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ORIGINAL ARTICLE

Photocatalytic degradation of organic dyes using composite nanofibers under UV irradiation

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Abstract

In this work, photocatalytic degradation of organic dyes such as methylene blue (MB) and indigo carmine (IC) have been studied by composite nanofibers systems containing cellulose acetate (CA), multiwall carbon nanotubes (CNT) and TiO_2 nanoparticles under UV light. The amino factionalized TiO_2–NH_2 NPs cross-linked to the CA/CNT composite nanofibers works as a semiconductor catalyst. The morphology and crystallinity were characterized by scanning electron microscopy, transmission electron microscopy (TEM), X-ray diffraction, and Fourier transform infrared spectroscopy. It was also seen that many factors affected the photodegradation rate, mainly the pH of the solution and the dye concentration, temperature, etc. The study demonstrated that IC degrades at a higher rate than MB. The maximum photodegradation rate of both organic dyes was achieved at a pH 2. In comparison to other studies, this work achieved high photodegradation rate in lower time and using less power intensity.

Keywords Photocatalytic · Electrospinning · Composite nanofibers · UV light

Introduction

Water pollution is a considerable threat to human health. Water is the most vital resource for people and for ecosystems. However, industrialization and urbanization led the water quality to deteriorate, thus negatively impacting humans and all other living organisms. The low quality of the water is also a major problem in agriculture and food production. Other sectors, such as the economy, are greatly impacted as well. The most common water pollutants are organic dyes and pigments, which are present in many industrial effluents such as textile, lather, paper, cosmetics, and printing (Zheng et al. 2008). Many techniques can be employed to eliminate those pollutants from the wastewater. Those techniques mainly involve chemical, physical or biological processes (Mohamed et al. 2016). Contaminants degradation using photocatalytic processes with the aid of composite nanofibers had been emerged in the 1970s and are still developing. The photocatalytic processes mainly use semiconductors catalysts such as (TiO_2, Fe_2O_3, ZnO) under light exposure (UV light or sun light) to degrade the organic and inorganic contaminants (Kuriakose et al. 2015; Mohamed et al. 2017). Most of the researchers is now focusing on the photocatalytic techniques using composite nanofibers for the treatment of the wastewater and degrading of the dyes due to its high efficiency and low-cost technique (Mohamed et al. 2016; Xu et al. 2010).

Many semiconductor catalysts can be used, but titania (TiO_2) is the most commonly used semiconductor catalyst due to its cheap cost combined with a high photocatalytic activity. Moreover, titania is readily available, non-toxic and can induce complete mineralization by degrading organic pollutants (Eskandarloo and Badiei 2014). It can be found in three crystalline phases: brookite, rutile and anatase. However, many previous studies have favored the use of the anatase form of titania in the photocatalytic process to degrade different types of dyes. Nasirian et al. (2017) have showed that the degradation efficiency of MO and CR removal using Fe_2O_3/TiO_2 composite nanofibers is 61.5 and 46.8%, respectively. Dhanya and Aparna (2016) have illustrated the importance of adding TiO2 to

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the chitosan for MO photocatalytic degradation and have obtained a 100% degradation efficiency. Muneer et al. (2005) have shown the effects of the structure and size of the UV100, PC500, TTP and Degussa P25 photocatalysts. They have found that Degussa P25 has the highest efficiency in the degradation of the dyes. In this regard, this research is based on the usage of Degussa P25 TiO_2 NPs as a semiconductor photocatalyst in the degradation processes of MB and IC.

The surface of the nanofibers has to be activated by reactive group such as amines, carboxyls, and hydroxyls to be able to exploit the advantage of the nanofiber mesh. Primary amines were considered the most effective group to promote cell adhesion, due to their high reactivity and high stability in water. Manakhov et al. (2015) have reported the results of adding the primary amine group onto nanofibers of polycaprolactone in the coating process, using CPA plasma polymerization. This study describes the amino factionalized TiO_2 NP_S cross-linking on the CA–CNT composite nanofibers surface. By analyzing the photocatalytic degradation of IC and MB, many observations can be generated to conclude on how different parameters affect the photodegradation rate. Hence, the goal of this study is to investigate the factors that affect the photocatalytic efficiencies of MB and IC using the synthesis CA–CNT/TiO_2–NH_2 composite nanofibers.

