

RAPID COMMUNICATION

## Fe-aminoclay-entrapping electrospun polyacrylonitrile nanofibers (FeAC-PAN NFs) for environmental engineering applications

Jae-Young Lee\*, Saehae Choi\*\*, Dongsu Song\*\*\*, Seung Bin Park\*\*\*, Moon Il Kim\*\*\*\*,  
Go-Woon Lee\*\*\*\*\*, Hyun Uk Lee\*\*\*\*\*,†, and Young-Chul Lee\*\*\*\*\*,†

\*Korea Railroad Research Institute (KRRRI), Railroad Museum Road #176, Uiwang-si, Gyeonggi-do 437-757, Korea

\*\*Sustainable Bioresource Research Center, Korea Research Institute of Bioscience & Biotechnology (KRIBB),  
Daejeon 305-806, Korea

\*\*\*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST),  
291, Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea

\*\*\*\*Department of BioNano Technology, Gachon University,  
1342, Seongnamdaero, Sujeong-gu, Seongnam-si, Gyeonggi-do 461-701, Korea

\*\*\*\*\*Quality Management Team, Korea Institute of Energy Research (KIER),  
152, Gajeong-ro, Yuseong-gu, Daejeon 305-343, Korea

\*\*\*\*\*Advanced Nano-Surface Research Group, Korea Basic Science Institute (KBSI), Daejeon 305-806, Korea  
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**Abstract**—Electrospun polyacrylonitrile nanofibers (PAN NFs) with entrapped water-soluble Fe-aminoclay (FeAC) [FeAC-PAN NFs] were prepared. Slow dropwise addition of water-soluble FeAC into a PAN solution, less aggregated of FeAC into electrospun PAN NFs was one-pot evolved without FeAC post-decoration onto as-prepared PAN NFs. Taking into consideration both the  $\text{Fe}^{3+}$  source in FeAC and the improved surface hydrophilicity, the feasibility of Fenton-like reaction for decolorization of cationic model dye methylene blue (MB) under 6 hrs UV-light irradiation was established. In the case where FeAC-PAN NFs were enhanced by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) injection, the apparent kinetic reaction rates were increased relative to those for the PAN NFs. Thus, our flexible FeAC-PAN NF mats can be effectively utilized in water/waste treatment and other environmental engineering applications.

**Keywords:** Fe-aminoclay (FeAC), Polyacrylonitrile Nanofibers (PAN NFs), One-pot Synthesis, Fenton-like Reaction, Water Treatment

### INTRODUCTION

Utilization of electrospun polymer fibers has specifically focused on bio-medical applications such as (bone) tissue engineering [1-3] and drug delivery [4,5] applications, owing to the availability of biocompatible synthetic- and biopolymers and the ease of organizing three-dimensional (3D) map formation [6-8]. Also, the industrial upscaling of electrospun polymer micro- and nano-fibers has shown the potential for removal of heavy metals [9,10] and harmful gas [7,11] as well as the degradation of organic pollutants [12-14] in environmental engineering applications. To impart additional unique properties to these polymer fibers, various nanoparticles (NPs) such as Ag, Au,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$  and  $\text{V}_2\text{O}_5$ , among others, can be decorated onto electrospun polymer fibers' surfaces [14,15], entrapped inside them, or both [12,16,17]. As for the "entrapment" option, one approach is one-pot synthesis of electrospun polymer fibers, for example, whereby graphene oxide is dispersed in a polymer solution, thus producing graphene-entrapping one-dimensional

(1D) polymer fibers [11,18].

In 1998, Mann et al. reported the synthesis of water-soluble 3-aminopropylfunctionalized magnesium (Mg) phyllosilicate, that is, Mg-aminoclay (MgAC) [19]. Lee et al., having fabricated Mg-aminoclay, synthesized additional Al-, Fe-, and Ca-aminoclays (AlAC, FeAC, and CaAC) [20,21]. They found that whereas AlAC had a strong toxic effect in HeLa cells, both FeAC and CaAC showed little cytotoxicity. FeAC in fact, due to aminoclay's hydrophilicity, can be applied for efficient water treatment [22] and soil remediation [20]. Such typical clays [23] have been widely applied to the preparation of inorganic-organic hybrid electrospun polymer fibers to be employed in drug-delivery systems (DDS) or water purification. For example, MgAC and FeAC have been decorated on electrospun polyacrylonitrile nanofibers (PAN NFs) onto which rich-carboxylic groups are introduced by oxygen-plasma treatment to effect EDC/NHS amide bonding [24].

