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# Zwitter ionic modification of cobalt-ferrite nanofiber for the removal of anionic and cationic dyes



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#### ABSTRACT

In this paper, cobalt ferrite nanofiber was produced using electrospinning technique and the surface of prepared nanofiber was modified with L-arginine. We used [3-(2,3-Epoxypropoxy)-propyl]-trimethoxysilane as coupling agent. Bonding behavior, surface morphological and topography, crystalline phase, isoelectric point and chemical composition of nanofibers were investigated by FTIR, SEM, AFM, XRD, zeta potential and XPS analyses, respectively. FTIR spectra illustrated the formation of amino acid layer on the surface of nanofibers. Also, the average roughness of nanofiber surface and the amount of amorphous phase increased after surface grafting. XPS analyses showed a relatively large amount of nitrogen atoms due to the incorporated amine groups on the nanofiber surface. We examined the dye removal ability of prepared nanofibers for both anionic and cationic dyes using Direct red 80 (DR80) and Basic red 46 (BR46) as the model compounds. The effects of operational parameters such as adsorbent dosage, initial dye concentration, and solution pH on dye removal were evaluated. In order to determine the best fit isotherm for each system, two error analysis methods, namely, chi-square ( $\chi^2$ ) and composite functional error (HYBRD) were used. It was found that adsorption of dyes onto modified nanofibers are based on Langmuir isotherm. Finally, the pseudo-second-order kinetic model can be used to describe the adsorption behavior.

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#### 1. Introduction

Synthetic dyes are well-known water pollutants with high toxicity to aquatic life. They generally have complex aromatic structure and most of them are highly resistant to breakdown by different wastewater treatments [1]. Considerable efforts have been made by many researchers to find appropriate dye removal from wastewaters of different industries, in particular, textile industry. In this regard, many methods have been investigated extensively based on biological, chemical, and physical approaches [2–5]. Among them, discoloration based on physical adsorption is considered as a cost effective and simple method which can remove the dyes completely even at high concentrations from

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the textile effluents. For this purpose, various nano adsorbents are produced in different shapes and scales with specific physical and chemical properties [6–8]. Nanofibers with extremely high surface area and numerous reactive groups on the surface are demonstrated as strong adsorbents with high dye removal ability through chemical and physical phenomena.

An emerging wastewater treatment is recently introduced by utilization of magnetic nanoparticles to remove dyes according to adsorption mechanism. Magnetic adsorbents could be separated easily from solutions by applying a magnetic field. Therefore, their usage is a cost effective approach for separation of dyes from the solutions compared to biological and chemical compounds. In this regard, nanocrystalline ferrites are interested due to their intrinsic magnetic, electrical, chemical and thermal properties [9]. So far, some simple ferrites with the general formula MFe<sub>2</sub>O<sub>4</sub> (M=Co, Ni, Zn, Mn, Cu) were prepared in different forms of nanoparticle, nanowire and nanofiber [10–14]. Ambashta and Sillanpaa have recently reviewed the application of iron-based nanomaterials and ferrites for water treatment and environmental remediation [15].

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Table 1

The maximum adsorption capacity of different ferrite compounds.

Compound	Maximum adsorption capacity (mg/g)	Dye	Reference
Ni-Fe <sub>2</sub> O <sub>4</sub>	71.3	Congo red	[32,33]
	0.5	Basic blue 41	
Mn-Fe <sub>2</sub> O <sub>4</sub>	68	Congo red	[32]
Co-Fe <sub>2</sub> O <sub>4</sub>	170.1	Congo red	[32]
Zn-Fe <sub>2</sub> O <sub>4</sub>	111.1	Acid red 88	[34]

Generally, a disadvantage of iron-based materials is expressed with relatively low adsorption capacity for dyes due to lack of functional groups [16]. In this regard, surface modification can be an effective route to improve the adsorption efficiency using various functional groups with selective adsorption affinity [17–19]. Surfactant, polymer, monomer and inorganic compounds are used for modifying the inorganic materials [20]. Aminefunctionalized silica nanoparticle, amine-functionalized magnetic ferrite, aldehyde functionalized Fe<sub>2</sub>O<sub>3</sub>, iron oxide magnetic functionalized by lipophilic stilbene molecules, amino-functionalized Fe<sub>3</sub>O<sub>4</sub>–SiO<sub>2</sub> and chitosan-immobilized magnetic nanoparticles were synthesized and used for water treatment process [21–25].

