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TiO_2/amidoxime-modified polyacrylonitrile nanofibers and its application for the photodegradation of methyl blue in aqueous medium

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ABSTRACT

Polyacrylonitrile (PAN) nanofibers were prepared by an electrospinning technique. PAN nanofibers were chemically modified with amidoxime groups. The titanium oxide (TiO_2) was then introduced to amidoxime-modified PAN (OM-PAN), which was then used for the photodegradation of methylene blue in aqueous solution. The morphology and photodegradation study was investigated by using scanning electron microscopy (SEM) and UV-visible spectrophotometry, respectively. The SEM study showed the presence of TiO_2 particles on the surface of OM-PAN nanofiber mat in agglomerated form and was confirmed by energy dispersive X-rays analysis. The photodegradation study of methylene blue showed that the dye degradation was increased as increased in the irradiation time. The effect of pH on degradation efficiency showed that with an increase in pH the degradation efficiency increases.

Keywords: Photodegradation; Nanofibers; Methylene blue; Amidoxime-modified polyacrylonitrile

1. Introduction

Dyes and pigments are common water pollutants, which are frequently found in industrial effluents. The diversity in dyes structures comes from the use of different chromophoric groups, such as azo, anthraquinone, triarylmethane, and phthalocyanine groups; and different application technologies like reactive, direct, disperse, and vat dyeing. Most of these dyes are toxic, mutagenic or carcinogenic, and non biodegradable because of their large size and complex structures [1]. A small quantity of dye in water is not only visible but also interferes with transmission of sunlight into streams and therefore, reduces photosynthetic activity. Various physical, chemical, and biological methods such as precipitation, adsorption, ozonization, flocculation, reverse osmosis, and ultrafiltration are used for the removal of coloring material from aqueous solution [2–5]. Recently, extensive research is going on semiconductor photocatalysis, which is widely used for the degradation of organic dye. The photocatalytic degradation method is generally based on generation of hydroxyl radical and superoxide anion radical, which is responsible for the degradation of organic pollutants. Various research groups are working on photodegradation of dyes, for example, Deng et al. prepared rectorite-TiO_2 and used it as a photocatalyst for the degradation of methyl orange in aqueous solution under sunlight. They found that about 95% of dye was degraded within 8 h [6]. Pant et al. prepared TiO_2/nylon-6 electrospun nanocomposite mat containing silver nanoparticles and used it as photocatlyst

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against methylene blue. They also studied antibacterial properties (*Escherichia coli*) and found that the composites nanofibers showed good photocatalytic and antibacterial properties [7]. Moon et al. prepared Sb-doped TiO_2 photocatlyst by coprecipitation method, and used it for the degradation of organic dye in aqueous solution [8].

In the present study, the nitrile group of Polyacrylonitrile (PAN) nanofibers was chemically modified by amidoxim and then TiO_2 was introduced onto OM-PAN nanofibers. The amidoxime modified PAN (TiO_2/OM-PAN) nanofibers were used for the photodegradation of methylene blue in aqueous solution as function of time. In our knowledge, the OM-PAN nanofiber-supported TiO_2 is not used before for the photodegradation of methylene blue in aqueous solution. The selection of nanofibers is due to its large surface area and high aspect ratio, which may helpful for the better dispersion TiO_2 nanoparticles. The TiO_2 is selected because of its attractive applications in cosmetics, electrodes, capacitors, solar cells, and catalysis [9]. It is also a prominent semiconductor photocatalyst, which is extensively used for the decomposition of a wide variety of organic and inorganic substances due to its low cost, high photocatalytic activity, nontoxicity, and long-term stability against photo- and chemical corrosion. The TiO_2/OM-PAN was characterized by scanning electron microscopy (SEM) and energy dispersive X-rays (EDX). The degradation of dye was determined by UV–vis spectrophotometer. The photodegradation of methylene blue was also studied at different pH.

