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Research Article

Nanocellulose/Polyvinyl Alcohol Hydrogel with Adsorption and Photocatalytic Properties

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Abstract

Multifunctional Nanocellulose/Polyvinyl alcohol hydrogels with adsorption and photocatalytic properties towards an anionic dye Metanil Yellow (MY) was investigated. Office wastepaper was used as the raw material for synthesizing nanocellulose. The hydrogels were fabricated via the sol-gel method. The adsorption and photocatalytic properties of the hydrogel were evaluated under dark and sunlight irradiation respectively. Photo-stability of the hydrogels was studied by evaluating their recyclability efficiency. This study clearly reveals the potential application of the present system for anionic MY dye degradation.

Keywords: *Hydrogel, Dye degradation, Photo catalysis*

1. Introduction

In recent years, we have seen a significant change in lifestyle as a result of the development and progress of less costly products and effective methods. It is vital to use sustainable and renewable resources so as to keep up with this growing trend [1]. Cellulose is one of the most profuse polymers in nature with linear chain of glucose units composed of β-1, 4–glycosidic bonds which can be extracted from plant cell wall, cotton, woods and so on. Nanocellulose is a polysaccharide that achieved attention due to its renewability, biodegradability, low cost, availability, excellent stiffness, and high surface area [2,3]. Nanocellulose is mainly classified into three, based on their size, properties and synthesis method. They are cellulose nanofibers, cellulose nanocrystals, and Bacterial Cellulose. Among these, cellulose nanofibers (CNFs) have gained wide attention due to their nanoscale size composed of elongated cellulose chains, their characteristic mechanical strength, high flexibility, large number of hydroxyl groups which are accessible for surface modification [3-6]. The mass production and wide use of paper essentially requires suitable methods to recycle the large amount of wastepaper produced. Wastepaper has the potential as a source material for the production of nanocellulose due to their cellulosic content [2,7]. Hence, the present work focuses on the synthesis of CNFs from waste office paper as an environmentally friendly approach of raw material.

A hydrogel is a three-dimensional hydrophilic network of polymers made from synthetic or natural polymers that can hold a significant amount of water while maintaining its structure as a result of physical or chemical cross-linking of individual polymer chains [8]. The growing need for green and cost-effective products prompted the development of natural polymer-based hydrogels. The unique properties of nanocellulose make it favorable to form hydrogels that have the potential to be used as an ecofriendly adsorbent [9]. Studies have shown that cellulose is an excellent reinforcing agent for Polyvinyl Alcohol (PVA) polymer matrix. Because of nanocellulose's high surface area and abundance of hydroxyl groups, it interacts with PVA [10].

An enormous amount of artificial dyes is manufactured each year all over the world, and they are often divided into three categories: anionic dyes, cationic dyes, and non-ionic dyes. Industries have made substantial use of anionic dyes, particularly in the manufacture of textiles, leather, cosmetics, and plastics [11,12]. The anionic dye Metanil Yellow (MY) is toxic and carcinogenic with high solubility in water and it is widely used because of its low cost. These dyes discharged together with industrial waste water are dangerous to humans and environment [13]. Thus, dyes must be effectively detached from the discharged wastewater to tackle the biological, ecological and industrial issues [14]. Dye wastewater treatment has recently received much attention, and many technologies, such as adsorption, chemical degradation, photocatalysis, and coagulation, have been developed. One of the best approaches to eliminating dyes is photocatalytic degradation, which has the benefits of an environmentally friendly procedure, high photo-degradation efficacy, and reusability [15]. Also, much attention has been given to produce dye adsorbents using nanocellulose [16,17]. Since the hydrogels have a three-dimensional polymeric network that can absorb a lot of water and are hydrophilic, they are suitable for the removal of dyes [18].

