



Synthesis of polyacrylonitrile/polyamidoamine composite nanofibers using electrospinning technique and their dye removal capacity



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ABSTRACT

In this paper, polyacrylonitrile (PAN)–polyamidoamine (PAMAM) composite nanofibers were synthesized using electrospinning technique and their dye removal ability was investigated. The functional groups, morphology, total surface area and pore diameter distribution of nanofibers were studied by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), the Brunauer–Emmett–Teller (BET) and the Barret–Joyner–Halend (BJH) methods, respectively. Direct red 80 (DR80) and Direct red 23 (DR23) were used as the model compounds. The effects of adsorbent dosage, initial dye concentration, and solution pH on dye removal were evaluated. Kinetics and isotherm of dye adsorption were found to conform to pseudo-second order kinetics and Langmuir model, respectively. The maximum dye adsorption capacity (Q_0) of PAN/PAMAM composite nanofiber was 1666.66 and 2000 mg/g for DR80 and DR23, respectively.

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1. Introduction

Synthetic dyes have been recognized as one of the most important water contaminants. It is well-known that some of the dyes produce toxic and carcinogenic intermediates in wastewater. Several methods including enzyme [1], coagulation [2], ultrafiltration [3], oxidization [4,5], membrane [6], photocatalytic degradation [7] and adsorption [8–10] procedures are used to remove dyes from wastewaters. Adsorption process is highly interested due to its efficiency, simplicity and flexibility of design. Various types of adsorbents such as activated carbon, mineral oxides, resins and biosorbents are used [11–14]. Among them, polymeric adsorbents have been increasingly used to remove and recover organic pollutants from wastewater due to their high adsorption capacity.

Polyacrylonitrile (PAN) is a common, inexpensive and environmental stable polymer, and it can be easily electrospun into nanofibers. Many attempts are performed on surface modification of PAN in different forms of nanoparticle [15], membrane [16], and nanofiber [17]. In this regard, ethylenediamine and diethylenetriamine as amine compounds are mostly considered.

Dendrimers, known as a family of highly branched three-dimensional polymers, have recently received considerable attention for functionalization of substrates due to their superior properties compared to linear polymers. Dendrimers have empty internal cavities and many functional groups, which are responsible

for their reactivity. Polyamidoamine (PAMAM) dendrimers are known as promising candidates for different applications of catalysis reactions, molecular recognition, drug delivery and purification of water [18–22]. The combination of linear polymers with different materials containing functional groups of carboxyl, amine, and hydroxyl enable more effective use of adsorbents for dye removal from wastewaters [23].

A literature review showed that there was no report on surface modification of PAN with PAMAM to remove dyes from wastewater. In this study, PAN–PAMAM composite nanofiber was synthesized by electrospinning technique and the structure was demonstrated by FTIR, SEM and BET methods. The anionic dye adsorption of the synthesized nanofibers was described by studying the influence of several parameters including contact time, adsorbent dosage, dye concentration, and pH of solution. Furthermore, the data are analyzed using different well-known adsorption isotherms and kinetics.

2. Experimental section

2.1. Materials

Polyacrylonitrile copolymer (93.7% acrylonitrile and 6.3% vinylacetate with $M_w = 100,000$ g/mol) was purchased from Isfahan Polyacryl Inc. (Iran). N, N-dimethylformamide (DMF) and PAMAM dendrimer, Generation 3, 20 wt.% solution in methyl alcohol were used as received from Merck and Aldrich, respectively. DR80 and DR23 were supplied by Alvan Sabet Co. Iran. The chemical structures of the dyes are shown in Fig. 1.

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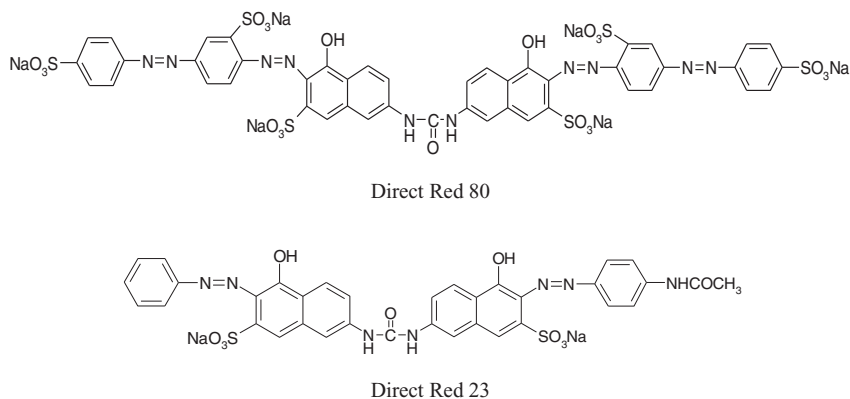


Fig. 1. The chemical structure of dyes.

