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Adsorption of iron (III) onto chemically modified polyacrylonitrile nanofibers from aqueous solution and used as photocatalyst for the degradation of bromophenol blue dye

Khalid Saeed[a,b,*], Nasib Khan[a], Soo-Young Park[c]

[a]*Department of Chemistry, University of Malakand, Chakdara, Dir (Lower), Khyber Pakhtunkhwa, Pakistan, emails: khalidkhalil2002@yahoo.com (K. Saeed), nasib4u@yahoo.com (N. Khan)*
[b]*Department of Chemistry, Bacha Khan University, Charsadda, Khyber Pakhtunkhwa, Pakistan*
[c]*Department of Polymer Science, Kyungpook National University, #1370 Sankyuk-Dong, Buk-Gu, Daegu 702-701, South Korea, email: psy@knu.ac.kr*

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ABSTRACT

Hydrazine modified polyacrylonitrile (F-PAN) nanofibers were used as an adsorbent for the removal of iron ions (Fe(III)) from aqueous medium and then iron adsorbed F-PAN nanofibers (Fe/F-PAN) is used as a photocatalyst for the degradation of bromophenol blue in aqueous medium. The F-PAN nanofibers were analyzed by scanning electron microscope, energy dispersive X-rays (EDX), and Fourier transform infra-red spectrometer. However, the iron adsorption and photodegradation study were carried out via atomic absorption and ultraviolet–visible spectrophotometers, respectively. The morphological study presented that the Fe were adsorbed on nanofibers mat, which present both in agglomerated and in dispersed form. The presence of Fe was also confirmed by EDX. The adsorption study presented that the equilibrium adsorption data were best fitted to Freundlich model as compared with Langmuir isotherm model. The saturation adsorption capacity for iron was 112 mg g^{-1}. The Fe/F-PAN nanofibers were employed for the photocatalytic degradation of bromophenol blue dye in aqueous media under UV-irradiation as a function of time, concentration of dye, pH, and Fe/F-PAN catalyst dosage. The photodegradation study showed that Fe/F-PAN nanofibers degraded about 88% of bromophenol blue dye in aqueous medium within 20 min. The photocatalytic degradation capability of recovered Fe/F-PAN catalyst was also investigated. It was found that the recovered Fe/F-PAN catalyst significantly degraded bromophenol blue, but its catalytic activity was slightly lower than original Fe/F-PAN nanofibers.

Keywords: Adsorption; Photodegradation; Nanofibers; Recovered catalyst; Bromophenol blue; Adsorption isotherms; Iron oxide nanoparticles

1. Introduction

Water pollution is a serious environmental problem arises worldwide due to industrialization and urbanization. The effluents from different industries contain various types of organic and inorganic harmful pollutants. Heavy metals and dyes are most common carcinogenic pollutants of industries, which enter into the water sources without any proper treatment and violate environmental policies in developing countries [1]. Heavy metals are well-known pollutant, which comes from various sources such as chemical industries, textile industries, cosmetics industries, mining, electroplating, and contaminate our water sources. The heavy metals can causes various problems like dehydration, stomachache, nausea, dizziness, lack of coordination in muscles, destroying the nervous systems of young children, lung irritation, eye irritation, skin rashes, vomiting, lung insufficiency, and liver damage [2]. To overcome the heavy metals pollution problem, various physical and chemical techniques such as filtration,

* Corresponding author.

evaporation, ion-exchange, reverse osmosis, electrochemical treatment, oxidation-reduction processes, and adsorption are applied for the removal of heavy metals from water effluents. Among these techniques, adsorption is widely used for the removal of heavy metals and organic pollutants from waste water due to high loading capacity for targeted heavy metals, more effective and low-cost technique [3–5]. During the adsorption process, the pollutants get attached through physical or chemical interactions on the surface of adsorbents.

Dyes and pigments are also important water pollutants, which arise from the rapid development of textile industries, leather, food processing, paper, cosmetic, and dyes manufacturing industries [6]. Dyes consist of two main groups of compounds: chromophores and auxochromes. Chromophores determine the color of dye while the auxochromes determine the intensity of color [7]. Various dyes (organic functional groups) have its own harmful effect, which not only affect marine plants and animals but also cause various serious diseases like cancer in human being [8,9]. Dyes contaminates can be removed by various techniques such as adsorption [10], chemical precipitation, ozonation [11], biosorption [12], and photoxidation. Among these techniques, photocatalytic degradation is the best technique where macromolecules are degraded into to simplest/nontoxic species by photons. Photocatalytic degradation is mainly related with structure of dyes and auxiliary functional groups attached central aromatic nuclei of dyes [13]. Various metals and metal oxides nanoparticles such as Fe_3O_4 nanoparticles [14], TiO_2 nanoparticles [15], CoO [16], etc. are used as a photocatalyst for the photocatalytic degradation of dyes in aqueous medium.

