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Preparation of polyacrylonitrile–Titania electrospun nanofiber and its photocatalytic dye degradation ability

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ABSTRACT

In this paper, polyacrylonitrile (PAN)-Titania (TiO_2) electrospun nanofiber (PAN/TiO_2 nanofiber) was prepared via a facile electrospinning method. The characteristics of the PAN/TiO_2 nanofiber were investigated using SEM and FT-IR. The nanofiber showed retained nanofibrous structures and high photocatalytic efficiency under UV light for degradation of Direct Red 80 (DR80) and Direct Red 23 (DR23) in water. The photocatalytic dye degradation kinetics followed first-order model. The reaction rate constant (k) at 20 mg/L dye concentration was 0.0184 min^{-1} for DR 80 and 0.0328 min^{-1} for DR23. The dye degradation rate constant decreased by increasing initial dye concentration. The results indicated that polyacrylonitrile - Titania electrospun nanofiber could be used as a photocatalyst to decolorize colored wastewater. Prog. Color Colorants Coat. 10 (2017), 23-30© Institute for Color Science and Technology.

1. Introduction

Dyes are widely employed in various industries such as the textile, paper, leather, food, plastics, cosmetics, printing, etc. Their discharges into ecosystem have a significant threat due to their non-biodegradable and recalcitrance nature. The release of these compounds in water will reduce sunlight penetration and resist photochemical and biological attacks to aquatic life [1-7]. Some azo dyes containing one or more azo bands (-N=N-) are toxic because of the presence of toxic amines in the effluent [8, 9].

Photocatalysis as an advanced oxidation process emerged as a useful and effective method to degrade pollutants in water and wastewater [10-13]. It has many advantages over competing methods, including complete mineralization, and has no waste-solids disposal problem. In addition, only mild temperature and pressure conditions are necessary.

Several nanomaterials were used as catalysts. Recently, researchers have focused on nanofibrous photocatalysts because they can be easily recovered after a degradation reaction. In addition, electrospinning is a simple and effective technique to produce nanofibers using electrostatic force [14]. Electrospun Titania nanofiber has attracted considerable attention as an efficient photocatalyst. It opened a spectrum of new possibilities for high photocatalytic activity and easy recovery catalysts. Also, the electrospun nanofibers with both high porosity and large reaction surface area are promising catalysts [15].

In this paper, polyacrylonitrile (PAN) - Titania (TiO_2) electrospun nanofiber (PAN/TiO_2 nanofiber) was prepared via the electrospinning process and its photocatalytic activity for degradation of Direct Red 23 (DR23) and Direct Red 80 (DR 80) in water was

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investigated. The prepared PAN/TiO_2 nanofiber was characterized using SEM and FT-IR. The effect of catalyst dosage, solution pH, dye concentration and salt on photocatalytic degradation was investigated.

2. Experimental

2.1. Materials

Direct Red 23 (DR23) and Direct Red 80 (DR 80) were used as model dyes. The chemical structure and characteristics of dyes are shown in Figure 1 and Table 1, respectively. Polyacrylonitrile copolymers (93.7% acrylonitrile and 6.3% methyl acrylate with MW 70,000 g/mol) were obtained from Isfahan Polyacryl Inc. (Iran). Titania nanoparticle as a photocatalyst was obtained from Evonik Co. The main characteristics are: average particle size = 21 nm, phase = anatase and surface area = 50 ± 15 m^2/g. Other chemicals were achieved from Merck and used without further purification.

Table 1: The main characteristics of dyes.