Electrospun polycaprolactone (PCL) or PAN nanofibers have been used in environmental applications only rarely, with the exception of filtration and biomedicine etc. Recently, mass-produced NP-decorated electrospun polymer nanofibers have been applied to the removal of heavy metals [25] and the adsorption of harmfulness gas and dye. In other studies,  $\text{F}^{3+}$  ions with polymer nano-

†To whom correspondence should be addressed.

E-mail: leeho@kbsi.re.kr, dreamdb@gachon.ac.kr

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fibers were one-pot electrospun for the attempted reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^0$  [12]. However, organic-contaminant degradation based on flexible electrospun polymer nanofibers has been little studied.

In the present study, FeAC-entrapping PAN NFs were prepared by slow dropwise addition of FeAC into dimethylformamide (DMF) solution containing a PAN NF precursor for minimal agglomeration of FeAC NPs, thus simply affording a one-pot FeAC-PAN solution with NFs. Taking into the consideration that water-soluble FeAC could not be recovered easily, one-pot FeAC immobilization onto PAN NFs was successfully proved to be a heterogeneous catalyst system. The FeAC-PAN NFs were then employed to induce a Fenton-like reaction between FeAC and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), thereby generating free radicals that discolored methylene blue (MB) under 365 nm wavelength irradiation at (near-)neutral pH.

## MATERIALS AND METHODS

### 1. Preparation of Fe-aminoclay (FeAC)

According to the procedure available in the literature [20], 8.4 g of ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich, MO, USA) was dissolved in 200 mL of bulk ethanol (Samchun Pure Chemicals, Gyeonggi-do, Korea) in a 500-mL glass beaker. After 10 min vigorous stirring, the ferric chloride hexahydrate, manifesting as a brown color, was fully dissolved in the then brown-colored solution. Subsequently, 13 mL of 3-aminopropyltriethoxysilane ( $\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$ , Sigma-Aldrich) was dropwise added to the solution, immediately forming a slurry. The slurry was centrifuged at  $6,000 \times g$  for 10 min. The precipitated product, Fe-aminoclay (FeAC), was oven-dried at  $60^\circ\text{C}$  for 24 hrs. The dried Fe-AC was then pulver-