Experimental

Material

Cellulose acetate/carbon nanotube composite nanofibers were prepared using electrospinning technique as discussed in the previous work (Mohamed et al. 2017). Titanium dioxide NPs (TiO_2 Degussa P-25), 3-aminopropyltriethoxysilane (APTES), glutaraldehyde (GA), indigo carmine (IC) and methylene blue (MB) dyes, hydrochloric acid (HCI) and sodium hydroxide (NaOH) were purchased from Sigma Aldrich.

Characterization

The morphology, and crystalline were characterized by scanning electron microscopy (SEM) (Quanta FEG 250, Republic Czech), transmission electron microscopy (TEM) (JEM-2100 JEOL Japan), X-ray diffraction (XRD) (D/MAX-2500 diffractometer, Rigaku, Japan), and Fourier transform infrared spectroscopy (FTIR) (Jasco, FT-IR 6100, Japan). The diameters of the fibers were measured by image processing software (Image J, 1.48v).

Samples preparation

Cellulose acetate/carbon nanotube composite nanofibers fabricated using electrospinning technique were cross-linked to TiO_2–NH_2 NPs. The composite nanofibers was submerged in the cross-linking medium which, consisting of 100 mL distilled water and 2.5 wt% glutaraldehyde (GA) and mechanically shaken for 24 h at room temperature. After this process, the composite nanofibers were washed by the distilled water. The surface functionalization TiO_2–NH_2 NPs were added to 5 mL distilled water, and sonicated for 2 h, then added to the composite nanofibers and shaken for 24 h. The CA–CNT/TiO_2–NH_2 composite nanofibers was finally washed with distilled water and dried in air at room temperature (Mohamed et al. 2015).

Photodegradation experiments

Using a UV lamp (315–400 nm) of 40 watts for the UV light irradiation, the photocatalytic activity of CA–CNT/TiO_2–NH_2 composite nanofibers was studied by recording the photodegradation of IC and MB. Different MB and IC concentrations were used (10, 30, 50 mg/L) and at different pHs starting from 2 to 8. The composite nanofibers (diameter of 12 cm) were placed in a column (2 cm × 13 cm). A 50 mL solution of IC or MB was added to the composite nanofibers and kept shaking for 30 min in the dark. After that, 3 mL volume of the dye solution was taken at uniform intervals of time, while shaking under the UV light irradiation. Using the UV–Vis/NIR spectrophotometer, the dye concentration was obtained. After each experiment, the composite nanofibers were washed many times using distilled water to be able to be reused again (Seo et al. 2017; Mohamed et al. 2017; Nguyen and Juang 2015). The photodegradation efficiency was calculated accordingly:

$$\text{Photodegradation efficiency } (\%) = \frac{C_i - C_t}{C_i} \times 100, \quad (1)$$

where C_i is the initial concentration and C_t is the concentration at time (t).

Results and discussion

Characterization of CA–CNT/TiO_2–NH_2 composite nanofibers

The SEM images of CA–CNT/TiO_2–NH_2 are shown in Fig. 1. The figure shows continuous and smooth morphology and free of aggregates nanofibers having an average diameter about 430 ± 20 nm. The figure also shows the distribution