Name	Molecular Formula	Molecular Weight (g/mol)	λ_{max}
Direct Red 23	$C_{35}H_{25}N_7Na_2O_{10}S_2$	813.72	507
Direct Red 80	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$	1373.08	528

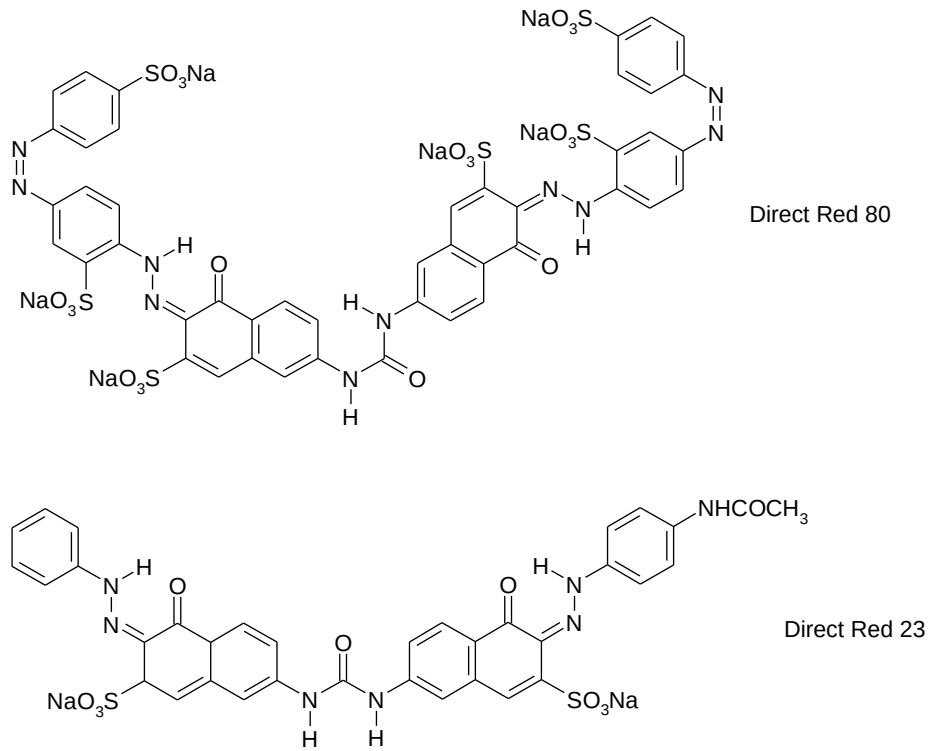

Figure 1: The chemical structure of dyes.

2.2. PAN/DMF/TiO_2 mixture electrospinning

Solution of PAN in DMF (10wt %) was prepared and stirred for 4 h. The TiO_2 nanoparticle (1 wt %) dispersion was gradually added to the PAN/DMF solution. The resulting mixture was stirred for another 24 h and used for fiber preparation. The electrospinning setup consists of a 10 mL glass syringe with a needle tip (0.51 mm diameter), a syringe pump, a ground electrode (aluminum sheet) and a high voltage power supply (Gamma High Voltage Research, RR60). The applied voltage was 21 kV and the distance from the tip to the collector was 15 cm. The feeding rate of the mixture solution was 1 mL/h.

2.3. Photocatalytic dye degradation

The PAN/TiO_2 nanofiber (0.03 g) was added into a photoreactor (light source: a UVC lamp of 9W) containing 800 mL of 20 mg/L dye. The reactor was first kept in a sealed container for 20 min to minimize the impact of adsorption process. At different time intervals, the solution sample was withdrawn and its absorbance was measured at dye maximum wavelength (507 nm for DR23 and 528 nm for DR80) by a spectrophotometer (CECIEL 2021). The effect of PAN/TiO_2 nanofiber dosage (0.01–0.04 g), different solution pH values (3-8) and the initial dye concentration (20-50 mg/L) on the dye degradation was investigated. The experiments were carried out three times.

3. Results and discussion

3.1. Catalyst characterization

Figure 2 presents SEM images of the PAN/TiO_2 nanofiber, showing that the nanofiber retained the fibrous shape, with fiber diameters ranged from approximately 200 nm. We observed that once PAN/TiO_2 nanofiber was deposited on the collecting foil, they quickly combined to form larger fibers because the outer layer of the fibers was not yet fully solidified [16].