The aim of the present study was to prepare an eco-friendly and low-cost adsorbent using nanocellulose as the key ingredient and also evaluate its photocatalytic degradation efficiency. Here CNFs were extracted from waste office paper via simple chemical method. Then cellulose based hydrogels were synthesized using CNFs and Polyvinyl Alcohol (PVA) by sol-gel method. In this work, the adsorption and photocatalytic degradation performance of cellulose-based hydrogel towards Metanil Yellow (MY) dye was evaluated. The reusability of the hydrogel was also evaluated to study its efficiency.

2. Materials and methods

2.1. Synthesis of Nanocellulose from waste office paper

CNFs were prepared according to previously reported work [7]. The desired amount of office wastepaper was washed with hot water several times. Then required amount of washed slurry and 2wt% NaOH solution were mixed well at 90 ^{0}C for 2 hours. A neutral pH was attained by filtering and washing the alkali-treated slurry with distilled water. The slurry was processed via acid hydrolysis and dried at 80 ^{0}C for 90 minutes and the obtained sample was powdered well. The powdered sample was kept for further use. This sample was labelled as CNFs.

2.2. Synthesis of CNFs/PVA hydrogel

The PVA solution (5wt %) and CNFs (100 mg) were mixed well under continuous stirring at an rpm of 5000 for 15 minutes. Then sulfuric acid (0.5M) and glutaraldehyde (2wt %) were added to it. After mixing well, the prepared samples were placed in a mold and heated for 3 hours in an oven at 90 ^{0}C. Then it was washed with distilled water to remove excess impurities present in it [19]. This sample was labelled as CPH. CPH stands for Cellulose-PVA hydrogel.

2.3. Characterization techniques

The structural confirmation of CNFs was studied by FTIR analysis using Perkin Elmer Spectrum Version 10.5.2 over the range 500 cm^{-1} to 4000 cm^{-1}. The morphology of CNFs/PVA hydrogel (CPH) was analyzed by SEM, JEOL JSM 6390 LV. The optical characterization of dye degradation was done using UV-Visible Absorption Spectroscopy using Shimadzu UV 1800 spectrophotometer. The intensity of sunlight was measured using MTQ 1010A lux meter.

2.4. Adsorption experiments of dye

A calculated amount of MY dye was dissolved in the required amount of distilled water to make the stock solution. The Beer-Lambert plot (graph of absorbance versus concentration) was used as the calibration curve to determine the concentration of remaining dye in the solution [20]. These experiments were performed in a 100 mL beaker with constant stirring at room temperature. The prepared hydrogel (~1.250 g) was immersed into the dye solution (15 mL with a certain concentration). As polluted wastewater in this case, dye solutions with different concentrations (5, 10, 15, and 20 mg/L) were used. The concentration of MY dye was evaluated by UV-Vis spectrophotometer at λ=437 nm. The equilibrium adsorption capacity, q_e (mg/ g), the adsorption capacity at time t, q_t (mg/g) and dye removal efficiency (E %), were calculated using the following equations [21].

$$q_e = \frac{(C_0 - C_e)V}{W} \text{ ………. (1)}$$

$$q_t = \frac{(C_0 - C_t)V}{W} \text{ ………. (2)}$$

$$E\% = \frac{(C_0 - C_e)}{C_0} \text{ ………. (3)}$$

where C_0 is the initial concentration of the dye, C_t is the concentration of dye at time t, C_e is the equilibrium concentration of dye, V is the volume of the dye solution (mL) and W is the amount of the adsorbent (g).

2.5. Photocatalytic degradation of MY dye using CNFs/PVA hydrogel

The photocatalytic degradation of MY dye was carried out under direct natural sunlight irradiation. The intensity of sunlight prior to the degradation reaction is found to be 56000 W/m^2 and throughout the experiment, the intensity of the sunlight was monitored. The intensity is increased with increase in the irradiation time and reached the maximum value of 60000 W/m^2. The CPH was taken in a 100 mL beaker containing 15 mL of MY dye solution (25mg/L) and stirred for 1 h under dark conditions to make the hydrogel and MY solution reach the adsorption and desorption equilibrium. Then, the system was exposed to sunlight and the remaining dye concentration was determined by UV-Vis spectrophotometer at λ=437 nm.