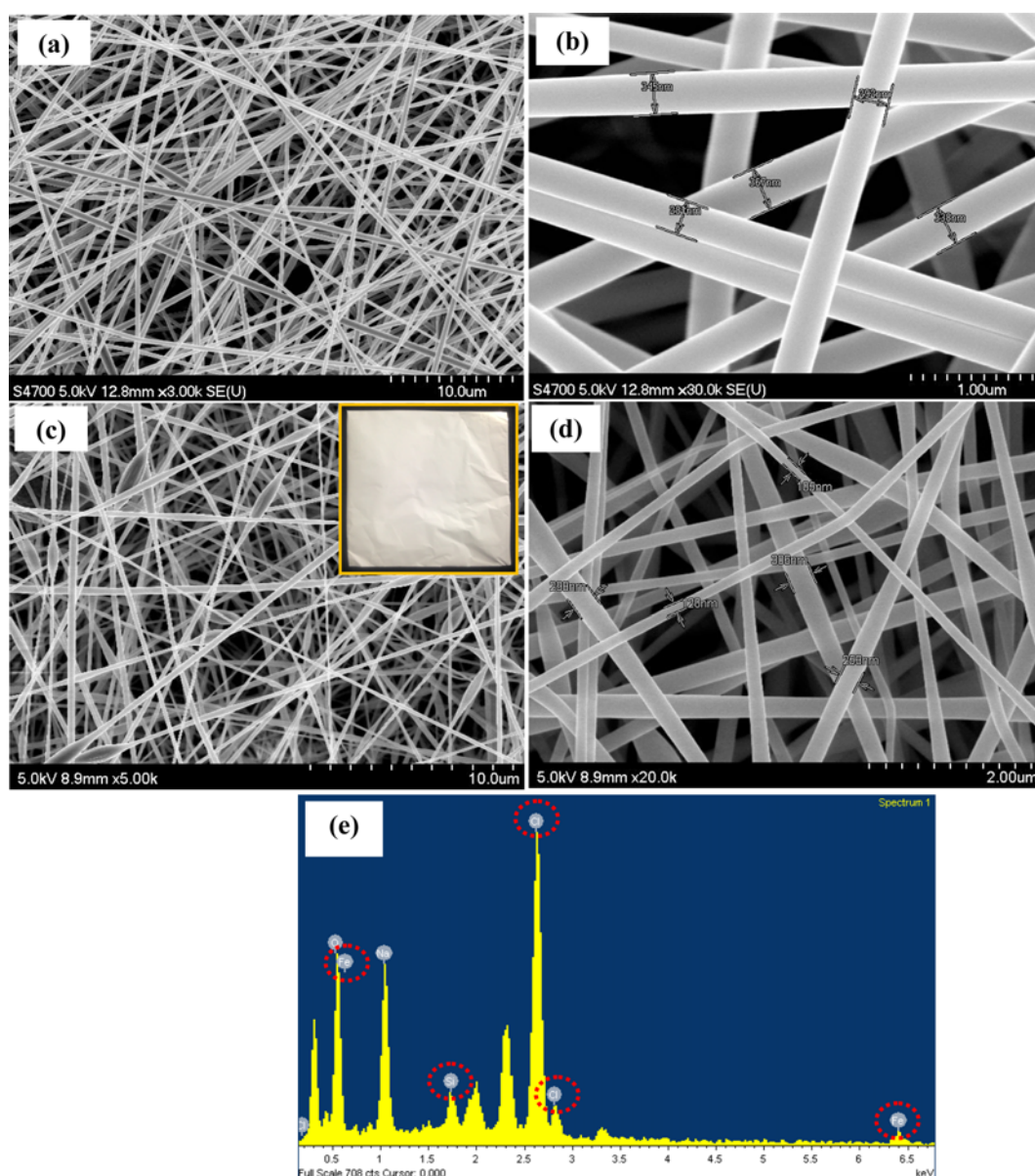


Fig. 1. Morphological observations of PAN and FeAC-PAN NFs under low (a) and (c) and high (b) and (d) scanning electron microscope (SEM) magnifications. (e) Energy-dispersive X-ray (EDX) analysis of FeAC-PAN NFs, the red-dotted circles indicating the presence of FeAC NPs.

ized into a powder by pestle and mortar preparatory to its utilization.

## 2. Synthesis of Electrospun FeAC-PAN NFs

FeAC (amount: 5.0 wt%) was mixed with double deionized (DI) water/DMF (ratio: 40 vol%: 60 vol%) to prevent its aggregation. Next, 10.0 wt% PAN solution was prepared by dissolution in 180 mL of DMF solvent and 6 hrs stirring at room temperature (RT). Then, 180 mL of the as-prepared solution was mixed with 20 mL of FeAC solution by 6 hrs stirring at RT. At the same time, a 20 kV voltage was applied between the tip of a needle attached to the syringe and an aluminum collector. By adjusting a syringe pump, the FeAC-PAN solution was successfully electrospun at a feed-rate of 1 mL/h onto aluminum foils [26]. FeAC-PAN NFs were then harvested and dried in a vacuum at 30 °C for 1 week. Flexible two-dimensional (2D) FeAC-PAN NF mats were obtained for use in a Fenton-like reaction.

## 3. Fenton-like Reaction Using Flexible FeAC-PAN NF Mats

The cut FeAC-PAN NF mats (W×L: 13 cm×13 cm) were placed on the bottom of a rectangular petri dish, into which 100 mL of 10 mg/L MB ( $C_{16}H_{18}N_3SCl$ , Sigma-Aldrich) was poured. Various

$H_2O_2$  concentrations (0, 0.1, 0.5, and 1.0 M) (35%, Extra Pure, Junsei, Japan,) were tested under UV irradiation (hand-held, 4 W, 365 nm, VSLAB VL-4CL, Korea) and 6 hrs 100 rpm magnetic-stirring, maintaining a 10 cm distance between the UV light and transparent petri dish reactors, with no pH adjustment. Control experiments under identical conditions but in the absence of FeAC-PAN NF mats also were conducted. The MB-decolorization efficiency in the absence or presence of FeAC-PAN NF mats was evaluated with respect to time ( $\ln(C/C_0)=kt$ , where  $k$  is the apparent reaction rate constant, and  $C_0$  and  $C$  are the initial and preceding reaction concentrations, respectively) [27]. The MB concentration was recorded to check the absorbance intensity at the 664 nm wavelength.