As mentioned earlier, separation of adsorbents from aqueous solution thoroughly is an important matter in order to avoid secondary pollution. The separation methods including filtration, sedimentation and centrifugation are time-consuming and uneconomic [26]. Therefore, it is necessary to choose a rapid and effective separation method. Among the magnetic nanomaterials, cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) has been widely studied in different fields due to its high electromagnetic performance, excellent chemical stability, mechanical hardness, and high cubic magnetocrystalline anisotropy [27]. Also, a literature review showed that the Coferrite nanofiber has a higher maximum saturation magnetization  $(M_{\rm s})$  value than the other spinel ferrite compounds, indicating on easier and higher separation ability in the presence of a magnetic field. The M<sub>s</sub> value for Co-ferrite [17], Mn-Fe<sub>2</sub>O<sub>4</sub> [28], Zn-Fe<sub>2</sub>O<sub>4</sub> [29] Co<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> [30] and CuFe<sub>2</sub>O<sub>4</sub> [31] nanofibers were 71.7, 46.8, 2.31, 58.4 and 31.8 emu/g, respectively. Furthermore, the maximum adsorption capacity of CoFe<sub>2</sub>O<sub>4</sub> for dyes was higher than the other ferrite compounds. The maximum adsorption capacity of different ferrite compounds are presented in Table 1. In this regard,  $Co-Fe_2O_4$  was selected as the base material for modification and adsorption experiments.

Amino acids are organic compounds containing amine (-NH<sub>2</sub>) and carboxylic acid (-COOH) functional groups. Arginine is a wellknown amino acid which is rich in amino and carboxyl groups. Due to its strong positive charged side chains. L-arginine has good potential to bind with anions through electrostatic force. Moreover, amine-functionalized adsorbents are highly considered because of their ability in formation of strong complexes with pollutants [35]. Thereby, it can be expected that adsorbents modified with Larginine would have strong affinity with anionic dyes. On the other hand, most of the adsorbents modified with reactive containing compounds adsorb a specific type of pollutants. For example, amine-functionalized silica nanoparticle are synthesized and used for the removal of anionic dyes [36]. However, few attempts were made on the synthesis of adsorbent with potential to adsorb both anionic and cationic pollutants [37]. Amino acid is one of the organic compounds which can absorb both of anionic and cationic dyes at different pH<sub>s</sub> due to its amphoteric nature. Adsorbing of cationic dyes by L-arginine modified adsorbents can be due to the presence of carboxyl group on the surface. As far as we know, there is no research on synthesis of amino acid-modified, inorganic nanofibers as nano adsorbents for removing dyes from effluents. In this study, cobalt-ferrite nanofibers (Co-ferrite NF) were produced by electrospinning method. The surface of prepared nanofibers was modified by L-arginine and the dye removal



Fig. 1. The chemical structures of the dyes and L-arginine.

ability of nanofibers was investigated using anionic and cationic dyes.

#### 2. Experimental

#### 2.1. Materials

Poly vinyl alcohol (PVA) (degree of polymerization: 600, saponification value: 88.1 mol%), tetraethyl orthosilicate (TEOS), L-Arginine monohydrochloride, 2-propanol and [3-(2,3-Epoxypropoxy)-propyl]-trimethoxysilane (coupling agent) were supplied by merck, Germany. Ferric nitrate (Fe ( $NO_3$ )<sub>3</sub>.9H<sub>2</sub>O, 98%) and cobalt (II) nitrate hexahydrate (Co ( $NO_3$ )<sub>2</sub>.6H<sub>2</sub>O, 98%) were purchased from Aldrich. Direct red 80 (DR80) and basic red 46 (BR46) were supplied by Alvan Sabet Co. Iran. The chemical structure of the dyes and L-arginine are shown in Fig. 1. The maximum wavelength and molecular weight of DR80 and BR46 were 528 and 530 nm, 1373.07 and 403.31 g/mol, respectively.

#### 2.2. Preparation of Co-ferrite NF

First, PVA solution (10 wt%) was prepared by dissolving PVA (0.5 g) in distilled water (5 ml) at 90 °C under magnetic starring for 3 h. Then, 1.36 g of cobalt(II) nitrate hexahydrate and 3.6 g of ferric(III) nitrate nonhydrate were added to the PVA solution under vigorous stirring for 6 h (the molar ratio of Fe:Co was 2:1). This final solution was then electrospun under a fixed electrical field of 23 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 0.5 ml/h. the obtained nanofiber mat was placed in an electrical furnace at 500 °C for 6 h with the heating rate of 5 °C/min to removing the polymeric part.

## 2.3. Surface modification of Co-ferrite NF

0.5 g of Co-ferrite NF, 1.67 g of tetraethylorthosilicate (TEOS), 0.34 g of coupling agent and 0.34 g of L-arginine were reacted

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