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Preparation of aminated nanoporous nanofiber by solvent casting/porogen leaching technique and dye adsorption modeling

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ABSTRACT

In this paper, nanoporous polyacrylonitrile/calcium carbonate (PAN/$CaCO_3$) nanofiber was produced through a solvent casting/porogen leaching technique. Calcium carbonate ($CaCO_3$) nanoparticle was extracted from PAN/$CaCO_3$ nanofiber. The nanofiber was modified using triethylenetetriamine (TETA). The aminated nanoporous PAN (ANPAN) nanofiber was characterized by FTIR, SEM, AFM and DSC. The dye removal ability of ANPAN nanofiber from wastewater was investigated by studying the influence of adsorbent dosage, dye concentration, and solution pH on dye adsorption. Response surface methodology (RSM) was used to build up the equation of dye removal efficiency from water with respect to operational conditions (adsorbent dosage, pH and dye concentration). The dye removal isotherm and kinetics followed the Langmuir isotherm and pseudo-second order model respectively. The thermodynamic data indicated dye removal by ANPAN nanofiber was spontaneous, endothermic, and a physisorption reaction. The RSM data confirmed good agreements with the experimental results.

1. Introduction

Synthetic dyes are used in different industries and the exact amount of dyes discharged from various industries to the environment are unknown. However, the release of high amounts of dyes to the environment has posed severe challenges to scientists. Several methods such as adsorption, oxidation, electrochemical, biological and membrane separation are used to remove dyes from water and wastewater [1–13]. Various inorganics and biomaterials (chitosan as an N-deacetylated derivative of chitin [12], alginate, *etc.*) are applied to uptake dyes. Some adsorbents were modified using several materials including surfactants and used to remove dyes. In addition surfactant has corrosion inhibition effect [14].

Nanomaterials as absorbents are promising materials due to their small sizes which offer efficient adsorption performance that is different from bulk materials [15]. Electrospinning is a simple and versatile method to generate nanofibers [16]. The obtained nanofibers have potential advantages to remove pollutants from wastewater due to their specific characteristics including high surface area and porosity, which can provide more adsorption sites [16–22]. In addition the properties of nanofibers can be modified by chemical and physical reactions to improve their adsorption capacity [15–17]. Different specific functional groups have been introduced onto the adsorbent surface to obtain high dye adsorption ability [18].

A literature review showed that nanoporous nanofiber was not studied to remove dyes from wastewater in details. In this research, nanoporous polyacrylonitrile/calcium carbonate (PAN/$CaCO_3$) nanofiber was produced through a solvent casting/porogen leaching technique. Calcium carbonate ($CaCO_3$) nanoparticles were extracted from PAN/$CaCO_3$ nanofiber. The nanofibers were modified using triethylenetetriamine (TETA). The characteristics of the aminated nanoporous PAN (ANPAN) nanofiber were studied by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), atomic force microscopy (AFM) and differential scanning calorimetry (DSC). The ANPAN nanofiber was used to remove dye from colored wastewater. The influence of adsorbent dosage, dye concentration, and pH of solution on dye removal was investigated. The dye adsorption kinetics, isotherms and thermodynamics was studied. Response surface methodology (RSM) was used to build up the equation of dye removal efficiency from water with respect to operational conditions (adsorbent dosage (mg), pH, dye concentration (mg/L)).

2. Experimental

2.1. Materials

Polyacrylonitrile fiber made by copolymers (93.7% acrylonitrile and 6.3% methylacrylate with MW 70,000 g/mol) was purchased

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Nomenclature

w_g, w_0	the weight of the original and grafted PAN nanofibers (g)
M_1, M_0	M_1 is the molecular weight of triethylenetetramine, and M_0 is the molecular weight of the acrylonitrile monomer
C_0, C_e	concentrations of dye in the liquid phase at initial and equilibrium time (mg/L)
V	the volume (mL)
q_e	equilibrium adsorption capacity (mg/g)
Q	the maximum adsorption capacity (mg/g)
K_L	Langmuir constant (L/mg)
K_F, n	Freundlich constants
$B=RT/b$	Temkin constant (J/mol)
A	the Temkin isotherm equilibrium binding constant (L/g)
R	the universal gas constant (8.314 J/mol K)
T	the absolute solution temperature (K)
q_e, q_t	the amounts of the adsorbed dye on adsorbent at equilibrium and at any time (mg/g)
k_1	the pseudo-first order rate constant (1/min)
k_2	the pseudo-second order rate constant (g/mg min)
k_p	the intraparticle diffusion rate constant (mg/(g $min^{1/2}$))
I	the intercept (mg/g)
e_i	error in the model, $i=1$–3
$\triangle G$	free energy change (kJ/mol)
$\triangle H$	enthalpy change (kJ/mol)
m_F	adsorbent dosage (g)
R^2	correlation coefficient
R^2_{adj}	adjusted correlation coefficient
S	specific surface area (m^2/g)
$\triangle S$	entropy change (kJ/mol K)
t	time (min)