2. Experimental

2.1. Materials

Sodium carbonate and hydrxylamine hydrochloride were purchased from Scharlau (CAS number 5470-11-1) and Merck companies, respectively, and used as received. Methylene blue was purchased from Bio basic Inco. The dimethylformamide (DMF) (CAS number 319937) was also purchased from Aldrich. The PAN nanofibers mat was prepared by the same method as discussed somewhere else [10]. 15 wt% solutions were prepared by dissolving PAN in DMF and the solution added to a 10 mL glass syringe with a needle tip (0.5 mm diameter). The flow rate of the polymer solutions, voltage, and distance between the needle tip and collector was 1 mL/h, 20 kV, and 15 cm, respectively.

2.2. Functionalization of PAN nanofibers

Hydroxylamine hydrochloride (8 g), sodium carbonate (6 g), 100 mL deionized water, and 2 g of PAN nanofiber mat were taken in a flask and heated at 70°C for 75 min. After the required reaction time, the nanofiber mat was washed several times with distilled water in order to remove the unreacted materials, then dried in oven at 80°C and stored for further use [11].

2.3. Photodegradation of methylene blue

The OM-PAN nanofiber mat (0.7 g), TiO_2 (0.05 g), and distilled water (10 mL) were taken in a beaker and stirred for 1 h. The TiO_2/OM-PAN nanofiber mat was separated from aqueous medium and dried in oven at 80°C. After drying, the TiO_2/OM-PAN nanofiber mat was weighed and then the amount of TiO_2 was calculated from weight of OM-PAN before and after treatment with titanium oxide (about 0.25 g TiO_2 adsorbed onto nanofiber mat). The dried TiO_2/OM-PAN nanofiber mat and 10 mL of 30 ppm methylene blue solution were taken in a vial and sonicated for 30 min in dark in order to allow the adsorption–desorption equilibrium to be reached. The reaction mixture was then irradiated under UV light (254 nm, 15 W) as a function of time. After the specific irradiation time, the TiO_2/OM-PAN nanofiber mat was separated by centrifugation and then the UV–vis absorption measurements were performed. The percent degradation of methylene blue in aqueous media was calculated by the following equation [12].

$$\text{Degradation rate }(\%) = \frac{C_o - C}{C_o} \times 100$$

$$\text{Degradation rate }(\%) = \frac{A_o - A}{A_o} \times 100$$

where C_o is the initial dye concentration, C is the dye concentration after UV irradiation, A_o shows initial absorbance, and A shows the dye absorbance after UV irradaition.

2.4. Instrumentation

The morphological study of gold-coated PAN and TiO_2/OM-PAN nanofibers mats were analyzed using JEOL, JSM-5910 SEM. The EDX spectrometric study analysis of TiO_2/OM-PAN mat were performed on EDX (Model INCA 200/Oxford Instruments, UK, company oxford), in order to investigate the elemental composition of the samples. The photodegradation study of methylene blue was performed using UV–visible spectrophotometer (UV-1800, Shimadzu, Japan).

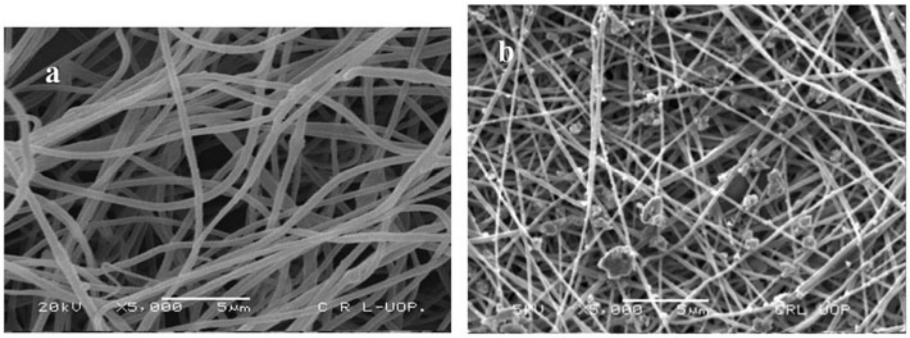

Fig. 1. SEM images of (a) OM-PAN nanofibers and (b) TiO_2/OM-PAN nanofibers.

