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Cobalt ferrite nanoparticles: Preparation, characterization and anionic dye removal capability

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ABSTRACT

$CoFe_2O_4$ nanoparticles were synthesized, functionalized with amine group, and used to adsorb Direct Red 80 (DR80), Direct Green6 (DG6), and Acid Blue 92 (AB92) dyes from aqueous solutions. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), zeta potential (ZP), and the Brunauer–Emmett–Teller (BET) were used to analyze the adsorbents surface characteristics. The effects of pH, adsorbent dosage, initial dye concentration and contact time on the dyes adsorption was studied at 25 °C. The Langmuir, Freundlich and Tempkin models were used for this study and the experimental results show that the Langmuir equation fits better than the other equations. At initial pH of 2, the adsorption capacity (Q_0) for DR80, DG6, and AB92 was 333.33, 384.61, and 625 mg/g, respectively. Furthermore, pseudo-first-order, pseudo-second-order, and intra-particle diffusion adsorption kinetics of three dyes were studied and the rates of sorption were found to conform well to the pseudo-second-order kinetics ($R^2 > 0.99$).

1. Introduction

Dyes and pigments have become part of human's life. They are widely used in the textile, paper, plastics, leather, food, and cosmetic industries, and can be released to the environment through colored wastewater from these industries. Such colored effluent can reduce light penetration and photosynthesis causing reduction in oxygen levels in water and, in severe case, resulting in the suffocation of aquatic flora and fauna. Therefore, they can be called eco-toxic substances, which need to be removed before discharging into receiving water bodies [1].

Different methods have been used to remove dyes from aqueous environment, such as oxidation [2], electrocoagulation [3], nanofiltration [4], photocatalysis [5], biosorption [6], and *etc*. Adsorption is another technique that has been developed to remove different types of coloring materials [7–13]. Adsorption methods for color removal are based on the high affinity of many dyes for adsorbent materials [14].

Due to their high surface area, nanoparticles can be effectively used as adsorbents. They are capable of improving the loading and catalytic efficiency of immobilized catalysts [15,16]. Compared with traditional adsorbents, OMCs[1] are promising candidates in pollutant removal because of their large surface area and pore volume, unique pore size, and excellent physicochemical and thermal stability [17]. Furthermore, the impregnation of metals into OMCs can intensify and expand the adsorption performance [18].

MNPs[2], recently, have attracted considerable attention [19]. The magnetic nature of such particles makes it easy for catalysts to be recovered and recycled by an external field. It optimizes the operational cost and improves the product purity. Various magnetic nanoparticles such as Fe [20], FePt [21], Fe_2O_3 [22], Fe_3O_4 [23], $MnFe_2O_4$ [23], $ZnFe_2O_4$ [24], $NiFe_2O_4$ [25], $CoFe_2O_4$ [23,26], *etc.* have been studied for their applications for biomedical purposes. The $CoFe_2O_4$ magnetic nanoparticles have been used as adsorbent and photocatalyst for the degradation of different environmental pollutants [27]. However, the adsorption property of these nanoparticles could be enhanced by adding some functional groups such as amine group.

Different methods have been used to synthesize CFNPs[3], such as sol–gel techniques [28], micro emulsion [29], hydrothermal synthesis [30], solvothermal [31], electrochemical [32], combustion methods [33] and co-precipitation [34]. Among them, co-precipitation is an easy and adaptable method [35].

Beside all the studies on the removal of pollutants from aqueous solutions using CFNPs, every special CFNPs requires individual

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[1] Ordered mesoporous carbons
[2] Magnetic nanoparticles
[3] Cobalt ferrite nanoparticles

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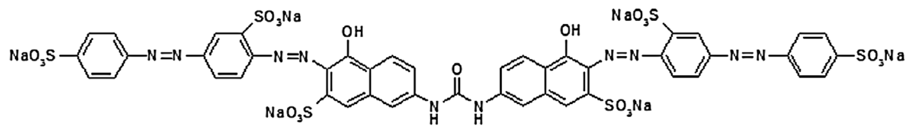
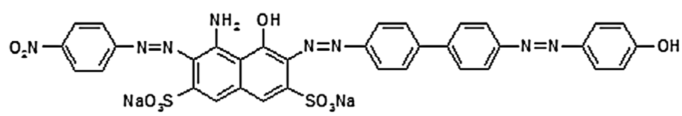
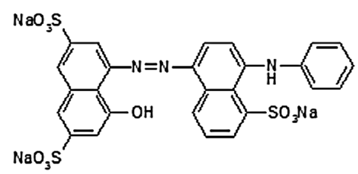