## 4. Characterization of PAN and FeAC-PAN NFs

To minutely examine the electrospun PAN and FeAC-PAN NFs, cold-type field-emission scanning electron microscopic (SEM-4700, operable at 0.5-30 V and 1 pA-2 nA with magnifications of 20-500,000 ×range) images were taken. Entrapped FeAC in the PAN NF morphology was observed on cross-sectioned transmission electron microscopic (TEM, Tecnai F20 model, Netherlands) images and

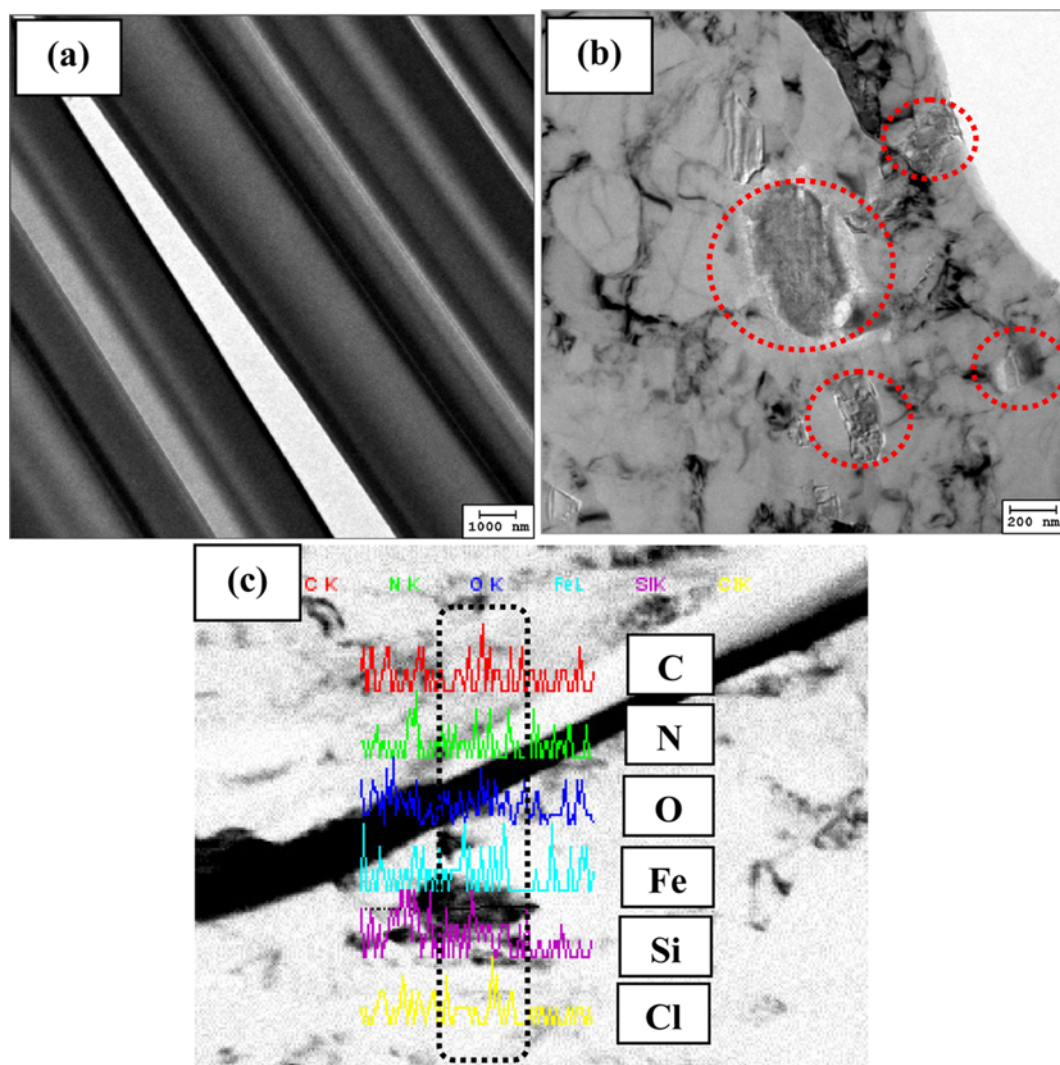


Fig. 2. Cross-sectioned images of PAN (a) and FeAC-PAN (b) NFs by transmission electron microscope (TEM) where the red dotted circles are the presence of FeAC NPs and elemental-composition (C, N, O, Fe, Si, Cl)-mapped line profiles (c) of FeAC-PAN NFs.

subjected to energy-dispersive X-ray (EDX) analysis. Additionally, the vibration modes in the organic functionalities of the respective PAN and FeAC-PAN NFs were determined by Fourier-transform infrared (FT-IR) spectrometry (FT-IR 4100, Jasco, Japan), following the KBr pellet protocol.

The wettability and surface free energy of the PAN and FeAC-PAN NF mats were evaluated by measurement of the contact angles (Dataphysics, OCA10) of liquid drops (DI water, ethylene glycol [Sigma-Aldrich] and n-hexane [Sigma-Aldrich]). Statistically, three independent determinations were averaged, and the surface energies were calculated by the extended Fowkes equation [28,29].