3. Results and Discussion

3.1. FTIR analysis

Figure 1 represents the FTIR analysis of CNFs prepared from waste office paper. A broad peak around 3400 cm^{-1} to 3600 cm^{-1} is attributed to the stretching vibration of –OH functional group and revealed the hydrophilic nature of the nanocellulose. The peak around 2800 cm^{-1} - 3000 cm^{-1} is due to C-H stretching vibration in $–CH_3$ and $–CH_2$- linkage. Characteristic peaks assigned to cellulose are observed in the region of 1630 cm^{-1} – 900 cm^{-1}. An aromatic C-C stretching is present at 1500 cm^{-1}. At 1641 cm^{-1} and 1163 cm^{-1}, OH bending of absorbed water is seen and attributed to the adsorbed water in the amorphous region of the cellulose. At 1325 cm^{-1} and 1371 cm^{-1} there is C-H bending. The amount of cellulose's crystalline structure is shown by the peak at 1420–1430 cm^{-1}, while the amorphous region is represented by the band at 897 $cm^{-1.}$ There is C-H stretching vibration at 1000 cm^{-1} and 2894 cm^{-1} [22,23].

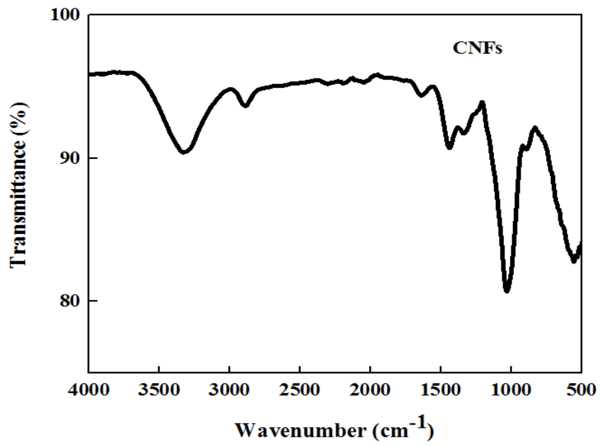

Figure 1: FTIR spectrum of CNFs prepared from waste office paper

3.2. Morphological study

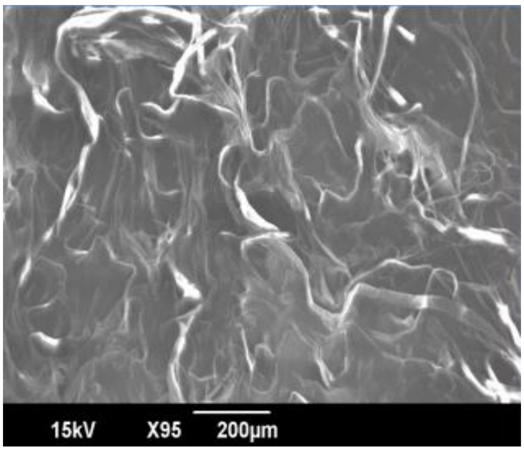

Figure 2: SEM image of CPH hydrogel

Figure 2 shows the SEM image of the prepared hydrogel. The hydrogel exhibited a uniform but rough surface. It showed that the fibrous shaped nanocellulose is cross-linked well with PVA in the hydrogel. This homogeneous dispersion could be attributed to the interaction between nanocellulose and PVA chains. It revealed porous structure, with pores which are connected, irregular and have denser walls indicating the cellulose content. Also, nanocellulose are cross-linked well with PVA matrix.