The FT-IR spectrum of PAN nanofiber (Figure 3a) exhibited the absorption peaks of a stretching vibration at 2243cm^{-1} (C≡N), 1736cm^{-1} (C=O), and 1452 cm^{-1} (C-O), which suggests that the PAN was a copolymer of acrylonitrile and methylacrylate [16]. The FT-IR spectrum of PAN/TiO_2 nanofiber (Figure 3b) shows the absorption peak at 3370-3525 cm^{-1} and 1668 cm^{-1} corresponding to stretching vibrations of the -OH and bending vibrations of the adsorbed water molecules, respectively. The main transmittance peak at 616.3 cm^{-1} was assigned to the Ti-O and Ti-O-Ti bonds [17].

3.2. Degradation of dyes by PAN/TiO_2 nanofiber

3.2.1. Effect of PAN/TiO_2 nanofiber dosage

The effect of PAN/TiO_2 nanofibrous catalyst dosage on the dye decolorization for DR80 and DR23 is shown in Figure 4. The decolorization percentage raised with increasing the PAN/TiO_2 nanofiber dosage up to a certain limit, then reached a constant value. The increasing of the dye decolorization with the catalyst dosage can be attributed to the increase in the catalyst surface and availability of more photocatalytic sites [18].

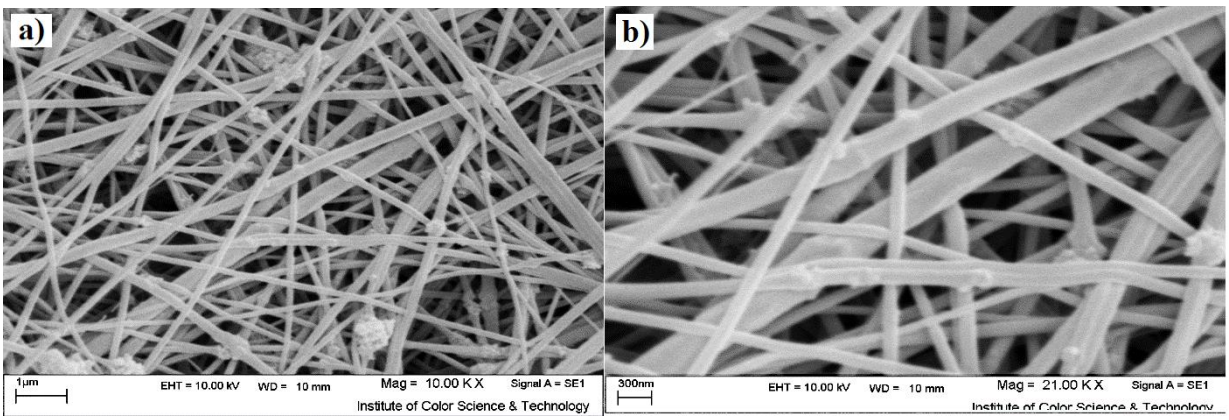

Figure 2: SEM micrographs of the PAN/TiO_2 nanofiber.

