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PAMAM grafted α-Fe_2O_3 nanofiber: Preparation and dye removal ability from binary system

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ABSTRACT

In this paper, polyamidoamine (PAMAM) grafted α-Fe_2O_3 nanofiber as a new adsorbent was prepared by a three-step method. (1): preparation of α-Fe_2O_3 nanofiber by electrospinning technique, (2): incorporation of vinyl group on the nanofiber surface by vinyltriethoxysilane (VTES) and (3): grafting of PAMAM dendrimer onto the nanofiber surface. For the first time, the possibility of reaction between the vinyl group of VTES and the amine group of PAMAM was evaluated and the optimum condition was reported. Characterization by Fourier transform infrared spectroscopy (FTIR) showed that the PAMAM molecules were covalently grafted to the surface through the formation of C–N group. The diameter of nanofibers was increased after the grafting process, confirming the deposition of a layer containing silica and PAMAM molecules on the surface. Decreasing in the total surface area values of nanofibers after the grafting process was detected by Brunauer–Emmett–Teller (BET) analysis. Moreover, dye removal ability of prepared nanofibers in single and binary systems were investigated. It was found that the number of functional group and size of dye molecule play important roles in selective adsorption in binary system. Adsorption of dyes in single and binary systems followed the Langmuir isotherm and pseudo-second order kinetics confirming monolayer and chemical adsorption, respectively. The maximum adsorption capacity of PAMAM grafted nanofiber was 1428.57 and 1250 mg/g for Direct Red 80 and Acid Red 18 at pH 3, respectively. It was concluded that the prepared nanofiber with a relatively large adsorption capacity can be a suitable alternative for elimination of dyes from aqueous media.

1. Introduction

Wastewater effluents released from different types of industries generally contain several organic pollutants and toxic substances. Textile industry as a major consumer of fresh water discharges significant amounts of colors and organic dyestuffs in its effluents. Dyes and their degradation products are mutagenic and carcinogenic, which are certainly harmful to aquatic microorganisms and human health [1].

Also, they are usually chemical resistant, light stable and non-biodegradable [2], thus; it is essential to find proper techniques and processes for efficient removal of these toxic chemicals from wastewaters.

In order to remove dyes from effluents, various treatment processes have been extensively studied [3–8]. Adsorption as a physical method has been proved to be an effective, proper and simple method for treatment of wastewater. Activated carbon because of its high surface is one of the mostly used adsorbents for separation of wide range of pollutants from waterways [9,10]. However, utilization of this adsorbent is limited in large scale applications because of its high cost of production and regeneration. In this regard, many alternatives low-cost inorganic materials such as magnetite [11], zeolite [12], natural clay [13] and agriculture wastes like rice husk [14] and wheat straw [15] are proposed.

A new emerged field in adsorption process is the application of iron-based material to remove pollutants. Also, properties such as good magnetic behavior, chemical stability, biocompatibility, amphoteric surface activity, enhanced catalytic activity, and dispersability have been reported for this material [16].The adsorbability of iron oxide nanoparticles to remove a wide variety of organic and inorganic contaminants has been studied [17]. Hematite is the most stable iron oxide which is widely used in different fields such as catalyst, sensor, and gas purification [18].

In recent years, many inorganic adsorbents were produced in different shapes and scales. A variety of nanostructured materi-

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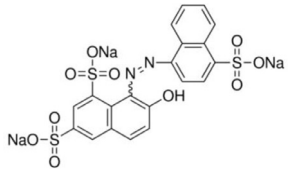
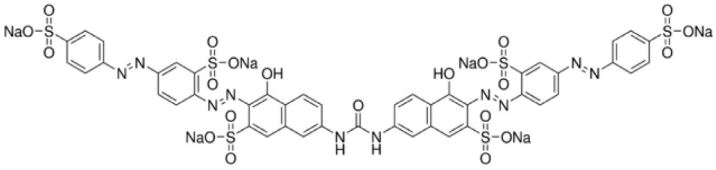
Table 1
Chemical structure of dyes.

Name	Formula	M_W	λ_{max} (nm)	Chemical structures
Acid Red 18	$C_{20}H_{11}N_2Na_3O_{10}S_3$	604.479	506	
Direct Red 80	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$	1373.07	528	

als, such as TiO_2 nanotube [19], hollow silica colloid [20] and nickel ferrite nanofiber [21] were reported. Also, self-assembled 3D flowerlike Fe_2O_3 [22], Fe/Fe_2O_3 core–shell nanowires [23], porous hematite hollow microspheres [24], ceria hollow nanospheres [25] and mesoporous magnetic γ-Fe_2O_3 nanoparticles [26] were synthesized and used as an adsorbent for water treatment. However, most of the inorganic adsorbent suffers from low adsorption affinity, selectivity, and capacity [27].