from Isfahan Polyacryl Inc. (Iran). Dimethylformamide (DMF), triethylenetetramine (TETA), calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3), and hydrochloric acid were all supplied by Merck. Distillated water was used for all preparation and washing stages. Direct Blue 78 (DB78) was used as a model dye. The properties of DB78 were show in Table 1.

2.2. Casting polymer/nanoparticles mixtures

Solutions concentrations of PAN in DMF (10 w%) were prepared and stirred for 6 h. Surface modified $CaCO_3$ nanoparticles were placed in an oven at 100 °C for 6 h. The $CaCO_3$ concentrations of 5 w% were gradually added to the stirred PAN/DMF solution to have 10 w%. The resulting mixture was stirred for another 24 h.

2.3. Electrospinning of PAN/DMF/$CaCO_3$ mixtures

PAN/DMF/$CaCO_3$ mixture with concentration of 10 w% was prepared. The electrospinning setup consisted 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 which could generate positive DC voltages up to 60 kV. The applied voltage between the tip of needle and collector was 23 kV and the distance from the tip to the collector was 16 cm. The feeding rate of the polymer solution was 1 mL/h.

2.4. Porogen leaching procedure

The extraction bath containing 5% v/v of HCl was prepared that was accompanied by deionized water with the purpose of extracting the area PAN/$CaCO_3$ nanofibers14 × 14 cm. The extraction procedure was done in a bath equipped with magnetic stirrer at 75 °C for 3 days. The recovered nanofiber web was allowed to dry thoroughly.

2.5. Aminated nanoporous PAN nanofibers (ANPAN)

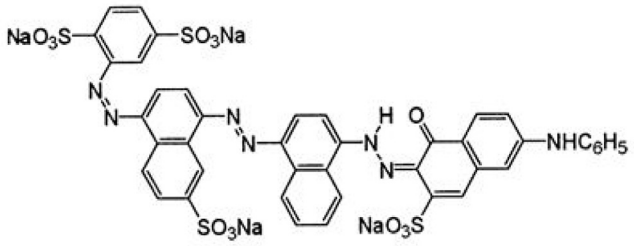
The nanoporous PAN nanofiber was immersed in a mixture of triethylenetetramine, sodium carbonate (1 g), and distilled water (100 mL) in a 250 mL beaker. The fiber was rinsed with distilled water until a pH level of 7 was reached. These were subsequently dried at 80 °C in an oven. In total, batches were treated using the same method. The degree of nitrile group conversion (to an amine group) was calculated by gravimetry. Therefore, the weight of the adsorbent was measured before and after the modification process. The conversion percent of the amine group on PAN was calculated as follows [23]:

$$\text{Conversion}\ (\%) = \left(\frac{w_g - w_0}{w_0}\right) \times \frac{M_0}{M_1} \times 100 \quad (1)$$

2.6. Characterization

The surface morphologies of the nanofiber were studied using scanning electron microscope (SEM, LEO1455VP, and ENGLAND). The topography of nanofiber was investigated using an atomic force microscope (AFM, Dual- Scope C-26, Denmark). A Fourier transform infrared spectrometer (ThermoNicolet NEXUS870 FTIR from Nicolet Instrument Corp., USA) was used to study the interactions over the wavenumber range of 4000–400 cm^{-1}. DSC experiments were carried out in dry nitrogen. The DSC curves were

Table 1
The characteristics and chemical structure of Direct Blue 78.

Name	Direct Blue 78 (DB78)
Molecular formula	$C_{42}H_{25}N_7Na_4O_{13}S_4$
Molecular weight	1055.91 g/mol
Chemical structure	

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