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A dual function magnetic nanomaterial modified with lysine for removal of organic dyes from water solution

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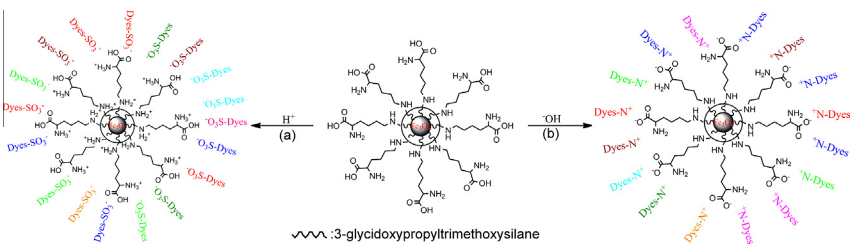
HIGHLIGHTS

- The improved adsorbent can enhance the maximum adsorption capacities for anionic dyes.
- Low toxicity and biocompatible lysine was used as raw materials.
- The adsorbent can be effectively reused to remove both anionic and cationic dyes.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel Fe_3O_4 magnetic nanoparticles (MNPs) modified with low toxic 3-glycidoxypropyltrimethoxysilane (GPTMS) and lysine (Lys) were synthesized. The MNPs were characterized by transmission electron microscopy, X-ray diffraction, infra-red spectra and thermogravimetric analysis. The MNPs were used to remove anionic dyes and cationic dyes, including methyl blue (MB), orange I (OR), acid red 18 (AR) and methylene blue (MEB), azure I (AZ), from aqueous solution. We investigated organic dye uptake capacity of Fe_3O_4@GPTMS@Lys as a function of contact time, dye concentration, and different pH. Furthermore, adsorption isotherms and kinetics were studied to understand the mechanism by which the MNPs adsorb dyes. To our delight, the improved adsorbent can not only enhance the maximum adsorption capacity for anionic dyes but also efficiently remove cationic dyes (AZ and MEB) from aqueous solution.

1. Introduction

Organic dyes are extensively used in various industries including dyestuff, paper, leather, cosmetic, and textile [1,2]. Nevertheless, organic dye effluents are the most significant identified contaminant amongst the various pollutants of wastewater, because the presence of these dyes in water even at very low concentration is highly observable. At the same time, they may cause allergic dermatitis or skin irritation, may be carcinogenic and mutagenic to humans and aquatic organisms [3], and are extremely resistant to biodegradation by native microorganisms. Thus, from an environmental point of view, the removal of organic dyes from waste water is of great significance [4,5].

To date, several techniques, such as chemical oxidation, biological treatment, coagulation, photocatalytic degradation and adsorption, have been explored to remove the dye contaminants from wastewater [6–9]. Adsorption is a more competitive method for removal of dyes due to its merits of simplicity, high efficiency and economy. Many kinds of adsorbents have been reported, such as zeolites, activated carbons, industrial by-products, agricultural wastes, clays, biomass and polymeric materials [10–14]. Recently, magnetic nanoparticles as new adsorbents have attracted considerable interest owing to their large specific surface area, short diffusion route, high separation efficiency and low cost [15–17]. Fe_3O_4 nanoparticles as the core of magnetic nanomaterials have also been proven to be biocompatible and with low toxicity. Therefore, many adsorbents based on the magnetic nanoparticles were synthesized through surface modification with various organic compounds, such as chitosan, cationic biopolymer, anionic

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biopolymer, ionic liquid and surfactant. Adsorption capacity of these adsorbents can be greatly enhanced because a large numbers of active sites are introduced [18–25]. In addition, we have reported three kinds of adsorbents modified with copolymers of acrylic acid and crotonic acid [20], aminoguanidine [26], and glycine [27].

The adsorbent modified with glycine (Fe_3O_4@GPTMS@Gly) could remove cationic and anionic dyes. However, the maximum adsorption quantity (q_m) for anionic dye is much lower than q_m for cationic dye. In this work, to enhance the maximum adsorption capacity for anionic dyes, we used lysine to modify Fe_3O_4 nanoparticles, because the number of amino group influences q_m for anionic dyes and lysine contains munch more amino groups than glycine. We also compared the adsorption results of the both adsorbents for anionic dyes. In addition, we studied the adsorption isotherms, kinetics, desorption and reuse of the new MNPs.

2. Experimental

2.1. Materials and reagents

All chemicals and reagents were of analytical grade and used as received without any further purification. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous sulfate ($FeSO_4{\cdot}7H_2O$), lysine, sodium carbonate, acid red 18 (AR), orange I (OR) and azure I (AZ) were purchased from Sinopharm Chemical. Methyl blue (MB), methylene blue (MEB) (Fig. 1), Sodium hydroxide and toluene were from Tianjin Guangcheng Chemical. 3-Glycidoxypropyltrimethoxysilane (GPTMS) was from J&K Chemical. Aqueous solutions of organic dyes were prepared with purified water.