In present study, polyacrylonitrile (PAN) nanofibers were prepared by electrospinning technique. The nitrile group of PAN is chemically modified by treatment with hydrazine. The F-PAN nanofibers were then used for the adsorption of iron from their aqueous solution. The selection of iron is due to its harmful effects when the concentration of iron increases from the permissible level, which accumulate in bone marrows, liver, pancreas, skin, heart muscles, and testicles and causes serious disorders in our body [17]. The Fe/F-PAN nanofibers were further used for photocatalytic degradation of bromophenol blue dye in aqueous medium. Recently, chemically modified polymeric materials and their composites are used only for the removal of heavy metal from aqueous solution or for the photodegradation of pollutants in aqueous medium. For example PAN/carbon nanotubes [18], rubber/silver [19] composites were used for the photodegradation of indigo carmine and methylene blue, and methyl orange dye, respectively. Similarly, Ethylenediaminetetraacetic acid modified PAN [20] and aminated PAN/γ–AlOOH [21] electrospun composite nanofibers were used for the removal of Cd and Cr and Pb(II), Cu(II), and Cd(II) ions in aqueous solution, respectively. To the best of our knowledge, the chemically modified PAN nanofiber is not used before for the adsorption of metal ion and then adsorbed metal ions PAN nanofibers are employed for the photodegradation of bromophenol blue in aqueous solution.

2. Experimental

2.1. Materials

Hydrazine, iron chloride ($FeCl_3 \cdot 6H_2O$) and dimethylformamide (DMF) were purchased from Sigma Aldrich, Germany, while bromophenol blue dye was purchased from Scharlau (Spain) and used as received. The PAN (copolymer of acrylonitrile (91.4% mol) and methylacrylate (8.6% mol)) were supplied by Taekwang Industry (South Korea).

2.2. Preparation of PAN nanofibers

The known amount of PAN polymer was dissolved in specific quantity of DMF to the prepared 15 wt.% solution of PAN polymer. The PAN solution was taken in glass syringe with a needle tip 0.5 mm diameter. The flow rate, distance between the collector and syringe needle, voltage, and electrospinning temperature were 1 mL h^{-1}, 15 cm, 20 kV, and 50°C, respectively. The PAN electrospun nanofibers were collected on metallic collector.

2.3. Functionalization of PAN nanofibers

The PAN nanofibers mat (fixed in Teflon frame) and 100 mL hydrazine was taken in a beaker and heated at 90°C to 94°C for 2.5 h. The F-PAN nanofibers were removed from the reaction medium and washed several times with distilled water. The F-PAN mat was also washed with ethanol in order to remove unreacted hydrazine from the surface of F-PAN nanofibers. The modified PAN is then dried in an oven at 60°C and stored for further use.

2.4. F-PAN nanofibers as an adsorbent

To study the adsorption capacity of F-PAN nanofibers, 0.02 g nanofiber mat was shacked in 10 mL $FeCl_3 \cdot 6H_2O$ aqueous solution (different ppm) for 120 min using mechanical shaker (Wrist action shaker model 75-Burrel, Scientific Pittsburgh, PA, USA). The amount of Fe adsorbed from their aqueous solutions of different concentration was investigated using atomic absorption spectrophotometer.

2.5. Photocatalytic degradation of bromophenol blue dye

The dried strip of Fe/F-PAN (0.01 g) was taken in beaker containing 5 mL bromophenol blue dye (50 ppm) and sealed with a colorless plastic to allow light and avoid evaporation. The solution was then placed in dark in order to achieve adsorption/desorption equilibrium. The dye solution was then irradiated under ultraviolet UV-light (254 nm, 15 W) as a function of time with constant stirring. After specific irradiation time, Fe/F-PAN nanofibers were removed from dye solution. The photodegradation study was performed by ultraviolet–visible (UV/VIS) spectrophotometer while the percent degradation of dye determined by following equations [22].

$$\text{Degradation rate}(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

$$\text{Degradation rate}(\%) = \frac{A_0 - A}{A_0} \times 100 \quad (2)$$

where C_0 is the initial dye concentration, C is the dye concentration after UV irradiation, A_0 shows initial absorbance, and A shows the dye absorbance after UV irradiation.

2.6. Instrumentation

The amount of Fe before adsorption and after adsorption was determined using atomic absorption spectrophotometer. The morphological study of F-PAN and Fe/F-PAN nanofibers was carried out by scanning electron microscope (SEM) (JEOL, JSM-5910, Japan). The percent elemental study of F-PAN and Fe/F-PAN nanofibers samples were performed by energy dispersive X-rays (EDX) spectrometer (Model INCA 200/Oxford Instruments, UK, Company Oxford). The degradation study of dye was performed by UV–VIS spectrophotometer (UV-1800, Shimadzu, Japan).