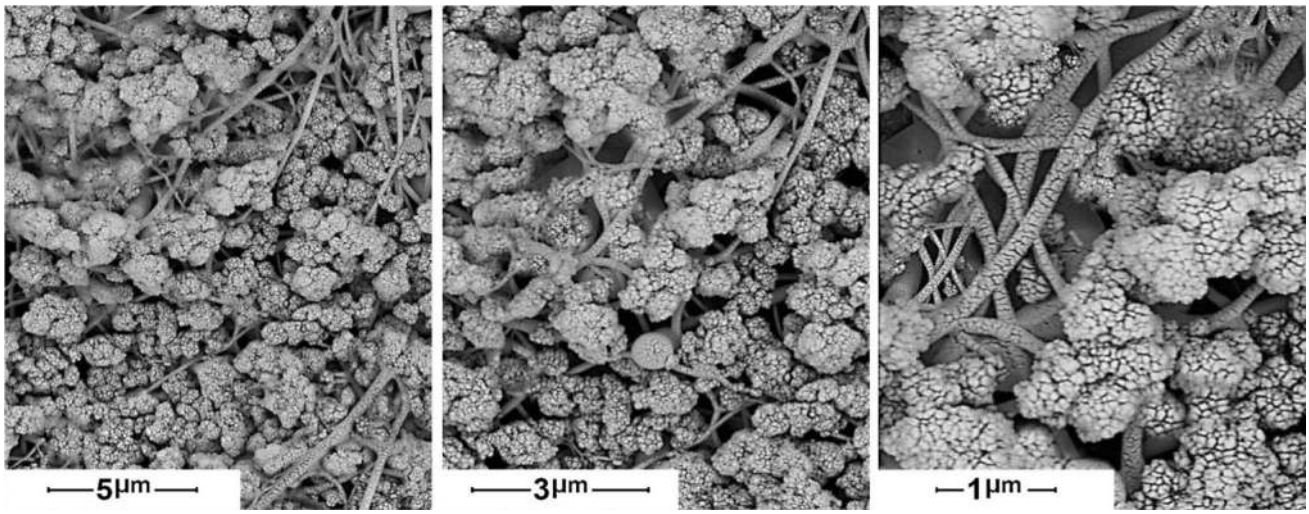

Fig. 1 SEM images of CA–CNT/TiO_2–NH_2 composite nanofibers

of the amino factionalized TiO_2 NPs on the surface of the CA–CNT composite nanofibers which occurred by the cross-linking process. In addition, Fig. 2 shows the TEM images of CA–CNT/TiO_2–NH_2, which, approved the presence of TiO_2–NH_2 and show the adhesion of TiO_2–NH_2 to the surface of the CA–CNT composite nanofibers.

The FT-IR spectral of CA–CNT and CA–CNT/TiO_2–NH_2 confirms the surface functionalization of the fabricated composite nanofibers. The IR spectral of CA–CNT shows the following peaks: (OH) peak at 3500 cm^{-1}, (C=O) peak at 1745 cm^{-1} and (N–O) peak at 900 cm^{-1} which are shown in Fig. 3a. After adding TiO_2–NH_2, the carbonyl and amino particles break down. The oxygen and nitrogen molecules are separated, which causes the formation of amidoxime (AO) after the molecules rearrangement. Figure 3b shows the IR spectral of CA–CNT/TiO_2–NH_2. The figure confirms the presence of NH_2 and illustrates the conversion of nitrile to amidoxime. More specifically, the conversion is confirmed by absorption in the range of 3300–3500 cm^{-1} which corresponds to N–H and O–H vibrations, and the bending vibrations of the amine group NH or NH_2 at 1600 cm^{-1}.

In addition, X-ray diffraction (XRD) analysis was performed to analyze the effect of CNT and TiO_2 on the crystalline structure of the CA. The reflection peaks of CA were found at 12° and 20° as shown in Fig. 4. Moreover, the graph shows the presence of CNT which causes a strong peak