## RESULTS AND DISCUSSION

### 1. Characterization of FeAC-PAN NF Mats

As shown in Figs. 1(a) and 1(b), the PAN NFs were of ~200–400 nm diameters, whereas the FeAC-PAN NFs had been slightly reduced to ~100–300 nm (Figs. 1(c) and 1d). The Fig. 1(c) inset provides a digital camera image of the light-brown-colored FeAC-PAN NF mats (size: 20 cm×20 cm) on aluminum foil, with their flexible and 2D characteristics. The entrapment of the FeAC into PAN NFs was confirmed by EDX analysis in the presence of Fe, Si, and Cl.

The FeAC NPs inside the PAN NFs were further studied by comparison of TEM images of cross-sectioned PAN NFs (Fig. 2(a)) with those of FeAC-PAN NFs (Fig. 2(b); marked by red dotted circles). The elemental-composition (C, N, O, Fe, Si, and Cl)-mapped line profiles (Fig. 2(c)) also were examined and consequently FeAC NPs were successfully entrapped or decorated onto PAN NFs.

The organic functional groups of the FeAC and FeAC-PAN NFs were recorded according to their FT-IR spectra (Fig. 3) [20,27]. Prominent vibration peaks of the pristine PAN NFs appeared at ~2,926/2,849  $\text{cm}^{-1}$  (-CH stretch), ~2,240  $\text{cm}^{-1}$  (C≡N stretch), ~1,450  $\text{cm}^{-1}$  (-CH<sub>2</sub> bend), strong ~1,745  $\text{cm}^{-1}$  (C=O stretch), and ~1,462  $\text{cm}^{-1}$  (C-O stretch). In the case of the FeAC, other vibration modes, namely, for Fe-O (477/697  $\text{cm}^{-1}$ ), Si-O-Si (1,040  $\text{cm}^{-1}$ ), Si-O-C (1,116  $\text{cm}^{-1}$ ), CH<sub>2</sub> bending (1,489  $\text{cm}^{-1}$ ), NH<sub>2</sub> bending (1,611  $\text{cm}^{-1}$ ), NH<sub>3</sub><sup>+</sup> (1,999

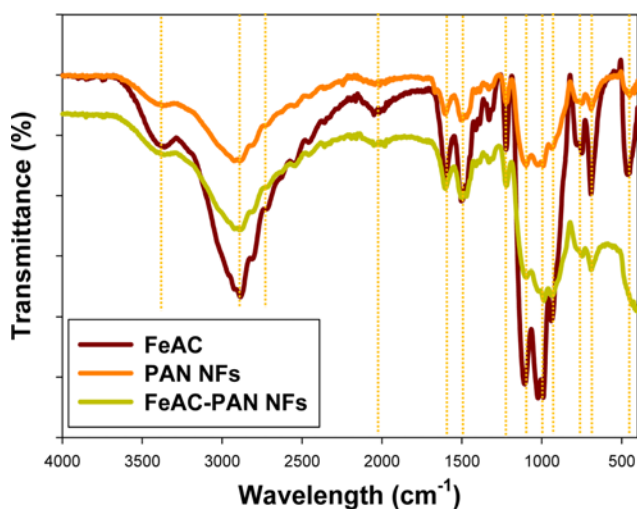


Fig. 3. Fourier-transform infrared (FT-IR) spectra of FeAC, PAN and FeAC-PAN NFs.