3. Result and discussion

3.1. Morphological study

The morphological study of cryofractured OM-PAN and TiO_2/ OM-PAN nanofiber mats are shown in Fig. 1. The Fig. 1(a) showed that the PAN electrospun nanofiber had uniform diameter (below 200 nm). The SEM image also showed that the surface of the PAN nanofibers was not damaged/degraded after the introduction of oxime group onto the PAN nanofibers (Fig. 1(a)). Fig. 1(b) showed the presence of TiO_2 particles on the surface of OM-PAN nanofiber. The SEM image also revealed that the TiO_2 are present in agglomerated form on the surface of nanofiber mat. The presence of TiO_2 onto TiO_2/OM-PAN nanofiber mats (Fig. 2) was also confirmed by EDX spectrum, which showed that Titanium and carbon are present in large quantity while oxygen in minute quantity.

3.2. Photodegradation of methylene blue

The photocatalytic properties of TiO_2/OM-PAN nanofibers were studied by degrading the methylene blue under UV irradiation as a function of time. Figs. 3–5 show the UV/visible spectra of methylene blue in aqueous solution before and after UV irradiation. The photodegradation of methylene blue was measured by the relative intensity of the UV/visible spectra, which gave maximum absorbance peak at 650 nm. The TiO_2/OM-PAN nanofibers showed that the degradation of methylene blue gradually increases with irradiation time (Fig. 3). The TiO_2/OM-PAN nanofibers mat degraded more than 50% of dye. While the neat OM-PAN nanofibers degraded about 30% of dye within 2 h under the same experimental conditions (Fig. 4) and after 2 h the dye degradation is almost constant. The kinetic study of photodegradation of methylene blue in aqueous solution vs. TiO_2/OM-PAN and OM-PAN is shown in Fig. 6.

The high TiO_2/OM-PAN nanofibers of photodegradation of methylene blue in aqueous solution is due to

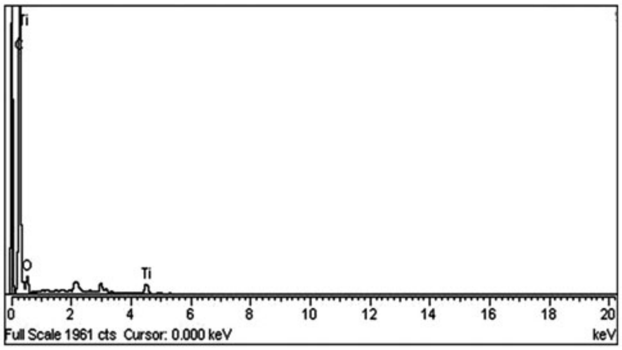

Fig. 2. EDX study of TiO_2/OM-PAN nanofibers.

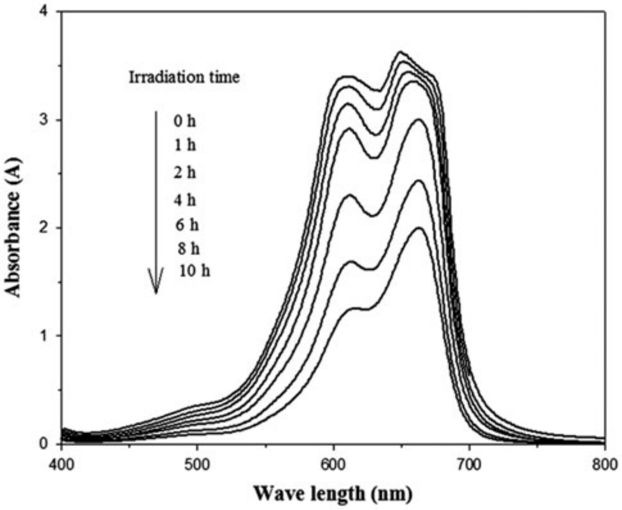

Fig. 3. UV–vis absorbance spectra of methylene blue photodegraded by TiO_2/OM-PAN nanofibers under UV irradiation vs. time.