2.2. Instrumentation

The particle size and morphology of the Fe_3O_4-MNPs were detected with a transmission electronic microscopy (TEM, JEM-1011). Infra-red (IR) spectra were recorded with an IR spectrophotometer Bruker VERTEX 70 FT-IR (Germany). The magnetic property of MNPs was studied by use of a vibrating sample magnetometer (VSM, JDM-13E). Thermogravimetric analysis (TGA) involved use of an SDTQ600 thermogravimetric analyzer (USA) at 10 °C/min under nitrogen flow. A Bruker D8 Advance X-ray diffraction analyzer (Germany) with Cu Kα radiation was used for X-ray diffraction (XRD) measurements. The values of pH were measured with a PHS-3C pH-meter (Tianyou, Shanghai). An AU-4100 spectrophotometer (Hitachi) was used for determining organic dye concentration in solution. Zeta potential measurements of synthesized MNPs were performed with Zeta PALS (USA).

2.3. Synthesis of MNPs

Fig. 2 shows the scheme of synthesis of Fe_3O_4@GPTMS@Lys. Fe_3O_4 magnetic nanoparticles were prepared by chemical coprecipitation method as reported in our previous work [28]. The preparation of GPTMS-modified Fe_3O_4 (Fe_3O_4@GPTMS) was achieved according to reported method [29]. Briefly, 1.000 g Fe_3O_4 MNPs were suspended in 100 ml distilled toluene by ultrasonator for 10 min. The dispersion was heated to reflux with vigorous stirring under nitrogen, and then 8 ml GPTMS was added. The mixture was kept refluxing for 8 h. The Fe_3O_4@GPTMS MNPs were separated by a magnet and washed 3 times with 150 ml anhydrous ethanol. At last, they were dried at 60 °C under vacuum for use in next step.

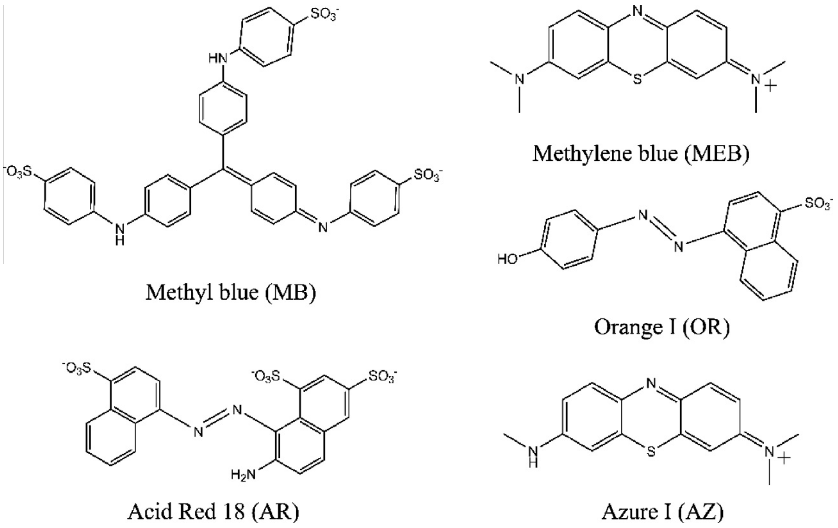
The Fe_3O_4@GPTMS@Lys MNPs were synthesized from Fe_3O_4@GPTMS and lysine by following a modified method [30]. Typically, Fe_3O_4@GPTMS MNPs (2.8 g), lysine (2.0 g), sodium carbonate (2.8 g) and deionized water (50 ml) were added into a flask with mechanical agitation under nitrogen. The mixture was stirred for 24 h at room temperature. The obtained product was separated by a magnet. After immergence of the precipitate in dilute acetic acid for 10 min the precipitate was washed several times with deionized water and anhydrous ethanol. The final product was dried in a vacuum system at 60 °C for 8 h.

2.4. Adsorption experiments

All adsorption experiments were carried out on a model SHA-B thermostat shaker (Changzhou, China) with a shaking speed of 300 rpm. Briefly, 0.05 g adsorbent (Fe_3O_4@GPTMS@lys MNPs) and 50 ml organic dye solution of known concentration were mixed by ultrasonication for 2 min, and then shaken at 298 K for 0–120 min. The adsorbent was separated by a magnet. The concentration of dye was analyzed by use of an AU-4100 spectrophotometer. The initial pH of dye solution was adjusted at different values with HCl or NaOH solution [31–33].

2.5. Desorption experiments

Desorption experiments were carried out as previously described, with some modifications [22]. The magnetic material


Methyl blue (MB)

Methylene blue (MEB)

Orange I (OR)

Acid Red 18 (AR)

Azure I (AZ)

Fig. 1. Structures of MB, AR, MEB, OR and AZ.