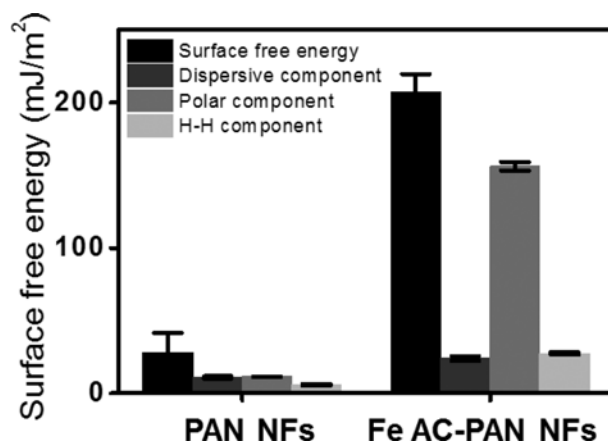


Fig. 4. Surface free energy ( $\text{mJ/m}^2$ ) of PAN and FeAC-PAN NFs.

$\text{cm}^{-1}$ ), CH<sub>2</sub> (3,042  $\text{cm}^{-1}$ ), and -OH (3,392  $\text{cm}^{-1}$ ), were assigned in a manner consistent with the relevant earlier reports. In the PAN NFs and FeAC, most of the vibration peaks were overlapped; however, in FeAC-PAN NFs, the intensities of the Si-O-Si and Fe-O vibration peaks in FeAC were increased [27].

As plotted in Fig. 4, the PAN and FeAC-PAN NFs' surface hydrophilicity as related to the surface free energy ( $\text{mJ/m}^2$ ) was plotted. The surface free energy (summation of dispersive component, polar component, and hydrogen-hydrogen component) in the PAN NFs was ~25  $\text{mJ/m}^2$ , the polar component of which was calculated as ~10  $\text{mJ/m}^2$ . By contrast, the surface free energy in the FeAC-PAN NFs attained ~200  $\text{mJ/m}^2$ . Demonstrably then, there was an increase in the surface free energy of the FeAC-PAN NFs relative to that of the PAN NFs, which, significantly, could be attributed to the entrapment of the hydrophilic FeAC NPs.

### 2. Photo-Fenton Reaction of FeAC-PAN NF Mats [27,30,31]

Next, apparent reaction rate constants were obtained in the absence and presence of FeAC-PAN NF mats (Fig. 5). According to 0, 0.1, 0.5, and 1.0 M H<sub>2</sub>O<sub>2</sub> concentrations under UV irradiation, the apparent reaction rate constants with the photo-Fenton-reacted FeAC-PAN NF mats were 0.0239 h<sup>-1</sup>, 0.0329 h<sup>-1</sup>, 0.1084 h<sup>-1</sup>, and 0.2113 h<sup>-1</sup>, respectively. At the 0.5 and 1.0 M H<sub>2</sub>O<sub>2</sub> concentrations, the apparent reaction rate constants in the presence of FeAC-PAN NFs (i.e., 0.1084 h<sup>-1</sup> and 0.2113 h<sup>-1</sup>, respectively) were enhanced approximately two-fold relative to the conditions under which FeAC-PAN NFs were absent (0.0444 h<sup>-1</sup> and 0.1036 h<sup>-1</sup>, respectively). The photographs of sampling vials displayed decolorization of MB at 0, 3 and 6 hrs at 1.0 M H<sub>2</sub>O<sub>2</sub> concentration from Fig. 5(b). Although the degradation of MB reached ~80% during 6 hrs reactions, flexible and recyclable FeAC-PAN NF mats can be inserted by a few foldings to induce fast dye degradation. For the decoloration mechanism, in the presence of H<sub>2</sub>O<sub>2</sub>, it reacted with Fe source in FeAC, both •OOH and •OH radicals generated from Fenton-like reaction ( $\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \bullet\text{OOH} + \text{H}^+ + \text{Fe}^{2+}$ ) and subsequent reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$ ) degraded for MB molecules [27]. After five runs, the FeAC-PAN NF-based photo-Fenton activity at the 0.5 M H<sub>2</sub>O<sub>2</sub> concentration had been only marginally reduced. This correlates with the fact that the observed morphology of the recycled FeAC-PAN NFs was still almost intact.

