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Mesoporous carboxylated Mn_2O_3 nanofibers: Synthesis, characterization and dye removal property

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ABSTRACT

In this study, the novel mesoporous carboxylated Mn_2O_3 nanofibers were synthesized by combination of electrospinning and sol–gel methods and *in situ* polymerization of acrylic acid monomer. The optimum amount of acrylic acid was determined by evaluating the results of microscopic and specific surface area analyses. The characteristic analyses exhibited the deposition of a layer containing silica and acrylic acid on the nanofiber surface. Also, Mn_2O_3 nanofibers showed a mesoporous structure which was maintained after the polymerization process. Although, the mean mesopore size on the nanofiber surface was decreased but the size of pores existing among the nanofibers increased because of increasing the nanofiber diameter. An investigation on the topography of nanofibers revealed that the average surface roughness values increased after the polymerization of acrylic acid. The coverage of Mn_2O_3 nanofiber surface by amorphous silica after the modification process was confirmed by X-ray diffraction (XRD) method. Moreover, the dye removal ability of synthesized nanofibers was evaluated and the effect of operational parameter including adsorbent dosage, pH, inorganic anions and initial dye concentration on dye removal was investigated. Adsorption isotherm and kinetic models were used to evaluate the adsorption mechanism and rate. To determine the best fit model for each system, non-linear regression along with error function were used. The results showed that the experimental data followed with Langmuir isotherm. Although the intra-particle diffusion was influenced on adsorption rate, the adsorption kinetic conformed to the pseudo-second order kinetic model. The result showed that synthesized nanofibers with high adsorption capacity might be a suitable alternative to remove dyes from colored aqueous solutions.

1. Introduction

Dyes are widely used in many industries such as textile, paper printing, leather, cosmetics and plastic industry [1]. Discharging of dyes into water resources even in a small amount can effect on the aquatic life and food web. High solubility of dyes facilitates their dispersion in irrigation and raw drinking water sources. The release of basic dyes into the environment is of concern due to their toxic, mutagenic and carcinogenic characteristics of the dyes and their biotransformation products. Methylene blue (MB) is the most commonly used substance for dying cotton, wood and silk [2]. It causes to increase the heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [3]. Malachite green (MG) dye is traditionally used for dyeing silk, leather and paper. MG is cytotoxic and tumor promoter. Also, it is shown that it induces mammalian cell transformation and lipid peroxidation [4].

Traditional methods such as photo-catalytic degradation [5], fenton degradation [6], electrochemical degradation [7], liquid–liquid extraction [8], ultrafiltration [9], ion exchange [10] cannot be efficiently treated the colored wastewaters because of complex aromatic structures of dyes. However, the decolorization of wastewaters by an efficient method is highly desired. Adsorption is known as a cost effective and simple method which can remove dyes completely even at high concentrations from the effluents [11]. In this regard, many adsorbents are synthesized in different scales and shapes such as nanofibers, nanoparticles, spheres and rods [12–15]. Among them, nano adsorbents with fiber like structure are attracted the attentions due to their specific physical and chemical properties [16]. Pure chitosan and nylon-6 nanofibrous membranes are prepared for the removal of anionic dyes from solutions [17,18]. Surface modified electrospun poly(acrylonitrile-co-styrene) nanofibers are synthesized and their basic dye removal property is investigated [19]. High surface area and the presence of numerous reactive groups on the nanofiber

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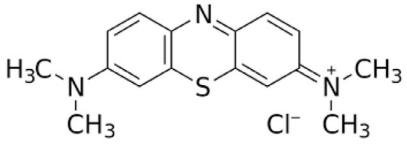
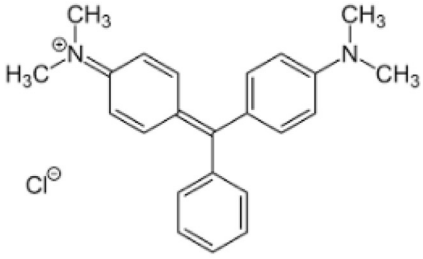
surface made them a strong dye adsorbent with high adsorption capacity.