2.2. Preparation of PAN/PAMAM composite nanofibers

Electrospinning solution was prepared by 10 w/w% PAN copolymer dissolved in DMF. Mechanical stirring was applied for 12 h at room temperature in order to obtain homogeneous PAN solution. The mixture of PAN–PAMAM solutions were then prepared by adding 5, 10, 20, 25 and 30 w/w% of PAMAM into 10 w/w% PAN copolymer solution, respectively. The mixtures were stirred on a magnetic stirrer, and the reactions were allowed to proceed at 80°C for 5 days and relative humidity of 65%. After the completion of reaction, the mixture of PAN copolymer and PAMAM solution was formed in a concentrated solution. In order to produce nanofibers, 2–5 mL of DMF was added to the mixtures, to maintain the viscosity and mechanically stirred for 6 h. The as-prepared solutions were then electrospun under a fixed electrical field in the range of 16–23 kV depended on the solution viscosity for different PAN–PAMAM. The electrospinning apparatus was a Gamma High Voltage Research RR60 power supply and nanofibers were collected onto aluminum (Al) sheet. The distance from the tip to the collector was 16 cm and the feeding rate of the polymer solution was 1.2 mL/h. The electrospun composite nanofiber mats were placed at a vacuum oven (75°C, 8 h) to ensure evaporation of the solvent.

2.3. Characterization

The FTIR spectrum of PAN copolymer and PAN–PAMAM composites was examined by the FTIR spectroscopy (ThermoNicolet NEXUS 870 FTIR from Nicolet Instrument Corp., USA). For this purpose, after the completion of reaction between PAN and PAMAM, the concentrated solutions of composites were poured into methanol to separate composites from PAN solvent. The composites were then placed in an oven 80°C for 4 h. The surface morphology of PAN copolymer and PAN/PAMAM nanofibers was investigated using a scanning electron microscope (SEM, LEO1455VP, and ENGLAND). The releasing amount of PAMAM from composites was tested by a total organic carbon (TOC) analyzer (TOC-L shimadzu, Japan). The surface area of the nanofibers was measured using standard Brunauer–Emmett–Teller (BET) analyzer (Micromeritics Gemini III 2375, USA). Pore size distributions were calculated using the Barret–Joyner–Halenda (BJH) model based on the nitrogen desorption isotherm by a porosimeter (autoporeIV9500, micromeritics Co., USA).

2.4. Adsorption studies

The composite nanofiber mat specimens were individually placed in a batch containing 120 mL solution of DR80 and DR23 with a concentration of 40 mg/L to evaluate the adsorption capacity of the composites. The pH of each solution was adjusted to the desired value using HCl or NaOH solution. Single beam UV spectrophotometer (CECIL CE2021) is used for adsorption measurements. The experiments

were done three times. The standard deviation is <5%. The amounts of dye removal from solutions were determined as a function of time according to the following equation:

$$\text{Dye removal(\%)} = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 and A are dye concentration at $t = 0$ and t , respectively.

The effect of adsorbent dosage (0.001–0.006 g) on the dye removal was investigated by contacting 120 mL of the dye solution with an initial dye concentration of 40 mg/L and pH = 2.1 at room temperature (25°C) for 60 min.

The dye removal of nanofiber mats (0.004 g) at different pH values (2.1, 6.5, and 9.1) was studied by contacting 120 mL of the dye solution with an initial concentration (40 mg/L) at room temperature (25°C) for 60 min.

The effect of the initial dye concentration (40, 60, 80 and 100 mg/L) on dye removal was investigated by contacting 120 mL of the dye solution with composites (0.004 g) at pH = 2.1 and room temperature (25°C) for 60 min.

3. Results and discussion

3.1. Characterization

The FTIR spectrum of PAN copolymer and various composite mats is shown in Fig. 2. The PAN spectrum (curve a) exhibited the peaks of stretching vibrations of OH groups at 3446 per cm, C≡N bond at 2242 per cm, C=O bond at 1737 per cm [24,25], CH stretching in CH, CH₂, and CH₃ groups at 2966 per cm [25–27] and C–O groups at 1200–300 per cm [28,29], which suggests that PAN is a copolymer containing both of acrylonitrile and vinyl acetate polymers. The band at 3438 per cm corresponded to overlapping of the stretching vibration bands of OH and NH groups. The peak intensity increased and shifted from 3446 per cm to the lower wavenumbers compared to PAN copolymer. This clearly states that the OH groups are generated by the hydrolysis of the ester groups in PAN. It is further supported by decreasing in the intensity of the band at 1736 per cm (PAN-5w/w PAMAM, PAN-10w/w PAMAM) and disappearance of the band (PAN-20w/w PAMAM, PAN-25w/w PAMAM, and PAN-30w/w PAMAM), confirming hydrolysis of the acetate ester groups. The composites also showed a new band at 1555 per cm, and shifting of a band at 1629–1668 per cm. It can be assigned to the bending vibrations of the secondary amine and the stretching vibrations of N–C=N group, respectively. The intensity of nitrile group peak of the composites at 2243 per cm also decreased for PAN–PAMAM composite (5w/w) and PAN–PAMAM composite (10w/w) samples. The peak of nitrile group disappeared for PAN–PAMAM composite (20w/w), PAN–PAMAM composite (25w/w), and PAN–PAMAM composite (30w/w) samples which indicate the reaction between nitrile and amine groups

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