3.3. Adsorption of dyes

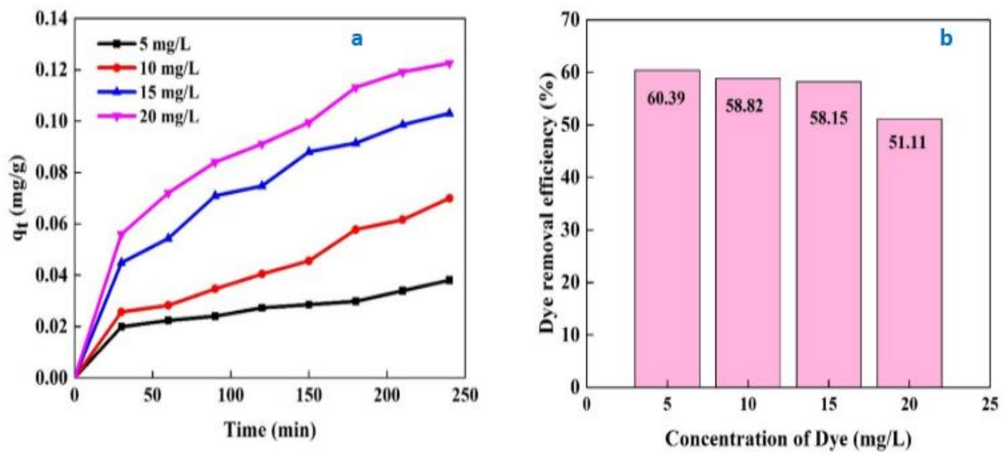

Figure 3: (a) Effect of the contact time on the adsorption of the dye for adsorption of MY on CPH and (b) Dye removal efficiency of CPH for different concentration of dye

The investigation of dye adsorption properties is of great importance in the practical application of hydrogel-based materials. MY dye was used in the adsorption test to confirm that the as-prepared CPH hydrogels are effective in water remediation. Batch adsorption experiments were done by continuously stirring the dye solution containing CPH for an interval ranging from 0 to 240 min. The equilibrium was achieved after 240 min of mixing. The results are shown in Figure 3a. The adsorption rate raised very fast at the initial stage then slowed down and finally reached the equilibrium. Such phenomenon could be explained that the hydrogels had many free functional sites at the first stage and would react with the MY dye molecules as soon as they contacted. The dye removal efficiency of CPH for different concentration of dye was shown in Figure 3b. The figure makes it evident that the hydrogel's ability to remove dye reduced as dye concentration increased. An important factor in driving mass diffusion and transfer between the aqueous and solid states is the dye's initial concentration. The decreasing trend suggests that the adsorbent's adsorbing sites are saturated [21].

3.4. Photo degradation performance

Metanil Yellow is an acidic, anionic azo dye. It is toxic, carcinogenic, highly water soluble and used widely as a pigment in textile industries, food processing industries and so on. The hydroxyl groups present in the CPH make the nanocellulose surface cationic in nature which results in the adsorption of anionic dyes on its surface via chemical as well as physical forces. The anionic dye Metanil Yellow has a polycyclic structure that contain C, S, N, O_2 or another non-carbon atom in their rings. The dye molecules with modest structure and low molecular weight are easily degraded. The photons from sunlight help in the promotion of electrons and thus in dye degradation. When the hydrogel was subjected under sunlight, the electrons in the valence band (VB) get excited and it is moved to the conduction band (CB) of the hydrogel which produce hole (h^+) in VB and an electron (e^-) in the CB. Then these pairs of photo induced species h^+_{vb} and e^-_{cb} moved to the surface of hydrogel and interact with dissolved oxygen, surface hydroxyl group and thus creates hydroxyl and superoxide radical anions. Later, these radicals decomposed the dyes into several chemical intermediates, and these intermediates were totally reduced into carbon dioxide, water, ammonium, and nitrate ion. [24,25]. The photocatalytic experiment was conducted in the presence of solar light to ascertain the hydrogel's possible applications. The photocatalytic degradation of MY dye showed that 98.3 % of degradation is observed in the presence of CPH under solar light irradiation for 80 minutes. Figure 4a shows the UV-Vis spectra of MY dye using CPH under direct sunlight irradiation. The main absorption peak for MY occurs at 437 nm and this peak decreased during reaction. About 60 % of dye is degraded after 50 mins of exposure of sunlight. The rate of dye removal increased steadily with time. In about 80 mins, approximately 98% of MY dye has been degraded efficiently by CPH. During the reaction the solution colour changed from an initial yellow to colourless within 80 min of sunlight exposure. Figure 4b shows the photocatalytic diagram of CPH. It clearly shows that the dye degradation is rapid under direct sunlight irradiation.