Since, the adsorption efficiency of adsorbents depends on their properties and surface functional groups, introduction of functional groups on the surface can enhance the removal property. It was previously stated that amino group is more effective than other functional group such as carboxyl, hydroxyl, *etc.* because of its high activity to form strong complexes with pollutants by its nitrogen atom [28].

Dendrimers are a family of highly branched organic compounds with three-dimensional structure characterized by a large number of end groups and empty internal cavities between the branches for taking up guest molecules. Polyamidoamine (PAMAM) dendrimers are known as promising candidates and used for different applications such as catalysis reactions, molecular recognition, drug delivery and purification of water [29–33].

A literature review showed that there is no study on modification of α-Fe_2O_3 nanofiber with PAMAM molecular. Also, the adsorption ability of the PAMAM grafted nanofiber in single and binary systems were not investigated. In this study, the surface of hematite nanofibers was modified by PAMAM dendrimer. Vinyl triethoxysilane (VETS) was used as the coupling agent. Also, the possibility of the reaction between vinyl group of VTES and amine group of PAMAM was studied.

2. Experimental section

2.1. Materials

Poly vinyl alcohol (PVA) (degree of polymerization: 600, saponification value: 88.1 mol%), vinyltriethoxysilane (VTES), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 98%), 2 propanol, and tetraethyl orthosilicate (TEOS) were all purchased from Merck, Germany. PAMAM dendrimer, Generation 3, 20 wt% solution in methyl alcohol was used as received from Aldrich. Two commercial anionic dyes, C.I. Direct Red 80 (DR80) and C.I. Acid red 18 (AR18) were obtained from Alvan Sabet Co. Iran and used without further purification. The purity (%) of Direct red 80 and Acid red 18 dyes was 97% and 99%, respectively. The characteristic and chemical structures of dyes are given in Table 1.

2.2. Preparation of α-Fe_2O_3 nanofiber

First, PVA solution (10 wt%) was prepared by dissolving PVA (1 g) in distilled water (10 ml) at 90 °C under magnetic string for 3 h. Then, 0.4 g of ferric nitrate was added to the PVA solution under vigorous stirring for 6 h. This final solution was then electrospun under a fixed electrical field of 21 kV. 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 0.3 ml/h. The obtained nanofiber was placed in an electrical furnace at 800 °C for 6 h with the heating rate of 5 °C/min to remove the polymeric part.

2.3. Surface modification of α-Fe_2O_3 nanofiber

2.3.1. Functionalization of α-Fe_2O_3 nanofiber by VTES

0.5 g of α-Fe_2O_3 nanofiber, 1.5 g of tetraethylorthosilicate (TEOS) and 0.5 g of VTES were reacted in the presence of water and 2-propanol at 85 °C for 2 h. After the evaporation of solvents, the resultant nanofiber was placed in an oven at100 °C for 2 h. At the end, the nanofiber was washed with deionized water and ethanol with the ratio of 2:1 and dried.

2.3.2. Grafting of PAMAM on the nanofiber surface

The PAMAM molecule (0.02–0.12 g) was grafted on the surface of vinyl-functionalized (0.5 g) nanofiber in the presence of water and 2-propanol at different times (2–18 h) and 85 °C under reflux condition. Then, the resultant nanofiber was placed in a vacuum oven at 100 for 2 h. Finally, it was washed with deionized water and ethanol with the ratio of 2:1 and dried.

2.4. Characterization

The FTIR spectra of α-Fe_2O_3 and amine-functionalized nanofibers were examined by the FTIR spectroscopy (ThermoNicolet NEXUS 870 FTIR from Nicolet Instrument Corp., USA). The surface morphology of nanofibers was investigated using a Scanning Electron Microscope (SEM, LEO1455VP, and ENGLAND). The BET surface area and pore size distribution were evaluated using the Barret–Joyner–Halenda (BJH) model based on the nitrogen desorption isotherm (Micromeritics Gemini III 2375, USA) and mercury intrusion technique (AutoPore III, Micromeritics Instrument Co., USA). The isoelectric point (IEP) of synthesized nanofibers was determined by the reported method [27]. For this purpose, 50 ml of a 0.01 M sodium chloride (NaCl) solution was prepared. Then, the pH was adjusted to initial values in the range of 2–12, by using either sodium hydroxide or hydrogen chloride

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