3. Results and discussion

3.1. Morphologies of F-PAN and Fe/F-PAN

Fig. 1 shows the SEM images of F-PAN and Fe/F-PAN nanofibers. The SEM image of F-PAN (Fig. 1(a)) nanofibers presented that the nanofibers were uniform pattern and had no crack/damage were found on the surface of F-PAN nanofibers. The size of the electrospun nanofibers were in the range of 200–300 nm. The morphological study of Fe/F-PAN nanofibers (Fig. 1(b)) illustrated that the Fe particles adsorbed on surface of nanofibers mat, which present both an agglomerated as well as in dispersed form. The F-PAN nanofibers provided large surface area for the attachment of Fe NPs.

The EDX study was performed in order to investigate the content elements of nanofibers. Fig. 2 illustrates the EDX spectra of F-PAN and Fe/F-PAN, which confirmed the presence of Fe on Fe/F-PAN nanofiber. The elemental analysis presented that F-PAN had only carbon and nitrogen, while in the case of Fe/F-PAN nanofibers, Fe and minute quantity of chlorine were also found along with carbon and nitrogen.

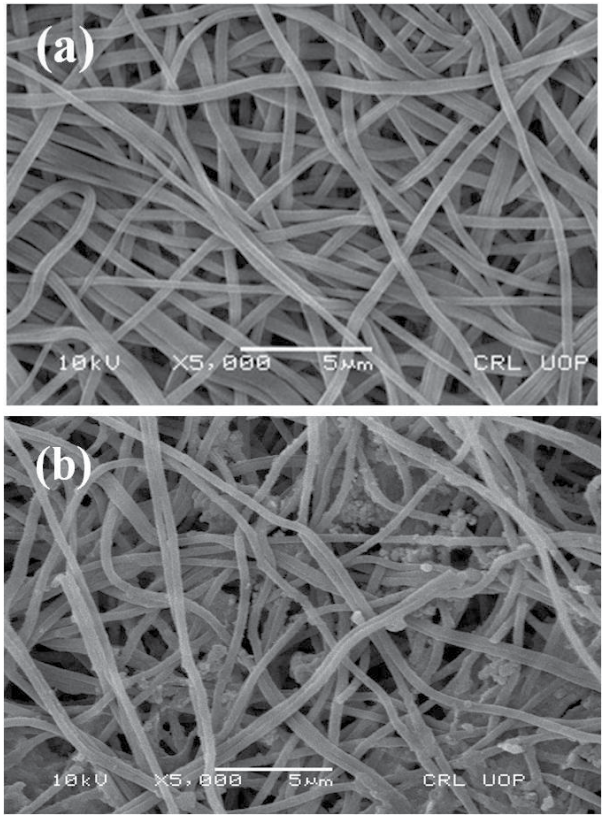

Fig. 1. SEM images of (a) F-PAN, and (b) Fe/F-PAN electrospun nanofibers.

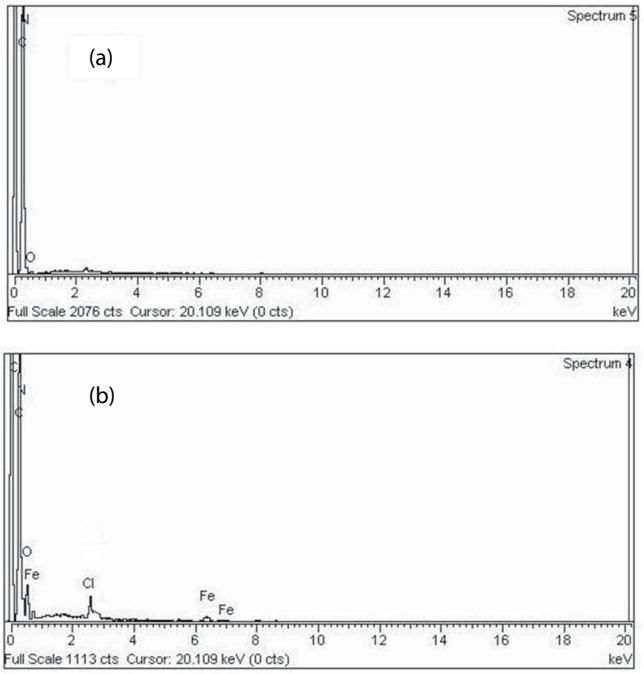

Fig. 2. EDX spectra of (a) F-PAN and (b) Fe/F-PAN nanofibers.

3.2. Fourier transform infra-red spectrometer study

The chemically modification of Nitrile group of PAN is confirmed by Fourier transform infra-red spectrometer (FT-IR) spectrometer and the results are shown in Fig. 3. The spectra presented that the nitrile peak (2,250 cm^{-1}) of PAN is disappeared after the treatment with hydrazine (Fig. 3(b)). While the peak in the range of 1,700–1,750 cm^{-1} and 1,150–1,050 cm^{-1} might be due to carbonyl and ether group. The carbonyl and ether bands came from the methylacrylate comonomer. The FT-IR of F-PAN also presented new peaks at about 3,100–3,400 cm^{-1}, which were due to the N–H stretching vibration of the secondary amino group [23]. The broad band in the region of about 1,700–1,630 cm^{-1} might be due to the coupling of carbonyl and C=N groups. The disappearance of nitrile peak and the appearance of new at 3,100–3,400 cm^{-1} presented that the PAN was chemically modified with hydrazine. The PAN was modified with hydrazine because the metal adsorption capacity of chelating fibers greatly depends upon the type and contents of the functional groups present on the adsorbent. The adsorbents, which have N-donor atoms, can strongly attach with metals ions.

