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Solvent free synthesized $MnFe_2O_4$@polyamid resin as a novel green nanohybrid for fast removing Congo red

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ABSTRACT

The development of environmental friendly techniques for synthesizing material is a main interest in green chemistry, as the absence of organic solvents in the synthetic routs is a major presage for realizing green ways. Based on this viewpoint, a solvent free green rout has been employed to prepare magnetic $MnFe_2O_4$ nanoparticles and $MnFe_2O_4$ reinforced polyamide resin. $MnFe_2O_4$ nanoparticles was synthesized through mixing the solid reagents with NaOH at room temperature. Polyamide and magnetic resin were synthesized through heating the mixture of citric acid, p-phenylenediamine and $MnFe_2O_4$ at 155 °C. The products were characterized with XRD, VSM, FT - IR, FE - SEM and TEM techniques. Characterization analysis revealed that the magnetic nanoparticles were less than 20 nm in diameter, and polyamide possessed stacked sheet structure with thickness in nano scale. Prepared magnetic resin was employed as a green adsorbent for removing Congo red from aqueous solution. Equilibrium was obtained within one minute as well as the sorbent showed a superior adsorption capacity of 1000 mg g^{-1}.

1. Introduction

It goes without saying that since the dawn of the industrial revolution regarding to increase in activities such as textile, paper, plastic, cosmetic, pharmaceutical, and food industries, discharge of huge volumes of wastewater into the environment has begotten a lot of detrimental effects which have been lead to the environmental pollution in that effluent contains highly colored compounds which are so poisonous[1–5]. Mixing of colored effluent with water leads to increase in the chemical oxygen demand (COD), which brings about a considerable decrease in photosynthetic activity. Moreover, poisonous chemicals in effluent such as dyes are responsible for severe health disorders in human beings, namely allergic dermatitis and skin irritation as well as they affect the function of kidneys, liver, and central nervous system [6–8]. Therefore, in order to diminish the aforementioned harmful impacts of dye-contained effluent, removal of colored agents is highly required [9].

In recent years, adsorption technology has been regarded as a preferable method for dye removal owing to its high efficiency, cost-effectiveness, and simplicity. Furthermore, this technology generates no secondary pollution [10–12]. Accordingly, several adsorbents such as rice husk [13,14], hen feather [15], Apricot stone [16], activated carbon [17,18], agricultural waste [19–21], and various other adsorbents [22–25] have been tested with the aim of removing the organic pollutants from wastewater. In spite of the fact that these materials have been useful for the end of remediation, most of them are not so efficient. Recent advances reveal that nanotechnology manage to resolve many issues involving environmental pollution and water quality in highly efficient and cost-effective approaches [26]. With this in mind, various nano-adsorbents have been proposed for remediation of dye pollutants and other waste effluents [27–30]. Among nanostructure compounds, magnetic nanocomposites are very popular advanced materials that could be magnetically recovered from solution. Hence, they have gained numerous multidisciplinary researchers` attention. That is to say, unsurpassed properties of nanomaterial provide routes to considerably mitigate detrimental effects of wastewater [31–34]. A wide variety of synthetic techniques for producing nano-particles consists of vapor, chemical, and biological sub-methods. Recently, solvent free, solid-state process has been successfully developed with the aim of synthesis, or functionalization of nanomaterial. Indeed, this technique has been considered as an efficient renewable route which presents more compatibility with green chemistry's tenet [35–37].

In this work, a solvent free, solid state synthetic route has been developed to prepare magnetic $MnFe_2O_4$. To this end, Citric acid-phenylenediamine based polyamide resin and its magnetic composite have been synthesized with thermal reaction of solid raw materials. The procedures are free of harmful gases and waste. In view of practical application, the prepared magnetic-resin nanohybrid has been employed for the removal of Congo red (CR) from aqueous solution. Effective parameter on dye adsorption such as working pH as

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well as interaction time have been optimized, and isotherm behavior has also been evaluated.

2. Experimental

2.1. Materials and instruments

Citric acid, $FeCl_3.6H_2O$, $Mn(NO_3)_2.4H_2O$, NaOH and p-phenylenediamine supplied from Merck (Darmstadt, Germany) and employed to preparing ferrite and magnetic resin. Congo red dye was supplied from chemistry & chemical engineering research center of Iran (Tehran, Iran). The pH adjustment was performed with 0.1 mol L^{-1} of HCl and NH_3.

Powder X-ray diffraction analysis was recorded by a Phillips powder diffractometer, X' Pert MPD, with Cu-Ka ($\lambda = 1.540589$ Å) radiation in 2θ range of 2–100°. FE-SEM and TEM analysis carried out using HITACHI S 4160 and Zeiss - EM10C instruments. Fourier transformed infrared spectra (FT-IR) were measured with Equinox 55 Bruker with ATR method over the wavelength of 400–4000 cm $^{-1}$. A digital pH-meter (model 692, metrohm, Herisau, Switzerland), was used for the pH adjustment. A Lambda – 25 UV – Vis spectrophotometer was used for recording the dye adsorption behavior of the magnetic polyamide.

2.2. Synthesis of $MnFe_2O_4$ and polyamide nanohybrid

$MnFe_2O_4$ was obtained through adding 1.5 g of NaOH to a mixture of 0.4 g of $Mn(NO_3)_2.4H_2O$ and 1.0 g of $FeCl_3.6H_2O$ and riled for 5 min, followed with drying at 100 °C for 10 min. Polyamide resin and magnetic nanohybrid were fabricated by solvent free rout with solid reagents. In a typical run, 0.5 g of citric acid and 0.6 g of 1, 4-phenylenediamine was mixed with together and/or with 0.3 g of the ferrite, and heated at 155 °C for 3 h. After cooling to room temperature, it was grinded and stored for subsequent work.