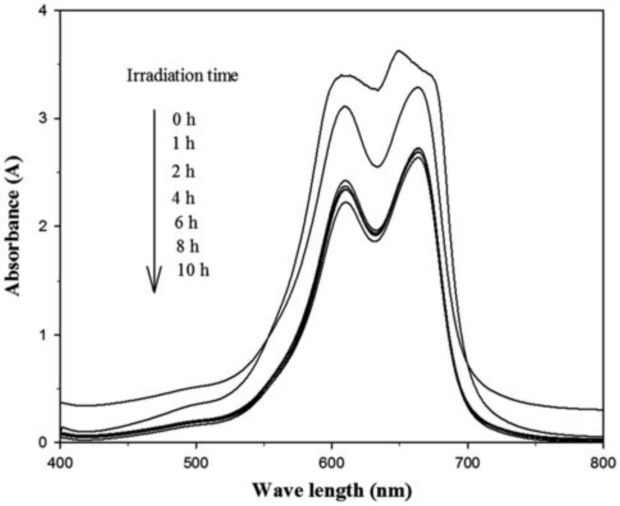

Fig. 4. UV–vis absorbance spectra of methylene blue photodegraded by neat OM-PAN nanofibers under UV irradiation vs. time.

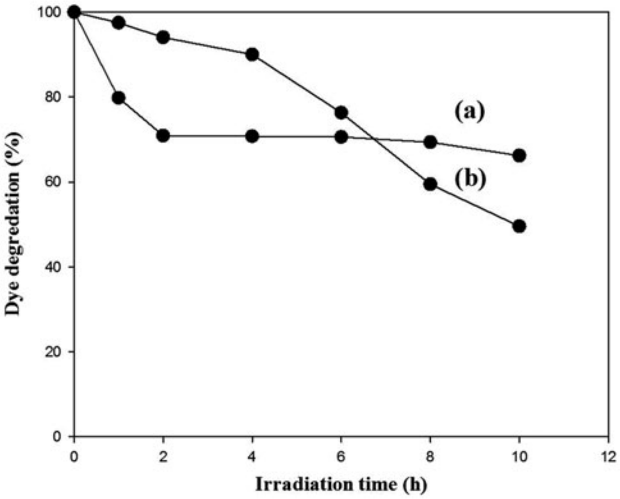

Fig. 5. Percent degradation of methylene blue by TiO_2/OM-PAN nanofibers under UV irradiation as a function of time.

the TiO_2 on the surface of OM-PAN, which was first photoexcited to produce conduction band electrons ($e-$) and valence band holes (h^+). The positive charged hole may react with water and result in the formation of hydroxyl radicals. These hydroxyl radicals are strong oxidizing agent, which react with dye molecules and finally degrade the organic dye [13,14].

$$TiO_2 + h\nu \longrightarrow TiO_2(e^- + h^+) \quad (1)$$

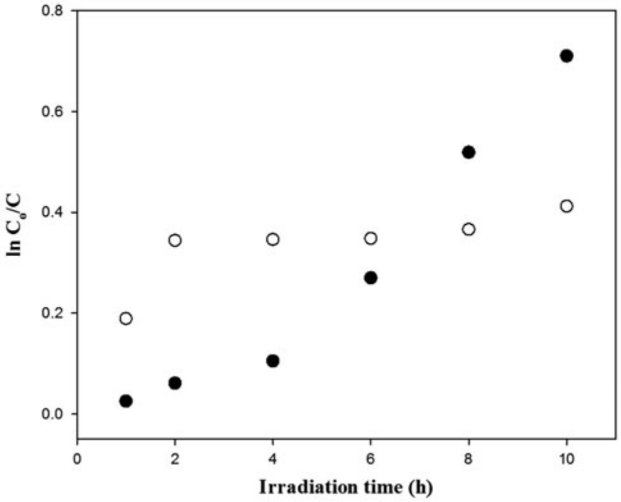

Fig. 6. Reaction kinetic of (●) TiO_2/OM-PAN and (○) OM-PAN with methylene blue.