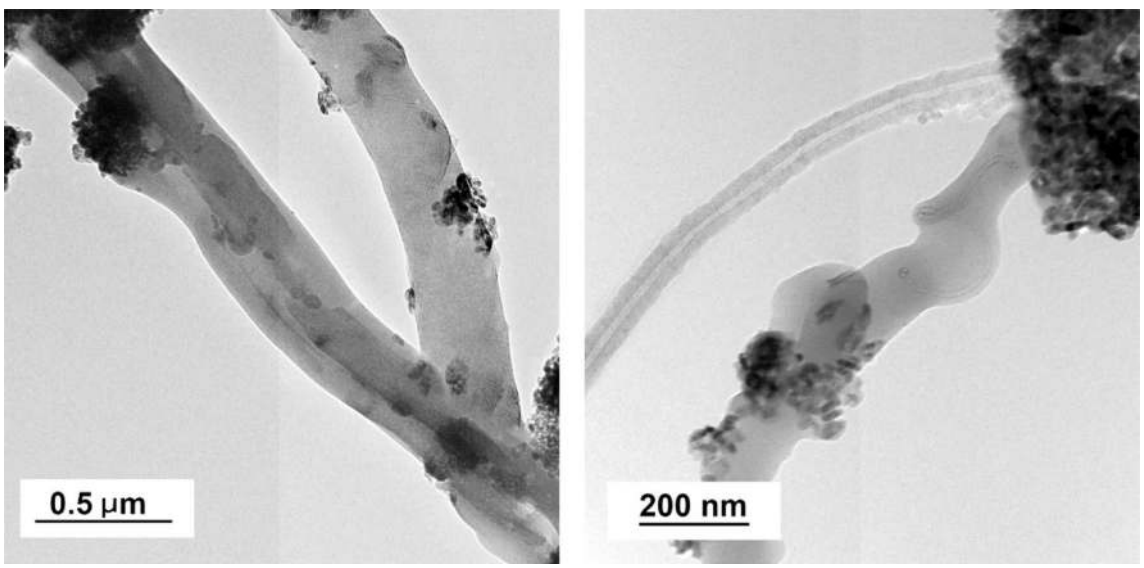

Fig. 2 TEM images of CA–CNT/TiO_2–NH_2 composite nanofibers

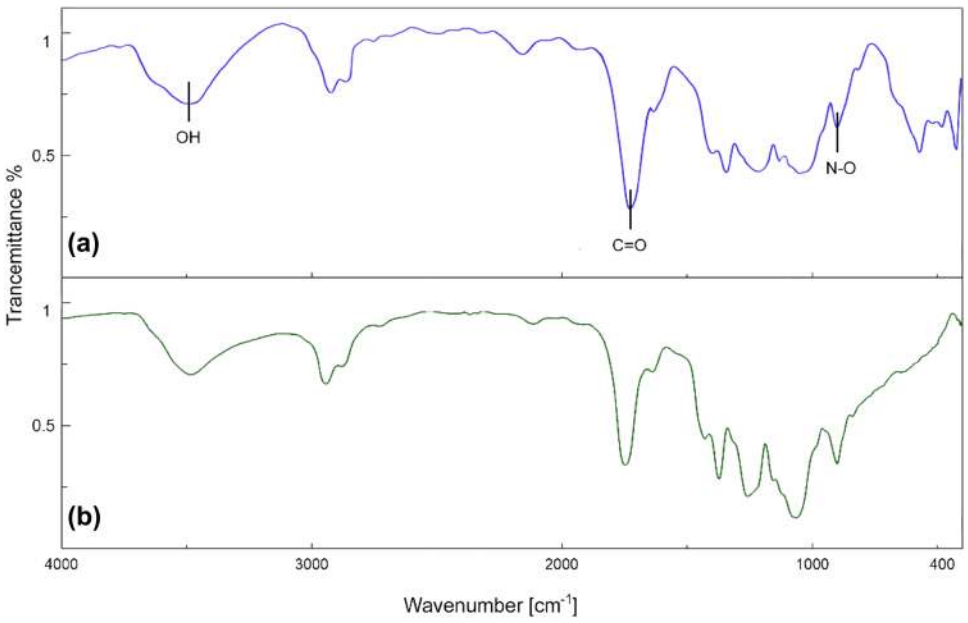

Fig. 3 FT-IR spectra of **a** CA–CNT and **b** CA–CNT/TiO_2–NH_2 composite nanofibers

