



## Rapid color degradation of organic dyes by Fe<sub>3</sub>O<sub>4</sub>@His@Ag recyclable magnetic nanocatalyst



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### ARTICLE INFO

#### Article history:

Received 1 December 2014  
Received in revised form 14 January 2015  
Accepted 16 January 2015  
Available online 23 January 2015

#### Keywords:

Magnetic recyclable nanocatalyst  
Methyl orange  
Methylene blue  
Catalytic reduction  
Magnetic nanomaterials

### ABSTRACT

In this study, we reported the degradation of organic dyes (methyl orange, MO and methylene blue, MB) by Fe<sub>3</sub>O<sub>4</sub>@His@Ag MRC in which histidine was used as linker. The size of crystallite of MRC was calculated as 19 nm. The M–H hysteresis loop of the product indicates that it exhibits superparamagnetic property at room temperature. Catalytic studies showed that this product could catalyze the degradation of MO and MB in a reasonable time. Moreover, the product can be recycled five times by magnetic separation without major loss of its activity. Thus, Fe<sub>3</sub>O<sub>4</sub>@His@Ag MRC can be served as an effective and convenient recyclable nanocatalyst for azo dye degradation and hence as an environmental protection application too.

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### Introduction

Dye pollutants and their disposal are a serious concern among many recent issues that remain a challenge to our environment globally. Organic dyes in general flow out of chemical industries and from many domestic discharge places. Dye textiles, plastic papers, leathers, foods, and cosmetics are the sources of toxic species in the form of colored wastewater [1]. Each day, natural and synthetic dye products are making our world spectacular, in spite of their uncontrolled discharge, which cause a destruction of ecosystem [2]. It was stated that over 700,000 tons of dyes are commercially produced every year; among them 15% of which are discharged by chemical industries as wastewater after their dyeing process [3]. Among these organic dyes, methyl orange (MO) as an organic sulfosalt and methylene blue (MB), as a heterocyclic aromatic dye, are quite dangerous to the environment [4]. Many methods, such as oxidation, adsorption, degradation, and catalytic reduction have been studied and developed to decolorize organic and inorganic dyes [5–8].

Nanoparticles (NPs) have attracted a considerable interest in different areas due to their excellent magnetic, optical, mechanical and catalytic properties. Due to the existence of these novel and versatile behaviours of nanoparticles, they have been used in ferrofluids, magnetic storage media, biomedicine and in other

technologies including targeted drug delivery, bio-sensing, contrast agents in magnetic resonance imaging and in chemical catalysts [9–14].

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is the most important and fundamental iron oxide which has been focused by many researchers because of its larger magnetic moments, high stability in aqueous media and excellent superparamagnetism [15,16]. In addition to that, Fe<sub>3</sub>O<sub>4</sub> NPs are used as a conventional support material for catalysts and they can be easily separated from the reaction system by using an external magnetic field (magnet) and those can be used to synthesize any new magnetically recyclable catalyst with good catalytic activities and they can easily degrade the organic dyes thereby reducing the hazardous effect of dye wastes on environment.

Noble metals (Ag, Pt, Pd, Au) are found to be effective catalytic material for the degradation of organic dye pollutants [17]. Due to that many studies have been done for the synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs with noble metals. Among these noble metals, silver nanoparticles are being used for several applications such as in many commercial products, textile, cosmetic, in catalysis processes, energy, biotechnology, electronics, food industries for packing and in biotechnology due to their excellent optoelectronic properties [18]. Both Silver and Fe<sub>3</sub>O<sub>4</sub> NPs have an individual catalytic effect and due to that reason several nanocatalysts have been synthesized and reported like, magnetically photocatalyst Fe<sub>3</sub>O<sub>4</sub>@C@Ag [19], Ag-coated-Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub> [20] Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Ag [21] etc.

In this work, we synthesized a new effective catalyst with a protein called Histidine (His) by hydrothermal method and

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demonstrated that recyclable  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC can be used to decolorize azo dyes pollutants rapidly such as methyl orange and methylene blue. The  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC showed an excellent catalytic performance in the reduction of dye pollutants and are also readily separated by the magnet and can be reusable. These properties showed that  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC have potentials that can form a new generation of catalysts for the degradation of azo dyes during the treatment of wastewater in chemical industries.

## Experimental

### Chemicals and instrumentations

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , Histidine,  $\text{AgNO}_3$ ,  $\text{NaBH}_4$ , and  $\text{NH}_3$  were sourced from Merck and were used without further purification.

The crystalline structure of resultant nanoparticles was determined with X-ray diffraction measurements (XRD) using Rigaku D/Max-IIIC with  $\text{Cu-K}\alpha$  radiation in the  $2\theta$  range of  $20^\circ$ – $70^\circ$ .

The surface morphology of the composites was analyzed with JEOL, JSM 7001F Scanning Electron Microscopy (SEM).

Ultraviolet–visible (UV–vis) spectrometer model Shimadzu UV–Vis 2600 was used in the range of 300–800 nm.

VSM measurements were performed by using a Vibrating sample magnetometer (LDJ Electronics Inc., Model 9600). The magnetization measurements were carried out in an external field up to 15 kOe at room temperature.

The thermal stability was determined by thermogravimetric analysis (TGA, Perkin Elmer Instruments model, STA 6000). The TGA thermograms were recorded for 5 mg of powder sample at a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of  $30$ – $800^\circ\text{C}$  under nitrogen gas.