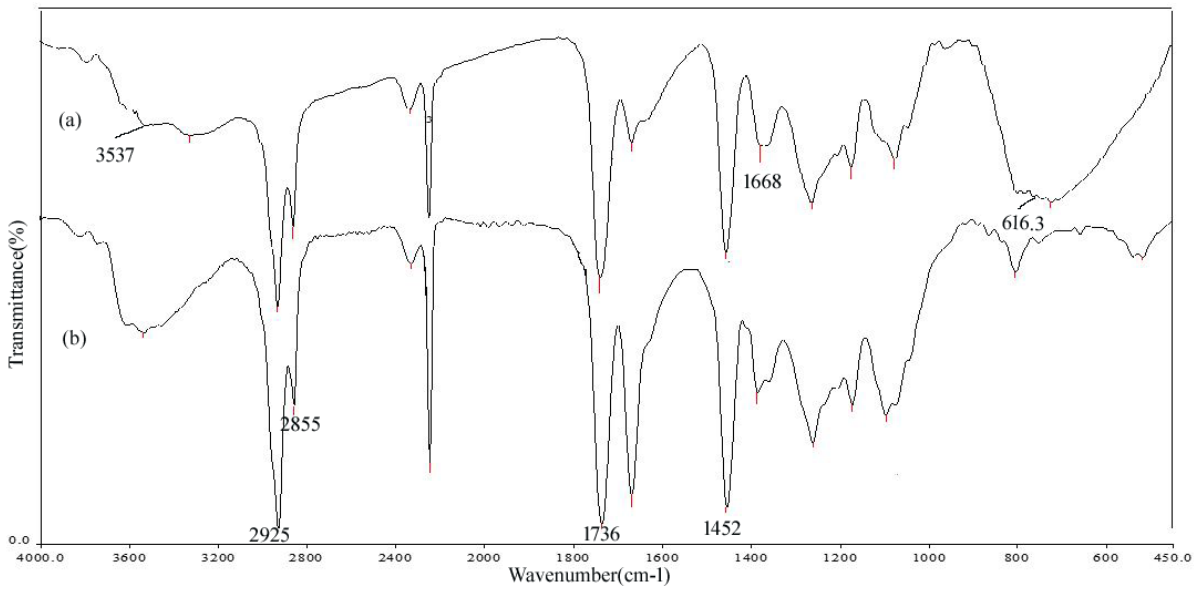

Figure 3: FT-IR spectra (a) PAN nanofiber and (b) PAN/TiO_2 nanofiber.

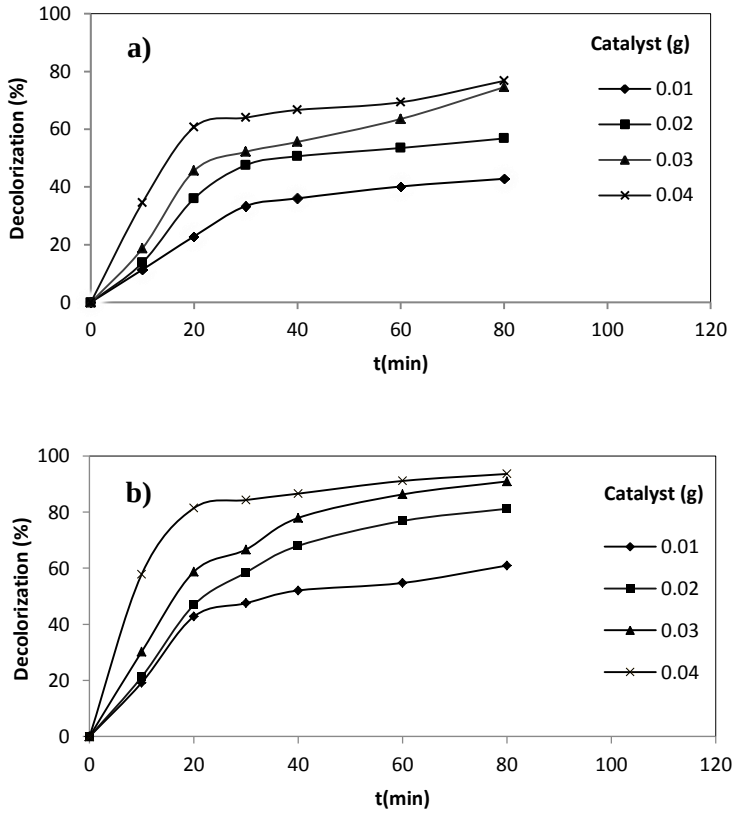

Figure 4: The effect of catalyst (PAN/TiO_2 nanofiber) dosage on the decolorization of dyes (dye solution = 800 mL, initial dye concentration = 20 mg/L, pH=3 and time = 80 min) (a) DR80 and (b) DR23.