In the last two decade, many inorganic materials such as ferric oxides, perlite, manganese oxides, aluminum oxides, etc. are used for removing pollutants because of their low cost and abundant [20]. Mn_2O_3 as an inexpensive and environment friendly metal has attracted considerable attention and it is utilized in many applications such as ion-exchange materials, catalysis, adsorption, and Li-ion batteries [21]. Moreover, manganese oxide and their modifications are widely used to remove heavy metal ions because of fairly good adsorption capacity and selectivity [22,23]. Previously, γ-MnOOH nanorods are synthesized and their removal ability for methylene blue is investigated [24]. The maximum adsorption capacity of the synthesized adsorbent was 41 mg/g. $Mn_2O_3/Al_2O_3/SiO_2$ hybrid nanocomposite is synthesized and it is used for the removal of methylene blue dye [25]. The adsorption capacity of the synthesized hybrid was around 90 mg/g. Mn_2O_3/MCM-41 composite with the adsorption capacity of 24.4 mg/g for removing the methylene blue is prepared [26]. Also, the Mn_2O_3 nanoparticle showed no adsorption capability toward methylene blue [26]. On the other hand, the change of morphology from particle to fiber decreases the agglomeration of particles. After the calcination process, the shape and morphology of nanofibers were fixed and the agglomeration was low. Also, the fixed structure of nanofibers is helpful for modification process. In this case, it is possible to modify the whole surface of nanofibers with minimum agglomeration which results to achieve a high BET surface area [27]. Also, the separation of nanofibers is easier than nanoparticle. However, the relatively low adsorption capacity for dyes due to lack of functional groups is the main disadvantage of inorganic adsorbents. High adsorption capacity for dyes can be obtained by introducing various functional groups (carboxyl, tetrazine, sulfonic, amino, and phosphoric groups) on the surface with selective adsorption affinity to targeted adsorbates [28,29]. A mesoporous polyvinyl alcohol (PVA)/SiO_2 composite nanofiber membrane functionalized with cyclodextrin is synthesized and its removal property for the indigo carmine dye evaluated [30]. Also, amino functionalized mesoporous nanofiber membrane is prepared for the removal of Cr^{3+} from aqueous solution [31]. In this regard, surfactant, polymer and monomer are used for modifying inorganic materials [32]. Hydroxylated α-Fe_2O_3 nanofiber is synthesized by polymerization of vinylacetate onto the surface of hematite nanofiber and its dye removal ability is investigated [33]. It is suggested that the *in situ* polymerization of monomers onto the surface of adsorbents can enhance significantly the adsorption capacity because of incorporation a large number of active sites on the surface [33]. Furthermore, layer-by-layer (LbL) self-assembly is one of promising method for enhancing the adsorption capacity of adsorbents toward pollutants. LbL self-assembly could be conducted several times to form sandwich-like multilayer structures. Sandwiched Fe_3O_4/carboxylate graphene oxide nanostructures are synthesized and used for the removal of dyes [34]. GO/polyethylenimine (PEI) hydrogels as efficient dye adsorbents are prepared through the self-assembly behavior of GO [35].

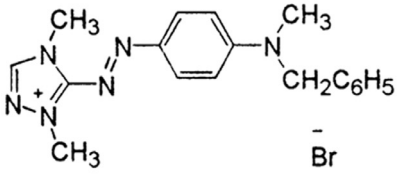
Acrylic acid monomer and poly acrylic acid polymer are organic compounds which are widely used in the removal of pollutants [36–38]. For example, kaolin/poly acrylic acid hydrogel [39] and zeolite-poly acrylic acid nanocomposite [40] are synthesized and their dye removal ability was evaluated. These materials possess ionic functional groups which can be helpful for absorbing ionic dyes. A literature review showed that the adsorption of metal ion and photocatalytic property of Mn_2O_3 inorganic material is investigated and few papers deal on its dye adsorption ability. In this study, Mn_2O_3 nanofibers aiming to produce a new dye adsorbent with high adsorption capacity was prepared by electrospinning method. Then, it was functionalized by an organosilane compound.



Methylene blue (MB)



Malachite green (MG)



Basic red 46 (BR46)

Fig. 1. The chemical structure of dyes.

Finally, the acrylic acid monomer was polymerized onto the surface of nanofibers. The optimum conditions for polymerization and dye removal of nanofibers were investigated.

2. Experimental

2.1. Materials

3-(Trimethoxysilyl) propyl methacrylate (silane A174), triblock copolymer Pluronic P123 and benzoyl peroxide (BP) were obtained from sigma Aldrich. Tetraethyl orthosilicate (TEOS), manganese (II) nitrate tetrahydrate, poly vinyl alcohol (PVA) (degree of polymerization: 600, saponification value: 88.1 mol%), 2-propanol and acrylic acid monomer were purchased from Merck, Germany. Methylene blue (MB), malachite green (MG) and basic red 46 (BR46) were obtained from Alvan Sabet Co., Iran and used without further purification. The chemical structure of dyes is shown in Fig. 1. The molecular weight of MB, MG and BR46 was 319.85, 364.91 and 401.3 g/mol, respectively.

2.2. Preparation of Mn_2O_3 and functionalized nanofibers

A PVA solution with the concentration of 10% *w/w* was prepared by dissolving 1 g polymer in 10 mL distilled water at 85 °C under vigorous stirring for 1 h. 0.4 g of manganese nitrate and 0.3 g of P123 were added to the PVA solution and the stirring was continued for 1 h at the temperature of 80 °C under reflux condition [41]. The solution was then electrospun under a fixed electrical field of 20 kV when the distance between tip of needle and collector was 16 cm. The electrospinning apparatus was a Gamma High Voltage Research RR60 power supply and nanofibers were collected onto aluminum (Al) sheet. The feeding rate of the polymer solution was 0.5 mL/h. In order to remove the polymeric

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