3.3. Adsorption equilibrium isotherm

Fig. 4 shows the equilibrium adsorption quantity of Fe (III) at 2 h under various equilibrium concentrations. It was found that initially the adsorption increased as increased

the Fe (III) concentration and then leveled off. The initial increase in Fe (III) adsorption with the increase in its concentration might be due to the availability of active sites on F-PAN nanofibers and then the adsorption equilibrium is reached to maximum because of saturation of F-PAN nanofibers active sites. The adsorption equilibrium data of Fe (III) were also analyzed by Langmuir and Freundlich isotherm models. These models provided the relationship between the amount of Fe (III) adsorbed on surface of adsorbent and the concentration of Fe (III) in solution at equilibrium.

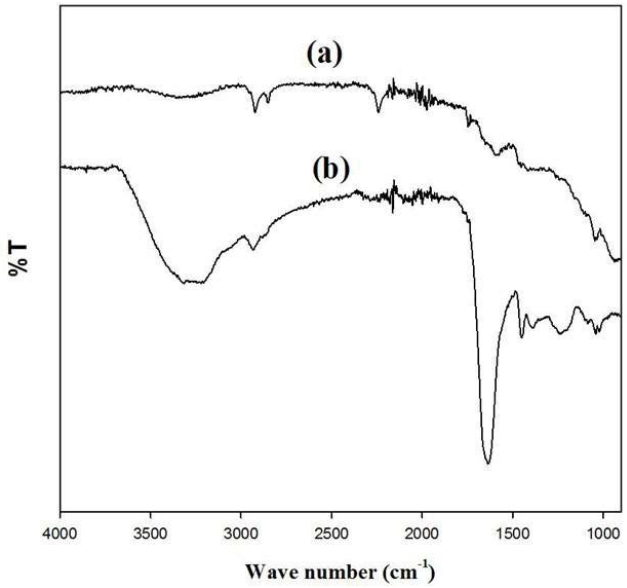

Fig. 3. FT-IR spectra of (a) PAN and (b) F-PAN nanofibers.

The linear form of Langmuir equation is given below:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

where C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the amount adsorbed per gram of adsorbent, K_L and q_m are the Langmuir adsorption isotherm constants, respectively.

The linear form of Freundlich equation is as follow:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{4}$$

where K_F is the Freundlich sorption isotherm constant (mg g^{-1}) and $1/n$ (g L^{-1}) is a measure of the adsorption intensity of heterogeneity factor. While q_e (mg g^{-1}) is the amount adsorbed per gram of adsorbent and C_e (mg L^{-1}) is the equilibrium metal ion concentration. The R^2 values are calculated for both Freundlich and Langmuir isotherms. The R^2 value for Freundlich isotherm was 0.953 while the R^2 value for