3.2.2. Effect of contact time

The efficiency of the degradation of dyes as a function of contact time with the PAN/TiO_2 nanofiber is given in Figure 5. The decolorization efficiency was 69% and 62% for DR80 and DR23 in 80 min of contact with PAN/TiO_2 nanofiber, respectively. After 80 min of reaction, the dye removal became negligible. So, subsequent experiments were performed for 80 min of reaction time.

3.2.3. Effect of initial dye concentration

The concentration of dye is a key factor which affects the rate of the PAN/TiO_2 nanofiber catalyzed oxidation. Studies were carried out at different concentrations of the dye (20–50 mg), keeping all the other parameters constant and the results are shown in Figure 6. The increase in dye concentration to 40 mg/L provides an effective increase in color removal. Subsequent increase in dye concentration above 40 mg/L resulted in negligible dye removal. Fewer photons reach the catalyst surface when the dye concentration increases, resulting in slower production of oxidants such as hydroxyl radicals. In addition, fewer oxidants are required to degrade more dye molecules [19].

3.2.4. Effect of pH

The pH value is one of the important factors influencing the rate of decolorization of organic compounds in the photocatalytic processes. It is also an important operational variable in actual wastewater treatment. The dye decolorization is highly pH dependent. The photocatalytic decolorization of dye at different pH values varying from 2 to 8, clearly shows that the photocatalytic decolorization efficiency is higher in acid media (Figure 7).

The zero point charge value for Titania is at pH 6.8. The surface of Titania is positive at pH below 6.8 and negative at pH above 6.8. It is well documented that Titania is negatively charged in basic medium, and so it attracts cations in basic medium and repels anions. As DR80 and DR23 dyes are an anion at acidic pH, the photocatalytic degradation of DR80 and DR23 dyes is higher than that at basic pH. At acidic pH, more hydroxide ions (OH^-) in the solution induced the generation of hydroxyl free radicals (HO^-), which came from the photooxidation of OH^- by holes forming on the Titania surface [19].

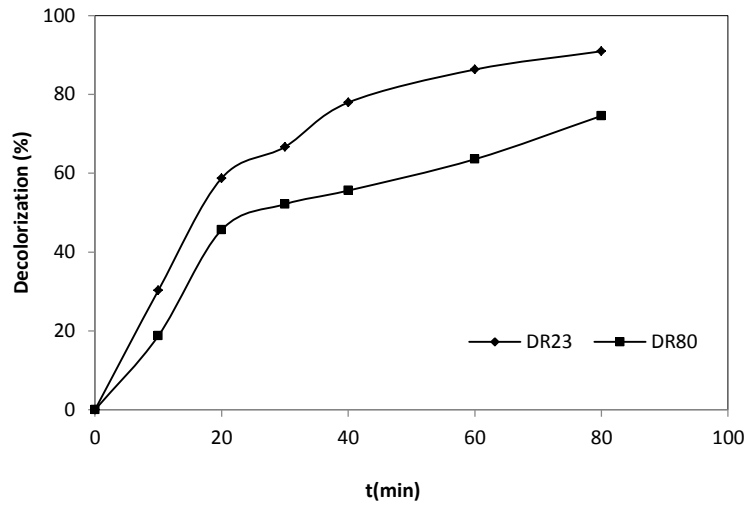

Figure 5: Effect of time on decolorization of dyes on the PAN/TiO_2 nanofiber (dye solution = 800 mL, initial dye concentration = 20 mg/L, pH=3 and catalyst dosage = 0.03 g).