2.3. Dye adsorption experiment

Congo red was employed as a sample anionic dye. Adsorption was performed in 50 mL volumetric flask, which contains 10 mg of $MnFe_2O_4$@polyamide as the adsorbent and known concentration of Congo red. pH of the mixture was conducted to pH = 2. After shacking for one min, the concentration of CR in aqua's phase was measured with UV–Vis spectrometer.

3. Result and discussion

3.1. Characterization of materials

3.1.1. XRD characterization

The X-ray powder diffraction analysis (Fig.1a) was used to verify the $MnFe_2O_4$, polyamide resin and magnetic nanohybrid. The pattern of $MnFe_2O_4$ showed typical main peaks at 2θ° = 29.64, 35.12, 35.48, 42.48, 52.72, 56.2 and 61.76 corresponding to (220), (311), (222), (400), (422), (511), and (440) planes of a cubic spinel structure [38]. The XRD pattern of resin showed a main broad scattering beginning from 2θ of 10° to 50° with a maximum height at 22°. The XRD pattern of magnetic nano-composite was dominant with the main peak of the resin and this confirmed the incorporation of nanoparticles within resin. However, the characteristic peak of the ferrite was also observable as a very small peak which confirmed the formation of the ferrite@ resin nanocomposite. It was obvious that the crystalline behavior of $MnFe_2O_4$ was approximately affected by growth of the resin on its surface. As a result, lower intensity of ferrite peaks was due to the masking of the diffraction peaks of the ferrite nanoparticles.

3.1.2. Magnetic characterization

The magnetic hysteresis loops are shown in Fig. 1b. The magnetic parameters of $MnFe_2O_4$, and nanohybrid including saturation magnetization (M_s)and remnant magnetization (M_r) which determined from the hysteresis loop's measurements. The values of $M_{s.}$ for as synthesized $MnFe_2O_4$ was 23.0 emu g^{-1} which were lower than that of bulk $MnFe_2O_4$ (80 emu g^{-1}) [39]. Bulk ferrites possess AB_2O_4 structure, which includes A (Mn^{2+}) and B (Fe^{3+}) magnetic sub-lattices sites (tetrahedral and octahedral sites) in which separated by oxygen atoms. The occupation ratio of Fe^{3+} to M^{2+} ions at the octahedral sites can affect the net magnetic moment as decrease the occupation ratio of Fe^{3+} ions at the octahedral sites can lead to an increase in the net magnetic moment [40]. In addition, saturation magnetization usually decreases with decrease in particle size, so the saturation magnetization of the nanoparticles is lower than bulk ferrites. Furthermore, the $M_{s.}$ value for magnetic resin (6.2 emu g^{-1}) is less than those obtained for pure ferrites. It is known that the Ms. of the nanocomposites are dependent on the volume fraction of the magnetic nanoparticles. In other words, lower Ms. value of the nanohybrid relative to the net ferrite was owing to the dilution effect of resin. The value of Mr. for nano ferrite was low (0.27 emu g^{-1}) which indicated that the particles posed likely superparamagnetic properties because the particle size is so small that each particle is a single magnetic domain.

3.1.3. FT – IR analysis

The FT-IR spectra of the ferrite and magnetic resin is shown in Fig.1c. The $MnFe_2O_4$ nanoparticles had peaks at 566 cm^{-1}, 1380–1390 $cm^{-1}$and 3000–3500 cm^{-1}that correspond to Fe - O stretching, OH bending vibration, and stretching vibration of residual hydroxyl groups [41]. Peaks of Mn – O at 400–420 cm $^{-1}$ and 520–596 cm^{-1} were ascribed to stretching vibration of octahedral and tetrahedral complexes. In addition, the peaks with high absorption intensity were owing to the high crystallinity of the ferrite. The spectrum of ferrite –resin posed new peaks around 3300–3500 cm^{-1}, 2929 cm^{-1}, 1725 cm^{-1}, 1570 cm^{-1} and 1400 cm^{-1} which could be assigned to $-NH_2$ stretching vibration, C–H stretching, C = O vibration, N–H bending units, and aromatic backbone vibration, respectively [42]. It was obvious that the peaks of magnetic ferrite are also observable at 400–600 cm^{-1} region in the spectrum of magnetic resin and confirmed that the ferrite presence of nanoparticles in the resin matrices.

3.1.4. SEM and TEM analysis

The SEM image of $MnFe_2O_4$ is shown in the Fig. 2a. The image indicated that synthesized ferrite was composed of discrete bundles. Moreover, the image suggested that the products contained some agglomeration of very small regular uniform spheres. Further analysis by the TEM image (Fig. 2d) showed high density of the nanoparticles which composed of fine particles with the diameter less than 5 nm. Formation of spherical shapes was owing to the equivalent growth rate along different directions of the nucleation. Fig. 2b showed the FE – SEM image of as prepared resin. It indicated that the resin exhibited sheet – like structure on the macrolevel. However, the TEM image (Fig. 2e) showed that the resin composed of very slim sheets as the thickness of them was less than 5 nm. Structure of citric acid and diamine contains several carboxylic acid and amine groups which can participate in condensation reaction. With this in mind, sheet-like structure was owing to proceed of amide-formation at various directions. Moreover, the combination of oxygen-containing functional groups, such as C–O, C = O, and — OH at the structure of resin, generated lamellar layers. According to the FE – SEM and TEM result (Fig.2c and f), dispersion of magnetic nanoparticles were obvious in composite structure. However, it was not homogeneous. In fact, magnetite nanoparticles can be chemically attached to the resin by esterification of hydroxyl groups on ferrite surface and citric acid.