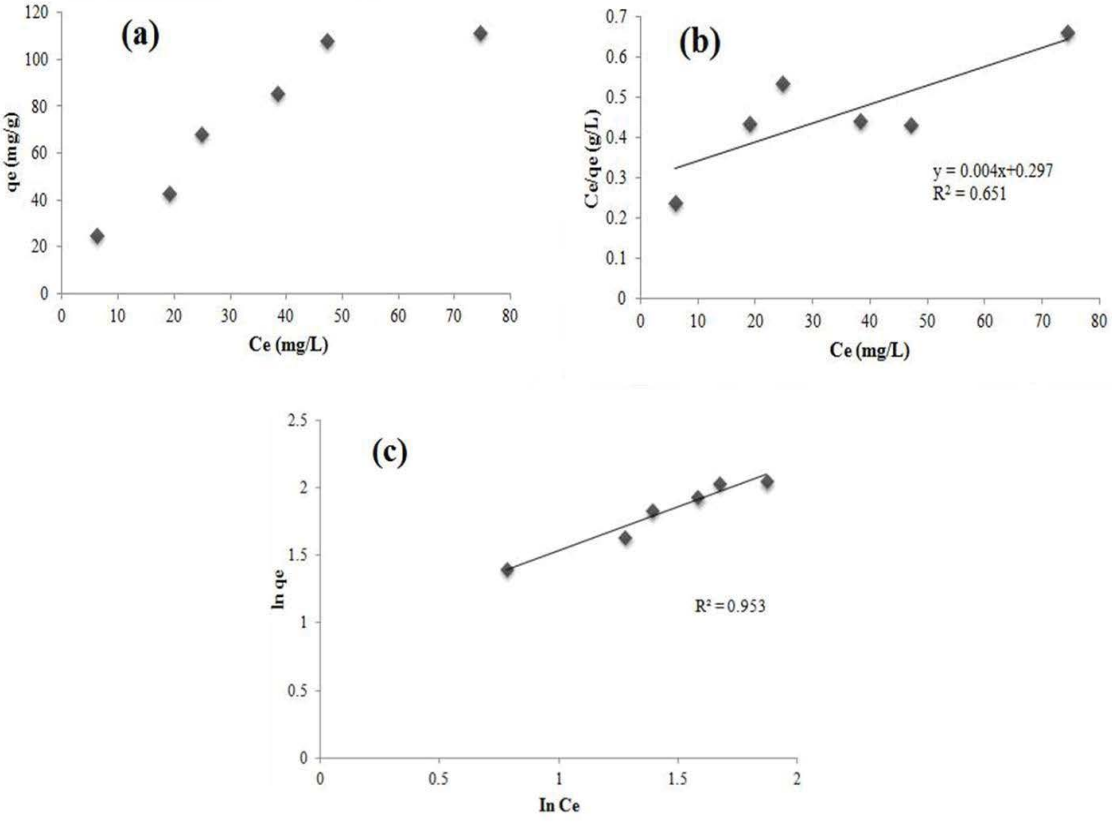

Fig. 4. (a) Adsorption isotherm, (b) Langmuir isotherm, and (c) Freundlich isotherm for the adsorption of Fe from aqueous solutions on F-PAN.

Langmuir isotherm was 0.651. It means that the values are best fitted to Freundlich isotherm as compared with Langmuir isotherm.

3.4. Photocatalytic degradation of bromophenol blue

The photocatalytic properties of Fe/F-PAN nanofibers were studied by photocatalytic degradation of bromophenol blue dye in aqueous media under irradiation of UV-light as a function of time, concentration of dye, pH, and Fe/F-PAN catalyst dosage. Figs. 5 and 6 show the spectra of bromophenol blue dye in aqueous solution before and after the UV-light irradiation in the presence of Fe/F-PAN nanofibers (used as photocatalyst). The UV–VIS spectra clearly showed that the degradation of dye increased as increased the irradiation time and after 15 min almost leveled off. The results (Fig. 6) also illustrated that about 88% of dye is degraded within 20 min. It means that the Fe/F-PAN nanofibers also use an efficient photocatalyst during the photodegradation and could be effectively applied for the removal of contaminates from effluents. The comparison of the Fe/F-PAN nanofibers as photocatalyst with the reported results is shown in Table 1.

The UV/VIS spectra of bromophenol blue in aqueous solution before and after UV irradiation by recovered catalyst are shown in Fig. 5(b). The results showed that the recovered Fe/F-PAN nanofibers significantly degraded dye but its catalytic activity was less as compared with original Fe/F-PAN nanofibers. This decrease in the photocatalytic activity of recovered Fe/F-PAN nanofibers might be attributed to the deposition of photo insensitive hydroxides on the Fe/F-PAN nanofibers surface, which block its active site [27].

The recovered catalyst degraded about 62% in 5 min and 81% of dye within 20 min. The comparison of %degradation of dye in aqueous solution by original and recovered Fe/F-PAN nanofibers is shown in Fig. 5(c). The results Fig. 5(c) presented that the Fe/F-PAN nanofibers mat might be reused various times as a photocatalyst because the efficiencies of the initially used and reused nanofibers mat are almost same. It means that Fe/F-PAN nanofibers might have great commercial potential because it is an economically friendly photocatalyst.

The propose mechanism is that when Fe/F-PAN is expose to UV irradiation, the Fe nanoparticles are first photoexcited to generate conduction band electrons (e^-) and valence band holes (h^+). The generated holes are ultimately trapped by surface hydroxyl groups (or H_2O) at the surface of Fe/F-PAN and as result generation of $OH^\bullet$ radicals occur. The dissolved