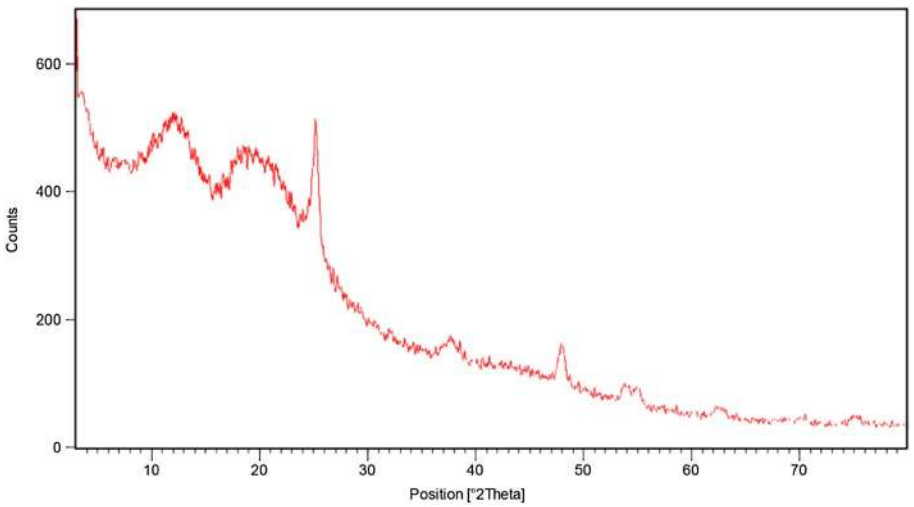

Fig. 4 XRD of CA–CNT/TiO_2–NH_2 composite nanofibers

at 25.6°. In addition, the peaks at 25.19°, 37.69°, 47.98°, 53.85°, 62.53°, and 75.12° confirm the presence of TiO_2.

Photodegradation performance

The effect of dye concentration

The photocatalytic degradation rate of a certain dye or pollutant depends on its concentration, nature and on the presence of other existing compounds in the water matrix. Figure 5 shows the effect of the dye's concentration on the photodegradation efficiency for MB and IC. The degradation efficiencies were studied at 10, 30, and 50 ppm. The result indicated that the degradation efficiencies were, respectively, 100, 80, and 70% for MB and 100, 90 and 80% for IC. High concentration of the dye activated the photocatalytic process,

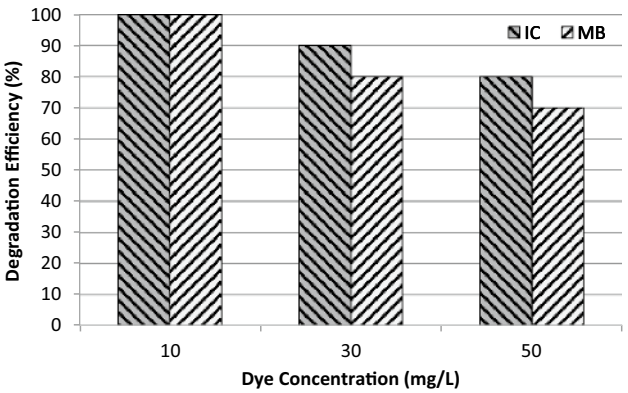

Fig. 5 The effect of the dyes concentration on the photodegradation efficiency

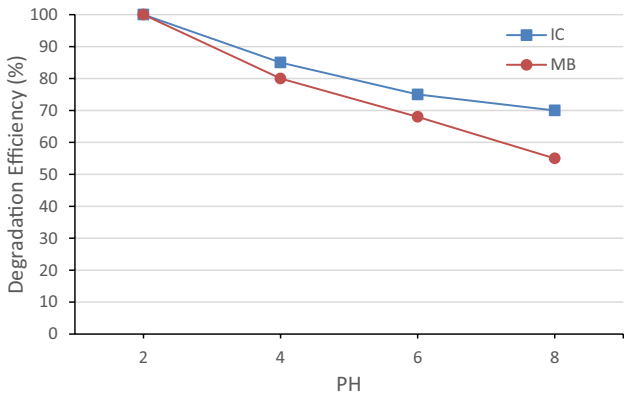

Fig. 6 The effect of the pH on the photodegradation efficiency for IC and MB at 10 ppm

but reduced the degradation rate. This result is due to the saturated surface of the TiO_2 which is caused by the high concentration of the dye. In this regard, the photocatalytic degradation reaction will be deactivated. Furthermore, the nature of the dyes is such that they adhere effectively to the surface of the photocatalyst, making the process of removing the dyes from the solution would be more effective.

The effect of the pH of the solution

The photocatalytic degradation of dye is mainly dependent on the pH value due to its effect on the catalyst charge, aggregates' size, and valance and conductance bonds position. The TiO_2 maximum oxidizing capacity was found at lower pH value. In this regard, the degradation of IC and MB was studied at different pH values in range of (2–8) to find the value that gives the maximum degradation efficiency. The influence of pH on degradation efficiency for both IC and MB can be seen in Fig. 6. The figure shows that the acidic conditions help to reach higher degradation efficiencies for IC and MB. The maximum degradation efficiency occurred at pH 2. This results may be due to the electrostatic interactions between the positive catalyst surface and the