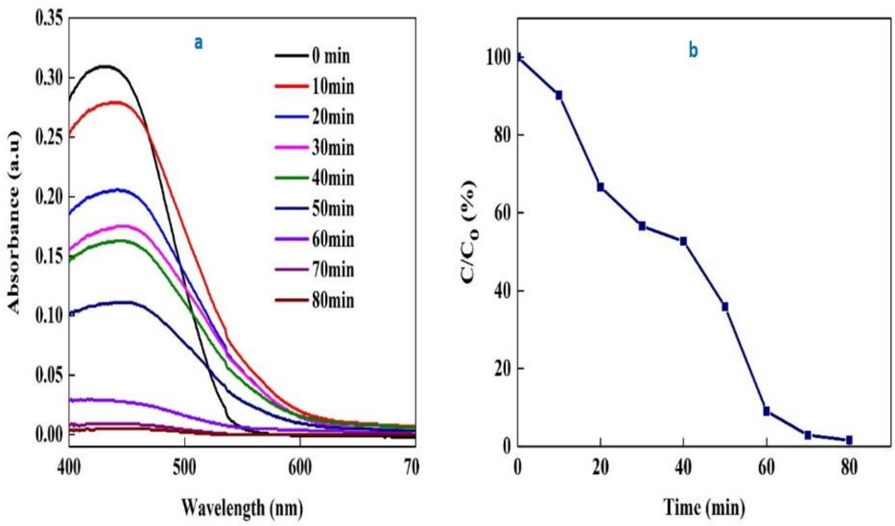

Figure 4: (a) UV-Vis spectra of MY dye using CPH under direct sunlight irradiation and (b) Photo degradation of MY dye using CPH

3.5. Reusability of CNFs/PVA hydrogel

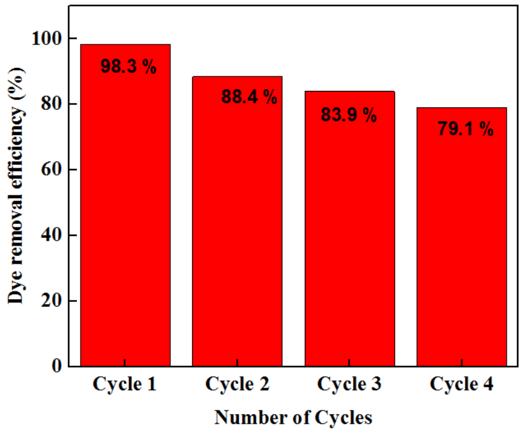

Figure 5: Reusability of CPH for 4 cycles under sunlight irradiation

In order to determine if an adsorbent can be used on a wide scale and to design adsorbents for the treatment of wastewater, it is essential to consider its reusability and stability. In the present study, the reusable cycle of CPH for the removal of MY dye is repeated four times without any other treatments under sun light irradiation and the results are shown in Figure 5. However, the dye removal efficacy was decreased as the cycles continued (e.g. CPH: 98.3 % to 79.1 %). This could be due to the shrinkage of hydrogel and the associated decrease in active surface area.

4. Conclusion

In summary, an eco-friendly and low-cost adsorbent using nanocellulose was prepared by a simple and cost-effective method. Both in the dark and under direct sunlight, the hydrogels were employed to remove the harmful azo dye Metanil Yellow. The results indicated that the sunlight irradiation enhances the rate of degradation of dye. The maximum dye removal efficiency of CPH was found to be 98.3% within 80 mins of sunlight irradiation. The reusability of the hydrogel was evaluated and it is observed that the hydrogels can effectively be reused without any other treatments up to 4 cycles. The advantages of excellent adsorption ability, photocatalytic properties and the reusability indicated the CNFs/PVA Hydrogel is a promising adsorbent for waste water treatment.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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