvested from Los Baños, Laguna, Philippines and hand-teared to remove seeds, wood fragments and other unnecessary speck. Aniline [$C_6H_5NH_2$] (Loba Chemie PVT. LTD.), hydrochloric acid (HCl) (Scharlab S.L.), ammonium persulfate [$(NH_4)_2S_2O_8$] (HiMedia Laboratories) (APS), zinc acetate dihydrate [$Zn(O_2CCH_3)_2(H_2O)_2$] (Techno PharmChem), sodium hydroxide (NaOH) (Macron Fine Chemicals), sodium chlorite ($NaClO_2$) (Sigma-Aldrich), chloroform ($CHCl_3$) (RCI Labscan Limited), acetic acid [CH_3COOH] (Macron Fine Chemicals) (AcOH) and methyl orange [$C_{14}H_{14}N_3NaO_3S$] (UniChem Laboratories LTD.) (MO) were used as received without further purification. Methanol and ethanol (Univar), and deionized water (dH_2O) was frequently used in this experiment for washing purposes and dilution of chemicals, respectively.

2.2. Preparation of hand-made kapok paper

In a typical experiment, 1 g of kapok fibers was pre-treated with $CHCl_3$ to remove cutin and wax from the surface [40,41]. The fibers were again dispersed in $CHCl_3$ and refluxed for 4 h at 60 °C under constant magnetic stirring. Afterwards, kapok fibers were removed from the solvent, washed with methanol, and air dried for at least 12 h. The fibers were then treated with $NaClO_2$ to remove the lignin and produce holocellulose fibers [40–44]. The $CHCl_3$-treated fibers were placed in 60 mL of buffer solution made from 60 mL acetic acid and 32.4 mM NaOH solution. Then, 6 mL of 20 wt% $NaClO_2$ solution was added in the mixture and placed in a water bath at 75 °C. Additional, 6 mL of the $NaClO_2$ solution were added after 0.5, 1.0, 1.75, and 2.5 h. After the last addition, the bath was kept for additional 45 min to continue the digestion process. After cooling, the fibers were removed from the mixture via filtration. It was noticed that the fibers turned from yellow to white due to bleaching property of $NaClO_2$. The fibers were washed with cold water, 1% AcOH and methanol, followed by drying for 12 h. About 1 g dried fibers were soaked in 299 mL dH_2O to make 0.33% pulp consistency computed using the equation below.

$$\%Consistency = \frac{w_{fiber}}{w_{fiber} + w_{dH_2O}} \times 100\% \quad (1)$$

The slurry was beaten to a pulp using a commercial osterizer. After this process, the water was removed from the pulp using a Büchner funnel, dried and flattened. Three pieces of kapok paper (KP) with diameter of 7 cm and grammage of 60 g m^{-2} were made from 1 g of fibers. The synthesized kapok papers were cut to 1 × 5 cm^2 pieces prior to PANI and ZnO deposition.

2.3. Deposition of zinc oxide and polyaniline on kapok paper

The kapok sheet was dipped in 0.2 M $Zn(O_2CCH_3)_2(H_2O)_2$ solution for 1 h, then dried. The paper was then immersed in 0.1 M NaOH solution for 10 min. Finally, the kapok paper was annealed for 24 h at 80 °C to form ZnO. The ZnO-deposited kapok paper was coated with a layer of PANI using the same method. First, the paper was dipped in a 5% aniline-HCl (1 M) solution for 10 s to adhere aniline molecules. Then, the paper was immersed in dH_2O for 5 s to remove poorly attached aniline. Finally, the paper was placed into 0.25 M APS for 5 s to allow polymerization of aniline. This cycle of dipping was repeated for a number of times to ensure polymerization and attachment of aniline. To optimize the deposition parameters of polyaniline, the removal efficiency of adsorption of MO was tested on KP with different number of PANI deposition cycles. The optimized PANI deposition cycle was then used for the synthesis of KP-ZnO-PANI nanocomposite.

2.4. Adsorption and photocatalytic activity experiments

1 × 1 cm^2 of KP-PANI nanocomposite was immersed in 30 mL 25 mg L^{-1} MO dye solution under dark conditions with stirring at 100 rpm for 6 h. At appropriate time intervals, 2 mL of the solution was collected. For the photocatalytic experiments, 1 × 1 cm^2 of KP-ZnO-PANI nanohybrid was immersed in 30 mL 25 mg L^{-1} MO dye solution with stirring at 100 rpm for 24 h under dark and UV light (3 × 20 W). Similarly, 2 mL aliquots were collected at appropriate time intervals. The removal efficiency of nanocomposites for MO was calculated by:

$$R(\%) = \frac{(C_o - C_f)}{C_o} \times 100 \quad (2)$$

where C_o is the initial dye concentration (mg L^{-1}) and C_f is the