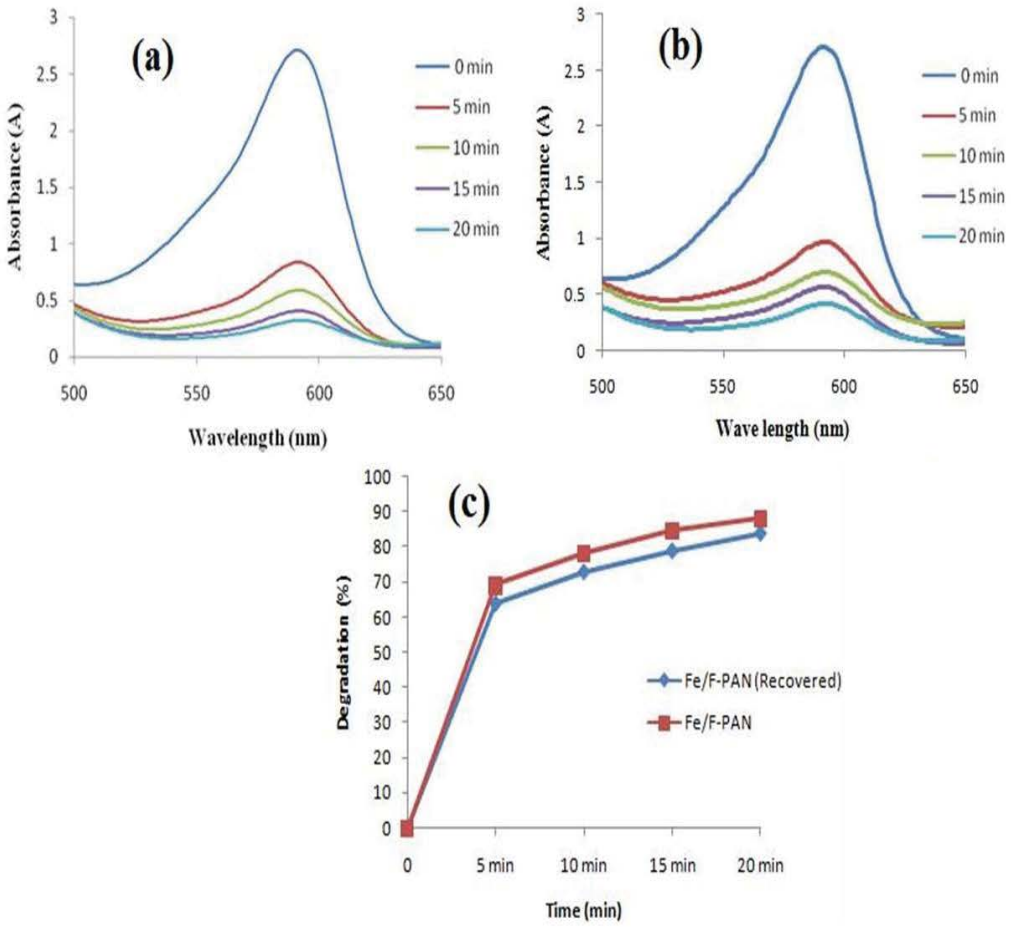

Fig. 5. UV/VIS spectra of bromophenol blue photocatalytic degraded by (a) Fe/F-PAN nanofibers, (b) recovered Fe/F-PAN nanofibers, and (c) percent degradation of dye at room temperature.