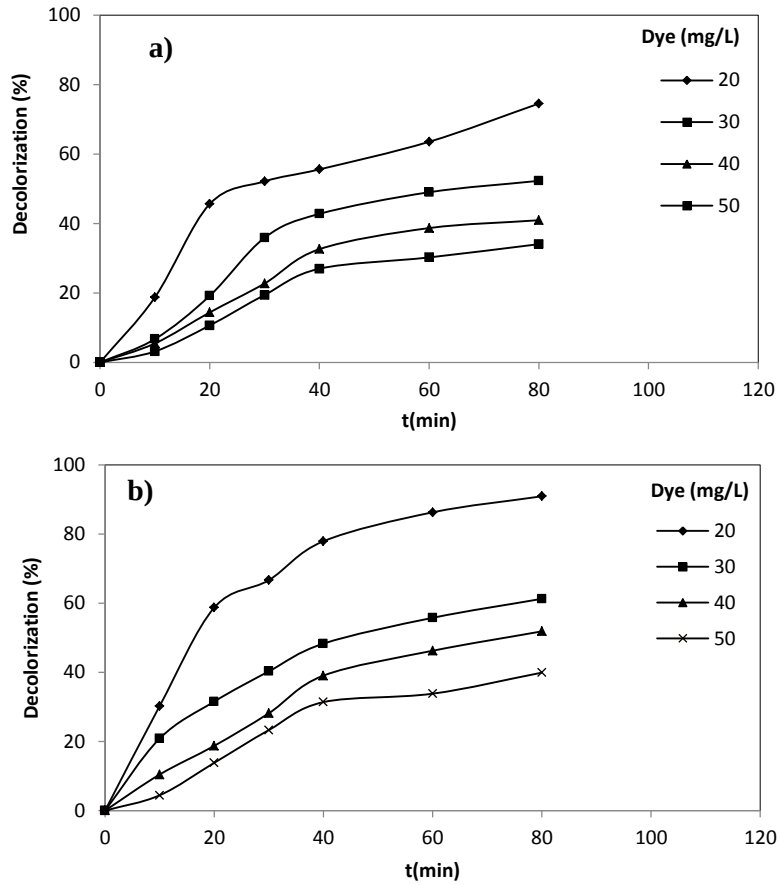

Figure 6: Effect of dye concentration on the decolorization of dyes by PAN/TiO_2 nanofiber (dye solution = 800 mL, pH=3, catalyst dosage = 0.03 g and time = 80 min) (a) DR80 and (b) DR23.

3.3. Kinetics of decolorization

In this paper, first-order kinetic model was used to investigate the photocatalytic dye decolorization by PAN/TiO_2 nanofiber. First-order kinetic model was utilized as follows:

$$-\ln (C/C_0) = kt \quad (1)$$

where C_0 = the initial dye concentration (mg/L), C = dye concentration at time *t* (mg/L), *t* = reaction time (min) and *k* = the first-order rate constant (min^{-1}).

The linear fit between the -ln (C/C_0) and reaction time at different dye concentrations can be approximated as first-order kinetics with good correlation coefficient values (Figure 8). The values of *k* and R^2 (correlation coefficient) of photocatalytic dye degradation by PAN/TiO_2 nanofiber are shown in Table 2. The results showed that photocatalytic dye degradation rate constant values decreased by increasing initial dye concentration. It could be attributed to the interference from intermediates formed upon degradation of the parental dye molecules. Such suppression would be more pronounced in the presence of an elevated level of degradation intermediates formed upon an increased initial dye concentration [20].

Table 2: The kinetic constant of photocatalytic dye degradation by PAN/TiO_2 nanofiber.

Dye (mg/L)	DR80		DR23	
	k	R^2	*k*	R^2
20	0.0184	0.9084	0.0328	0.9645
30	0.0108	0.9077	0.0136	0.9011
40	0.0076	0.9288	0.0101	0.9651
50	0.0059	0.9283	0.0071	0.9304