Fig. 7 The effect of reaction temperature on the photodegradation rate

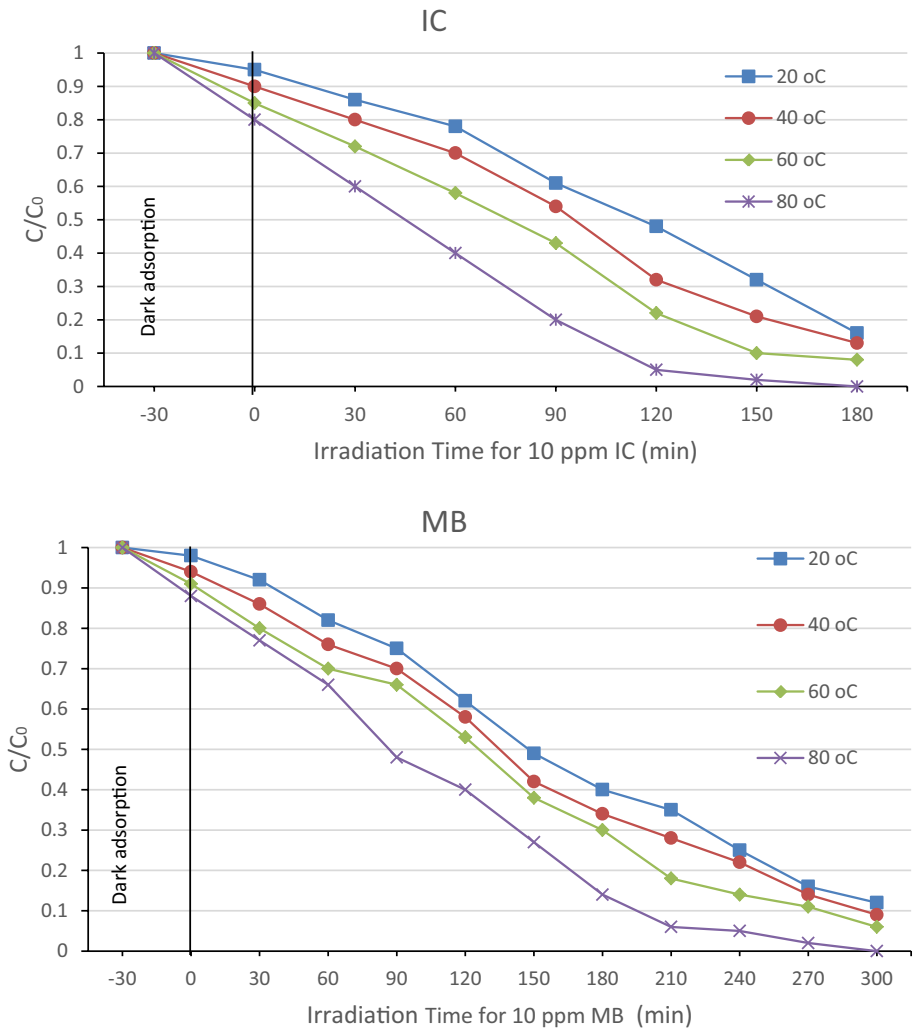

Table 1 Comparison of photocatalytic activities of materials used for photocatalytic degradation of dyes under UV light

Material	Model type	Model concentration (PPM)	Degradation (%)	Lamp power (W)	Max. time for max. degradation (min)	References
Cu_2O/Bi_2WO_6	Butyric acid	200	92	500	400	Zheng et al. (2017)
TiO_2/chitosan	MO		100		360	Dhanya and Aparna (2016)
$Cu_{0.6}Cd_{0.4}S$	Phenol	20	86		250	Boukhatem et al. (2017)
TiO_2-GO	MO		84	40	240	Atchudan et al. (2017)
Fe_2O_3/TiO_2	MO	30	61.5	45	210	Nasirian et al. (2017)
Fe_2O_3/TiO_2	CR	30	46.8	45	210	Nasirian et al. (2017)
CA–CNT/TiO_2–NH_2	IC	10	100	40	180	This work
CA–CNT/TiO_2–NH_2	IC	30	90	40	180	This work
CA–CNT/TiO_2–NH_2	IC	50	80	40	180	This work
CA–CNT/TiO_2–NH_2	MB	10	100	40	300	This work
CA–CNT/TiO_2–NH_2	MB	30	80	40	300	This work
CA–CNT/TiO_2–NH_2	MB	50	70	40	300	This work

dye anions which leading to strong adsorption of the dye anions on the metal oxide support. Moreover, the efficiency of the process increases by the formation of hydroxyl radicals, which formed when the hydroxide ions interact with the positive holes which are considered as the main oxidation species at low pH.