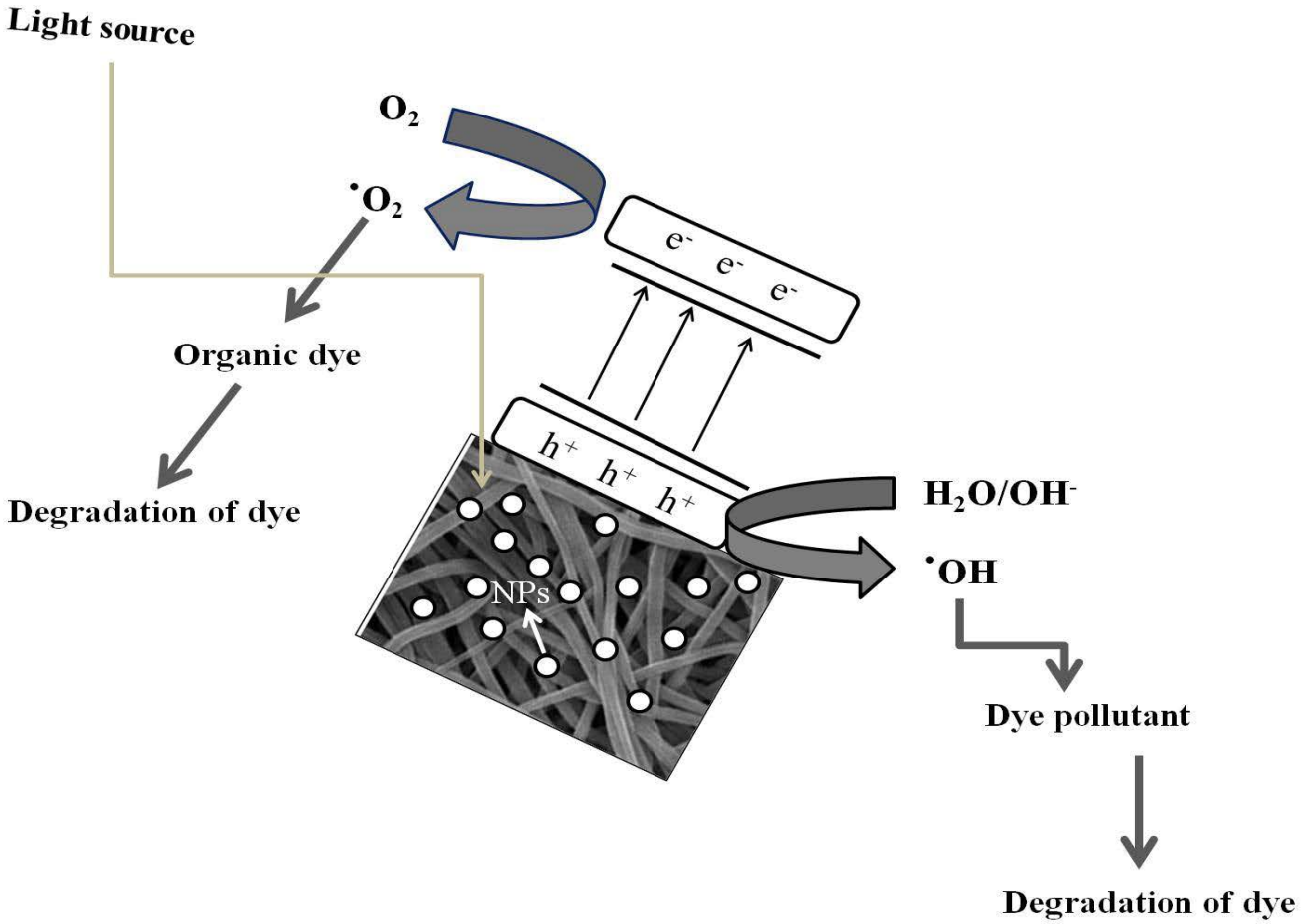

Fig. 6. Detail mechanism of bromophenol blue dye.

Table 1
Comparison study of F-PAN nanofibers as photocatalysts with other reported results

Adsorbent	Iron adsorption (mg g^{-1})	References
Fe/F-PAN nanofibers	35.3	Present study
Pre treated clinoptilolite	23	[24]
Zeolitic tuff	20.7	[25]
Kaolin	14.68	
Modified Orange peel	4.8	[26]
Activated Orange peel	6.0	

oxygen, which presents in aqueous medium might react with photogenerated electrons and results superoxide anion radical. Both $OH^{\bullet}$ and $O_2^{\bullet-}$ are strong oxidizing agents, which can easily attack any organic molecules and as a result degradation of organic pollutants occurs [28]. The detail mechanism of bromophenol blue dye is shown in Fig. 6.

$$H^{+}_{VB} + OH^{-} \rightarrow OH^{\bullet} \quad (5)$$

$$e^{-} + O_2 \rightarrow O_2^{\bullet-} \quad (6)$$

$$Dye + OH^{\bullet} + O_2^{\bullet-} \rightarrow CO_2 + H_2O + ... \quad (7)$$

3.5. Effect of Fe/F-PAN nanofibers dosage on photodegradation

The photocatalytic degradation of dyes depends upon the available surface area and active sites of photocatalyst. Fig. 7 shows the UV/VIS spectra and percent degradation of bromophenol blue dye in aqueous solution before and after UV irradiation. Fig. 7 clearly showed that photocatalytic degradation of bromophenol blue increased as increased Fe/F-PAN dosage. The result illustrated that 0.01, 0.02, 0.03, 0.04, and 0.05 g Fe/F-PAN nanofibers showed about 60%, 77%, 81%, 87%, and 88% degradation of bromophenol blue in aqueous medium, respectively.

3.6. Effect of pH of medium

Fig. 8 presents the effect of pH on photodegradation of bromophenol blue in aqueous medium. Fig. 8(a) shows the UV/VIS spectra of bromophenol blue in aqueous media before and after UV-light irradiation in the presence of Fe/F-PAN nanofibers. The results Fig. 8(b) showed that the photodegradation was gradually increased as increased the pH of the medium. It was found that only 48.8% of dye is degraded

at pH 2, which increased to 98.8% at pH 10. The increased photodegradation rate in basic medium might be due to the better formation of hydroxyl radicals and strong oxidizing specie [29].

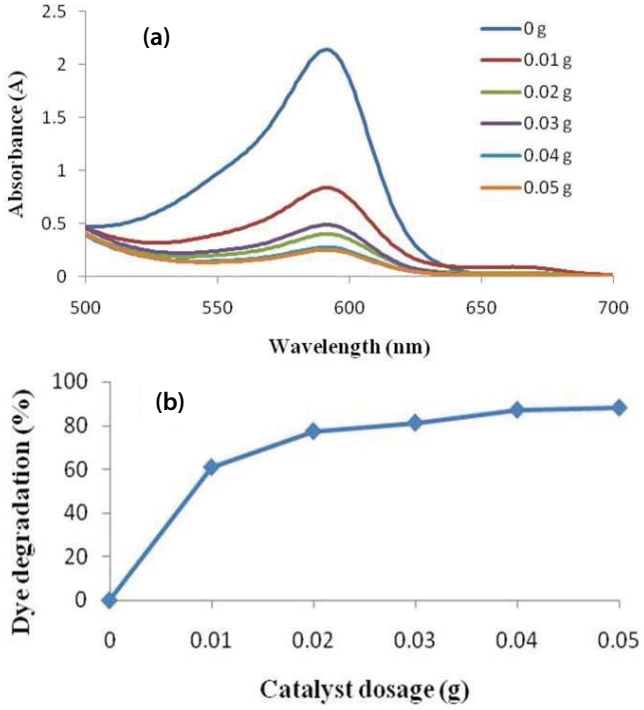

Fig. 7. (a) UV/VIS spectra and (b) % degradation of bromophenol blue photocatalytic degraded by Fe/F-PAN nanofibers under UV irradaition as a function of Fe/F-PAN nanofibers dosage; irradiation time: 5 min, room temperature.