DR80



DG6



AB92

Fig. 1. The chemical structure of dyes.

research. Therefore, in this study, CFNPs were synthesized and functionalized with amine groups. The adsorption efficiency of CFNPs against ACFNPs[4] was studied using three anionic model dyes. The surface characteristics of both adsorbents were determined. Effect of important parameters on the dyes adsorption was investigated. Isotherm and kinetic studies of the dyes' adsorption onto ACFNPs were also performed.

2. Materials and methods

2.1. Materials

Anionic dyes, DR80[5], DG6 [6], and AB92[7] were obtained from Ciba company, Iran, and were used without further purification. Their chemical structures are shown in Fig. 1. All other chemicals were of analytical grade and purchased from Merck, Germany.

2.2. Synthesis of nanoparticles (CFNPs and ACFNPs)

2.2.1. CFNPs preparation method

30 cc and 20 cc of deionized water was poured on 13.4 g of $Fe(NO_3)_3 . 2H_2O$ and 4.831 g of $Co(NO_3)_2.6H_2O$, respectively and then mixed together. A solution made up of 4.2 g NaOH dissolved in 70 cc deionized water and 4 cc ($C_2H_8N_2$) was added to the mixture and the resultant was stirred (200 rpm) for 45 min at 90 °C. After a precipitation time of 45 min, the newly formed nanoparticles were separated using a magnet, washed several times with deionized water, and then dried [36].

2.2.2. ACFNPs preparation method

1 g of ferrite cobalt was added into a mixture of *N*-(2-Amino-ethyl) 3-aminopropyl tri-methoxy-silane (2 mL), deionized water (1 mL) and ethanol (20 mL). Then the resultant was stirred for 3 h at 25°C at a constant stirring speed of 200 rpm. After a precipitation time of 3 h, the newly formed nanoparticles were separated using a magnet, washed several times with deionized water, and then dried [36].

2.3. Adsorption tests

The DR80, DG6, and AB92 adsorption experiments were carried out using CFNPs and ACFNPs. Batch experiments were conducted at 25°C and a constant stirring speed of 200 rpm using the optimum conditions of factors that influence adsorption efficiency such as pH (2–10), agitation time (2.5–60 min), dye concentration (50–200 mg/L), nanoparticle dosage (0.05–0.3 g/L), and inorganic ions (NaCl, Na_2SO_4, $NaHCO_3$, and Na_2CO_3). The pH of the solution was adjusted using HCl and/or NaOH (0.2 N). At the end of the adsorption experiments, the nanoparticles were separated from the suspension using a magnet and the dyes concentration in each sample was determined using a UV–Vis spectrophotometer CECIL 2021 at the maximum wavelengths (λ_{max}) of 549, 634, and 593 nm for DR80, DG6 and AB92, respectively. The results were verified with the adsorption isotherms (Longmuir, Freundlich, and Tempkin) and kinetics (pseudo-first-order, pseudo-second-order, and intra-particle diffusion).

2.4. Characterization

The FTIR[8] spectra of CFNPs and ACFNPs were achieved using Perkin-Elmer Spectrophotometer (Spectrum at 500–4000 cm−1). XRD[9] patterns of the CFNPs and ACFNPs samples were recorded in the range $5° \leq 2\Theta \leq 80°$ through a diffractometer (Bruker KAPPA APEX II) using Cu-Kα radiation ($\lambda = 1.5406$ °A). ZP[10] was measured using ZETASIZER Nano ZS, Malvern Instruments Ltd. UK. The specific surface

4 Amine functionalized cobalt ferrite nanoparticles
5 Direct red 80
6 Direct green 6
7 Acid blue 92
8 Fourier transform infrared
9 X-ray diffraction
10 Zeta potential