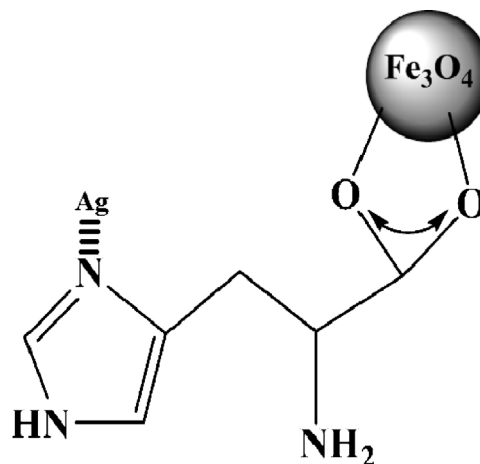
Transmission electron microscopy (TEM) analysis was performed using a FEI Tecnai G2 Sphera microscope. A drop of diluted sample in alcohol was dripped on a TEM grid.

### Preparation of $\text{Fe}_3\text{O}_4\text{@His}$ nanocomposite

$\text{Fe}_3\text{O}_4\text{@His}$  nanocomposite were prepared by hydrothermal method. Analytical grade chemical reagents,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were used as initial materials for the synthesis. Metal salts taken separately in required stoichiometric ratio were dissolved in 20 mL of distilled water; on the other hand 5 g of Histidine was dissolved with water in a small cleaned glass beaker using magnetic stirring. After dissolving all  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and Histidine was added and mixed them well. Analytical grade  $\text{NH}_3$  solution was added drop-by-drop under constant stirring so that the pH of the solution attains a value equal to 10 at which the precipitation of  $\text{Fe}_3\text{O}_4$  takes place. Then the solution was transferred to the teflon coated stainless steel autoclave. Then autoclave was closed very tightly so that no gas or vapor could go out or inside it. Then the autoclaves were placed inside an oven at  $250^\circ\text{C}$  for 24 h. After 24 h a black color  $\text{Fe}_3\text{O}_4\text{@His}$  nanocomposite was collected.

### Preparation of $\text{Fe}_3\text{O}_4\text{@His@Ag}$ MRC

The prepared  $\text{Fe}_3\text{O}_4\text{@His}$  NPs (150 mg) were dispersed in 50 mL of deionized water. Then these were sonicated for 30 min, followed by the addition of 30 mL of  $\text{AgNO}_3$  solution ( $0.2 \text{ mmol L}^{-1}$ ). The solution was vigorously stirred for 30 min and then 0.6 g of  $\text{NaBH}_4$  was quickly added and the mixture was allowed to react for 1 h under rapid stirring. The product was separated magnetically and washed several times with deionized water to eliminate impurities (Scheme 1).



Scheme 1. Synthesis of  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC.

## Results and discussion

### XRD analysis

Fig. 1 shows the XRD powder pattern of  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC. The deposition of Ag NPs on the surface of  $\text{Fe}_3\text{O}_4$  was confirmed by XRD, as illustrated in Fig. 1. Compared to the XRD patterns of the  $\text{Fe}_3\text{O}_4$ , four additional peaks are observed for the  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC at  $2\theta$  values of  $38.1^\circ$ ,  $44.3^\circ$  and  $64.4^\circ$  which corresponded to the (1 1 1), (2 0 0) and (2 2 0) lattice planes of face-centered cubic phase Ag NPs (labeled with the red color). As shown in Fig. 1, all of the diffraction peaks match well with Ag (JCPDS No. 87-0720) crystal and  $\text{Fe}_3\text{O}_4$  nanocrystals (JCPDS No. 75-0033). The average crystallite size ( $t$ ) was calculated from the diffraction line-width of XRD pattern, based on Scherrer's relation:

$$t, \text{ thickness} = \frac{0.9\lambda}{\beta \cos \theta}$$

where  $\beta$  is the full width at half maximum (fwhm) and found out as 19 nm [22,23].

### FT-IR analysis

The FT-IR spectra of FT-IR spectra of  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC, L-histidine and  $\text{Fe}_3\text{O}_4\text{@Histidine}$  are presented in Fig. 2a–c, respectively. The presence of the iron oxide nanoparticles is evidenced by the strong absorption bands at around  $570$ – $590 \text{ cm}^{-1}$  that confirm the metal-oxygen stretching, present in Fig. 2a and c [24]. In the spectrum of Fig. 2b (pure L-histidine), the characteristic  $\text{NH}_2$  stretching frequencies of L-histidine are observed at  $\sim 3330 \text{ cm}^{-1}$ , and asymmetric and symmetric stretching frequencies of carboxylate ( $\text{COO}^-$ ) are observed at  $1635 \text{ cm}^{-1}$   $\nu_{\text{as}}(\text{COO}^-)$  and  $1411 \text{ cm}^{-1}$   $\nu_{\text{s}}(\text{COO}^-)$  respectively [25]. The linkage of L-histidine to iron oxide surface has been already explained in our previous study [26]. According to these results, FT-IR analyses suggest that L-histidine remains chemisorbed on the surface of iron oxide. The formation of bond between  $\text{Cu}^{2+}$  and  $\text{Fe}_3\text{O}_4\text{@Histidine}$  nanocomposite was explained by Tang et al. [22]. According to this study,  $-\text{NH}_2$  groups were used to bind  $\text{Cu}^{2+}$  ions through  $\text{Cu}^{2+}-\text{NH}_2$  complex then the bound  $\text{Cu}^{2+}$  ions were reduced to Cu with  $\text{NaBH}_4$  to form  $\text{Fe}_3\text{O}_4\text{@Cu}$  nanocomposite. Fig. 2a and b revealed that the characteristic peak of C=N stretching noticed at  $1633 \text{ cm}^{-1}$  for L-histidine was shifted to  $1645 \text{ cm}^{-1}$  for  $\text{Fe}_3\text{O}_4\text{@His@Ag}$  MRC. This shifting is possible if Ag NPs bind with C=N group of L-histidine and thus indicating the immobilization of Ag NPs on  $\text{Fe}_3\text{O}_4\text{@His}$

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