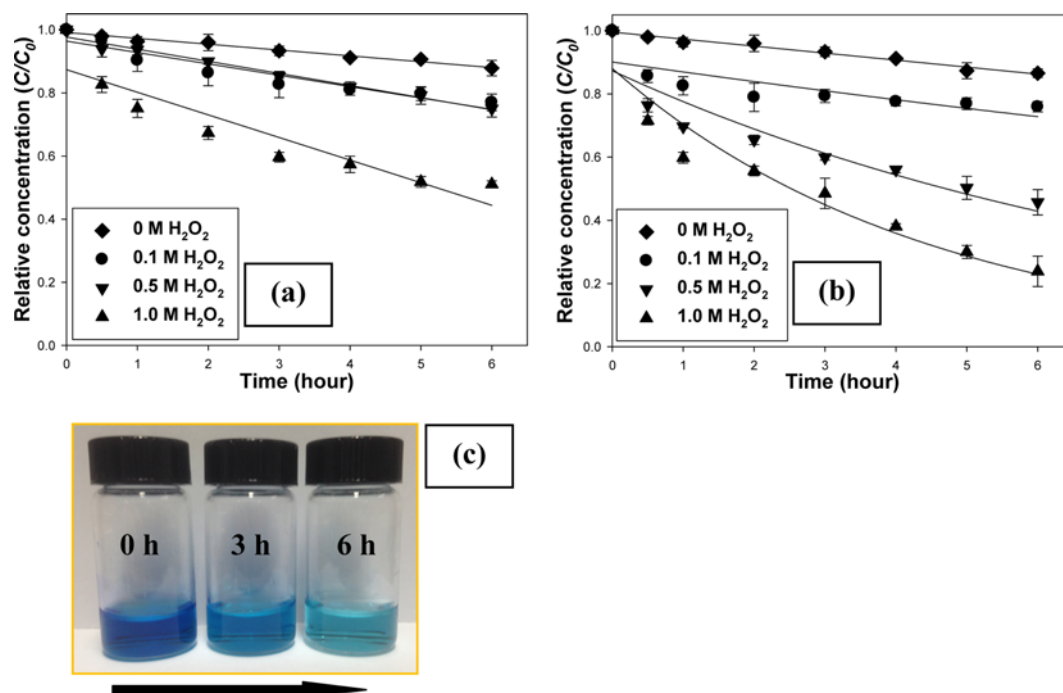


Fig. 5. Relative degradation of MB concentration ( $C/C_0$ ) by PAN (a) and FeAC-PAN (b) NFs according to  $H_2O_2$  concentration under 6 hrs UV irradiation and its corresponding photographs of in sampling vials (c) at 1.0 M  $H_2O_2$  concentration under 6 hrs UV irradiation.

## CONCLUSIONS

Slow dropwise addition of water-soluble FeAC into PAN DMF solution enabled successful one-pot synthesis of electrospun FeAC-PAN NFs. Due to the hydrophilicity of the FeAC-PAN NFs, their photo-Fenton reaction could, according to the  $H_2O_2$  concentration, decolorize MB under 6 hrs UV-light irradiation. At the 0.5 and 1.0 M  $H_2O_2$  concentrations, the apparent kinetic reaction rate in the presence of FeAC-PAN NFs was enhanced approximately two-fold relative to the condition under which FeAC-PAN NFs were absent. Thus, it can be concluded definitively that one-pot-synthesized FeAC-entrapping PAN NFs can be effectively utilized to oxidize organic pollutants in environmental engineering applications. To further develop our technique, research entailing the loading of larger amounts of water-soluble FeAC is planned for increase in the decoloration efficiency with recycling capacity, like the reported efficient single  $TiO_2$  and doped- $TiO_2$  photocatalysts.

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