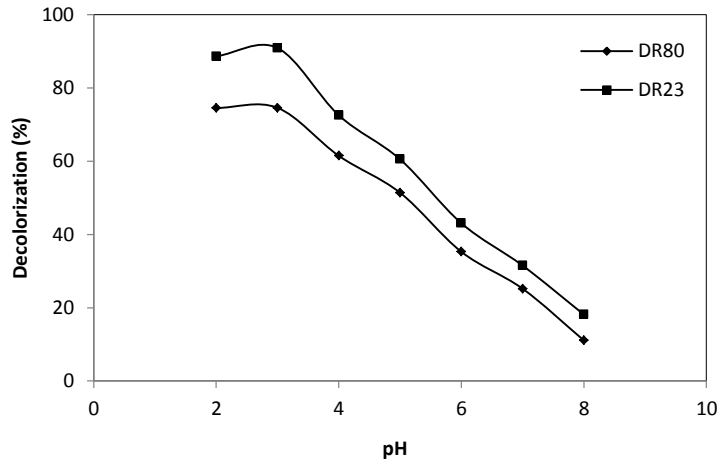

Figure 7: Effect of solution pH on the decolorization of dyes by PAN/TiO_2 nanofiber (dye solution = 800 mL, initial dye concentration = 20 mg/L, catalyst dosage = 0.03 g and time = 80 min).

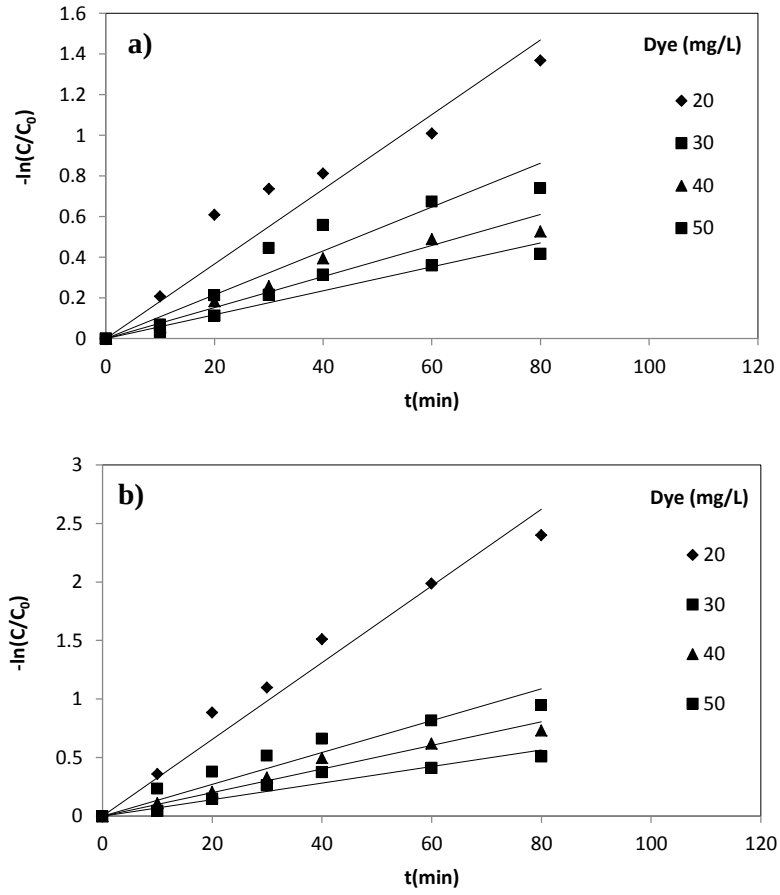

Figure 8: The first-order kinetics of photocatalytic dye decolorization by PAN/TiO_2 nanofiber: a) DR80 and b) DR23.

4. Conclusions

In this paper, PAN/TiO_2 nanofibrous catalyst was successfully prepared by electrospinning and characterized using FT-IR and SEM. The PAN/TiO_2 nanofiber was used as a photocatalyst for degrading DR23 and DR80 dyes. Dye degradation increases by increasing catalyst dosage. The reaction kinetics followed the first-order model. The photocatalytic dye

degradation rate constant (k) at 20 mg/L dye concentration was 0.0184 min^{-1} for DR 80 and 0.0328 min^{-1} for DR23. The results showed that PAN/TiO_2 nanofibrous nanomaterial could be used as a photocatalyst to treat colored textile wastewater.

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