$$TiO_2\ (h^+) + H_2O \longrightarrow TiO_2 + H^+ + OH^{\cdot} \quad (2)$$

$$Dye + OH^{\cdot} \longrightarrow \text{dye degradation} \quad (3)$$

The other possibility is the high oxidative potential of the hole, which directly oxidizes organic dye molecules.

$$h^+ + dye \longrightarrow dye^{\cdot +} \longrightarrow \text{dye degradation} \quad (4)$$

It was also reported that dissolved oxygen react with photogenerated electrons and results superoxide anion radical. The superoxide anion radical is also a strong oxidizing agent, which can easily attack any organic molecules adsorbed on, or located near to the catalyst surface, and as a result degradation of organic dyes molecules occur [13,15].

3.3. Effect of pH on photodegradation study

The effluents from various industries such as textile, paint, dyes, etc. are discharged at diffrenet pH, therefore, it is essential to study the effect of pH on the degradation of organic dyes. The pH not only plays a significant role during the degradation of textile wastes and generation of hydroxyl radicals but also affects the charge on the catalyst particles, and the positions of conductance, and valence bands [14,16].

The effect of pH on the degradation of methylene blue is shown in Fig. 7. The results show that the dye

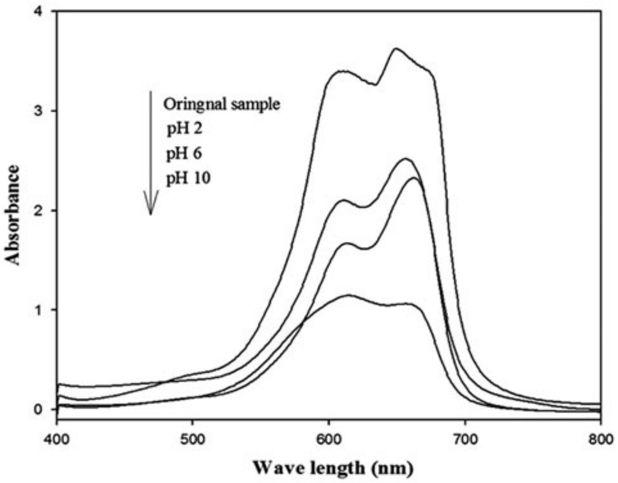

Fig. 7. UV–vis absorbance spectra of methylene blue photodegraded by TiO_2/OM-PAN nanofibers under UV irradiation at various pH.

Table 1
Effect of pH on the photodegradation of methylene blue

pH	Photodegradation (%)
2	32.35
6	41.43
10	71.09

degradation increases as the pH of solution increases. The result (Table 1) shows that the degradation of the dye is about 32% at pH 2, and it gradually increases up to about 41and 71% at pH 6 and 10, respectively. The high photodegradation of methylene blue in basic medium might be due to the enhanced formation of hydroxyl radicals. These hydroxyl radicals are strong oxidizing species, which are responsible for higher degradation rate at higher pH levels. Similary, Kansal et al. [17] used TiO_2 and ZnO as a photocatalyst for the decolorization/degrdation of Reactive Black 5 and Reactive Orange 4 and they also found that the degradation of dyes was increased as a function of pH of the solution.

4. Conclusion

The TiO_2 was adsorbed onto OM-PAN and used for the photodegradation of methylene blue in aqueous solution as a function of time. The SEM study showed that the morphology of nanofibers was not disturbed after the chemical modification. Both neat OM-PAN and TiO_2/OM-PAN nanofiber mat showed photocatalytic activities. The degradation rate of methylene blue in aqueous solution was increased as increased the UV irradiation time. It was also found that the neat OM-PAN degraded less quantity of dye as compared to TiO_2-OM-PAN under the same experimental conditions. It was also found that the high pH is favorable for the high degradation of dye and about 71% of dye was degraded at pH 10.

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