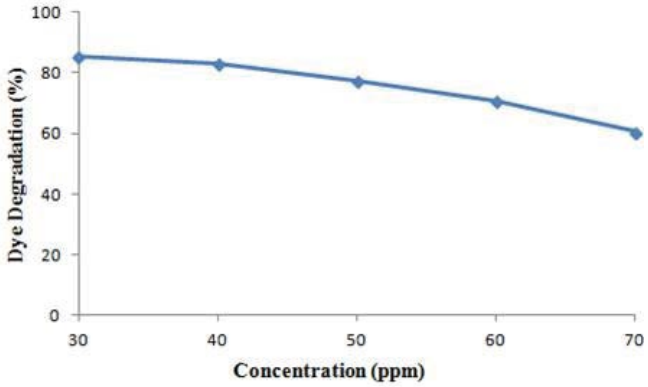

Fig. 9. Effect of Fe/F-PAN and Fe-Mn at different dye concentrations.

3.7. Effect of dye concentration on photodegradation

Fig. 9 illustrates the % degradation of dye at different dye concentrations (30, 40, 50, 60, and 70 ppm) at constant irradiation time and catalyst dosage. The results presented that the photodegradation of bromophenol blue dye decreased gradually as increased the initial dye concentration. The reason might be that as the dye concentration increased, molecules of dye adsorbed on the surface of catalyst, which absorb significant quantity of UV-light rather than metallic nanoparticles. The other reason is that when the initial dye concentration increased, the dye molecules might occupy active sites of photocatalyst and as a result less formation of hydroxyl radicals occurred [30].

4. Conclusions

It is concluded that the F-PAN is suitable adsorbent for the removal iron ions from aqueous medium and the Fe

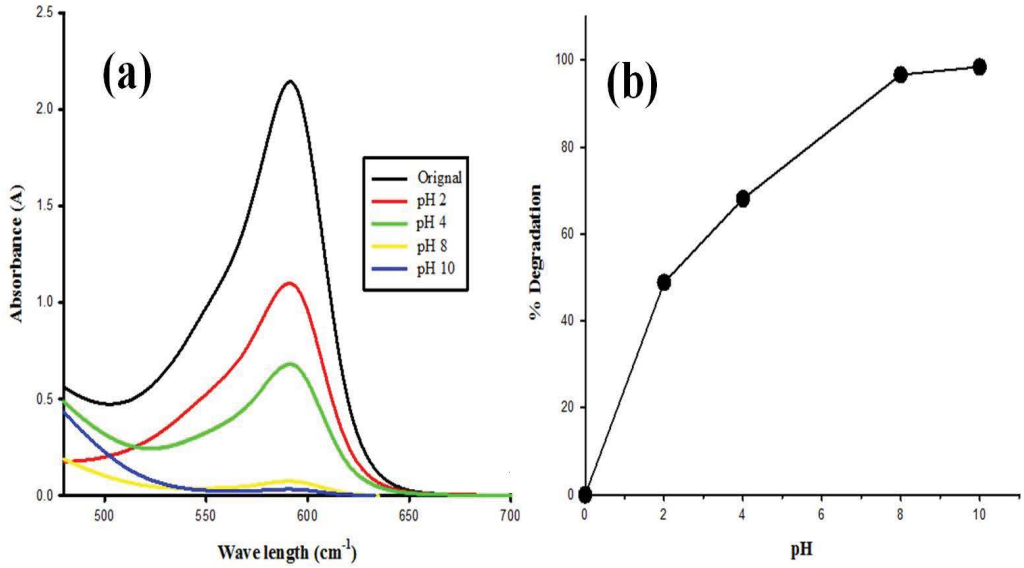

Fig. 8. UV/VIS spectra of methylene blue at different pH by (a) Fe/F-PAN nanofibers and (b) comparison of % degradation at different pH by Fe/F-PAN nanofibers; irradiation time: 5 min, room temperature.

adsorbed F-PAN is useful for the photodegradation of dyes in aqueous medium. The adsorption study presented that it follows the Freundlich isotherm model. The photodegradation study illustrated that both original and reused Fe/F-PAN nanofibers photodegraded more than 80% of bromophenol blue dye within 20 min, which indicated that Fe/F-PAN nanofibers is an economical and may have commercial potential. It was also found that the recovered catalyst degraded about 62% and 81% of dye within 5 and 20 min, respectively.

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