The effect of the reaction temperature

The photodegradation process is very sensible to changes in temperature. This correlates with the results of this study, which shows that high temperature positively affects the degradation rate. In this regard, most researchers use solar energy, since it doesn't only include UV light which activates the photocatalytic process, but also infrared light which increases the temperature of the photocatalytic process (Barjasteh-Moghaddam and Habibi-Yangjeh 2011; Hu et al. 2010; Barakat et al. 2013). Figure 7 illustrates the effect of the temperature with the UV light in range from 20 to 80 °C. The figure shows that the highest temperature corresponds to the optimal degradation rate. This is due to the fact that more thermal energy is available for molecules at higher temperatures, as well as sufficient energy to react.

The effect of the light intensity

The photodegradation rate is affected by the light intensity. Table 1 proves that the photodegradation rate increased with the increase in the light intensity and vice versa.

The effect of irradiation time

Figure 8 illustrates the influence of the irradiation time on the photodegradation rate. It has been found that during the first 90 min of effective irradiation, the degradation rate was high, reaching 80% for IC and 52% for MB. Then, the degradation

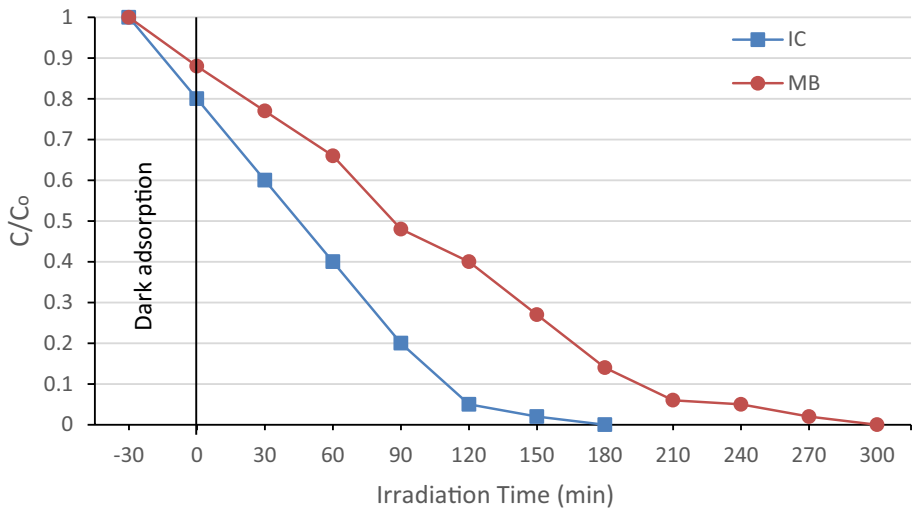

Fig. 8 The effect of irradiation time on the photodegradation rate

rate gradually decreased, reaching 95% after 120 min for IC and 210 min for MB. The full degradation occurred at 180 min for IC and 300 min for MB. The large degradation rate at the start of the process is caused by the high amount of the amino factionalized TiO_2 NPs on the surface of the CA–CNT composite nanofibers. The degradation rate is then reduced because of catalyst consumption.

Conclusion

The amino factionalized TiO_2–NH_2 NPs cross-linked to the CA/CNT composite nanofibers was successfully prepared. The results shows smooth morphology and free of aggregation nanofiber with an average diameter about 430 ± 20 nm. The results also illustrated the good adhesion of the TiO_2–NH_2 to the surface of the CA–CNT composite nanofibers. The above study demonstrated that the fabricated composite nanofibers CA–CNT/TiO_2–NH_2 is an effective photocatalyst in the degradation of water soluble dyes IC and MB. The full degradation was achieved at the lowest dye concentration (10 ppm), the lowest pH value (2), at a high temperature (80 °C), and a low power intensity of the UV lamp (40 W). The full degradation of IC and MB needs 180 and 300 min, respectively, to be achieved.

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