Comparative study of photocatalytic activity for three type Fe_3O_4 prepared in presence of different hydrolysis agent

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Abstract

The aim of this study was to compare morphology, size and photocatalytic activity of magnetic Fe_3O_4 nanopowders synthesized by solvothermal method utilizing different sources of hydrolysis factor (ammonium acetate, urea and dodecyl amine) in various temperatures. Prepared magnetic nanostructures were characterized by FT-IR and DRS spectra and SEM images. Influence of different conditions of synthesize on morphology, size and photocatalytic activity of Fe_3O_4 nanopowders was investigated.

Keywords: Fe_3O_4, ammonium acetate, urea, dodecyl amine, photocatalytic activity.

1. Introduction

The powder of Fe_3O_4 is increasingly important for applications as magnetic material, catalyst, biomaterial, and so on. Especially in the nanoscale region, the particles of Fe_3O_4 often demonstrate unique size-and shape-dependent physical and chemical properties that are of technological importance and scientific research interest. Consequently, so far, considerable effort has been devoted to designing novel methods for the preparation of Fe_3O_4 nanomaterials with different characteristics and purposes [1-4].

Among the various developed for synthesizing metal oxide nanomaterials, the metalorganic molecular precursor route has been regarded as one of the most convenient and practical techniques, because it not only enables to avoid special instruments and severe preparation condition, but also provides good control over purity, homogeneity, composition, phase and microstructure of resultant products [3-4]. Besides practical applications in industry such as in catalysis, ceramics, energy storage, magnetic data storage, and ferrofluids [2], Fe_3O_4 nanoparticles have already been applied in clinical diagnosis and medicine transporters. Conventionally, Fe_3O_4 nanoparticles are produced via aqueous or organic solution synthesis.

A hydrothermal reaction of $(NH_4)_2SO_4.FeSO_4.6H_2O$ in the presence of hydrazine produces Fe_3O_4 particles of about 70 nm [5]. Other aqueous solution synthesis methods, such as co-precipitation of ferrous (Fe^{+2}) and ferric (Fe^{+3}) ions, thermal decomposition of alkaline solution of (Fe^{+3}) chelate in the presence of hydrazine and sonochemical decomposition of hydrolyzed Fe(II) salt, have also been developed in the recent years. However, none of them cold prepare monodispersed nanoparticles with a satisfactory size distribution [7-12]. An organic solution phase decomposition route has been widely used in the synthesis of iron oxide nanoparticle. Although the decomposition of $Fe(cup)_3$, $Fe(acac)_3$, or $Fe(CO)_5$ followed by oxidation can bring to high-quality monodisperse γ-Fe_2O_3 nanoparticles [6-8], a relatively higher temperature and a complicated operation are required.

In this study, we present facile, one-step and magnet-induced solvothermal approach to obtain Fe_3O_4 nanoparticles, using ethylene glycol (EG) as reaction solvent and utilizing different sources of hydrolysis factor (ammonium acetate, urea and dodecyl amine) in various temperatures. Influence of different conditions of synthesize on morphology, size and photocatalytic activity of Fe_3O_4 nanopowders was investigated.

2. Experimental

2.1. Materials

In this study, iron(II) chloride ($FeCl_2.4H_2O$), iron(III) chloride ($FeCl_3.6H_2O$), ethylene glycol (EG), ammonium acetate (NH_4Ac), dodocyleamine (DDA), sodium hydroxide (NaOH), citric acid($C_6H_7O_8$), urea (CH_4N_2O) and ethanol were purchased from Merck Company and used as received without further purification to prepare the samples.

2.2. Preparation of Fe_3O_4 nanostructures

2.2.1. Preparation of Fe_3O_4 nanostructures by method 1: Fe_3O_4-DDA

Solution A was prepared by dissolving 0.541 g of $FeCl_3.6H_2O$ and 0.371 g of DDA in 20 mL of EG under magnetic stirring at a rate of ca. 750 rpm at 50 ^oC. Solution B was prepared by dissolving 0.160 g of NaOH in 10 mL of EG under magnetic stirring at a rate of ca. 750 rpm at 50 ^oC. Then the two solutions were mixed together and different dosages of stirring at a rate of ca. 750 rpm at room temperature, leading to the formation of a yellow suspension. The resultant solution was loaded into a 50 mL-Teflon lined stainless steel autoclave, sealed, and heated at 220 ^oC for a period of time. The black solid product was obtained by centrifugation, washed with water and ethanol three times and dried [9].

2.2.2. Preparation of Fe_3O_4 nanostructures by method 2: Fe_3O_4-NH_4Ac

Synthesis nanocrystals were obtained via a facile solvothermal synthetic route. The typical preparation procedure of hollow Fe_3O_4 nanospheres is as follows. $FeCl_3.6H_2O$

(2 mmol) and $FeCl_2.4H_2O$ (1 mmol) were added into ethylene glycol (30 mL) to form a clear solution. Then a protective agent such as NH_4Ac (15 mmol) was added into the solution to form a mixture under vigorous stirring at room temperature. Subsequently, the mixture was put into a Teflon lined stainless steel autoclave of 50 mL capacity and sealed and maintained respectively at 200 °C for 48 h. Finally, the system was allowed to cool to room temperature naturally. The resulting black precipitate was collected by filtration and washed with absolute ethanol and distilled water in sequence for several times. The final product was dried in a vacuum box at 50 °C for 4 h [10].

2.2.3. Preparation of Fe_3O_4 nanostructures by method 3: Fe_3O_4-Urea

Ferric chloride hexahydrate ($FeCl_3·6H_2O$) (6 g) and urea (10 g) and citric acid (1.6 g) were loaded into a 100 mL Teflon-lined stainless steel autoclave, which was then filled with 60 mL absolute EG. Then a square and stainless small magnet was added into the autoclave, and the autoclave was sealed and maintained at 200 ℃ for 18 h. After cooling to room temperature naturally, the black products were filtered off, washed with distilled water and absolute ethanol for several times and dried in vacuum at 50 ℃ for 12 h [11].

2.3. Characterization of products

The particle morphologies of the prepared Fe_3O_4 were observed by an Tescan (model Vega II) scanning electron microscopy (SEM). The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer. Furthermore, the structure of particles was analyzed by powder X-ray diffractometer (XRD, Bruker AXS D8 advance).

24. Photocatalytic experiments

Photocatalytic activity studies of the prepared Fe_3O_4 nanostructures were evaluated by the degradation MB solutions. In a typical process, the catalytic reaction was carried out in a 100 mL photoreactor, which contain 10 mL of MB dye (10 mg/L) solution and 0.01 g of catalyst. Before the irradiation, the solution was magnetically stirred in the dark (15 min) to allow equilibrium of the system. Irradiation was carried out using 7 W LED lamps as the light sources. All photocatalytic experiments were carried out at the same conditions. The distance between photoreactor and light sources was 10 cm. Samples (3 mL) were collected during the irradiation and MB solution were separated from the photocatalyst by centrifugation. The degradation was monitored by measuring the absorbance amount using a double beam UV–Vis spectrophotometer (Shimadzu UV-1700) at 664 nm wavelengths.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD pattern of Fe_3O_4 nanostructures. The position of all diffraction peaks match well with those of Fe_3O_4 peaks at $2\theta=29.86^\circ$, 35.21°, 56.68°, 62.25°. The lattice system of Fe_3O_4 is cubic, which is in good agreement with standard card JCPDS 01-088-0315.

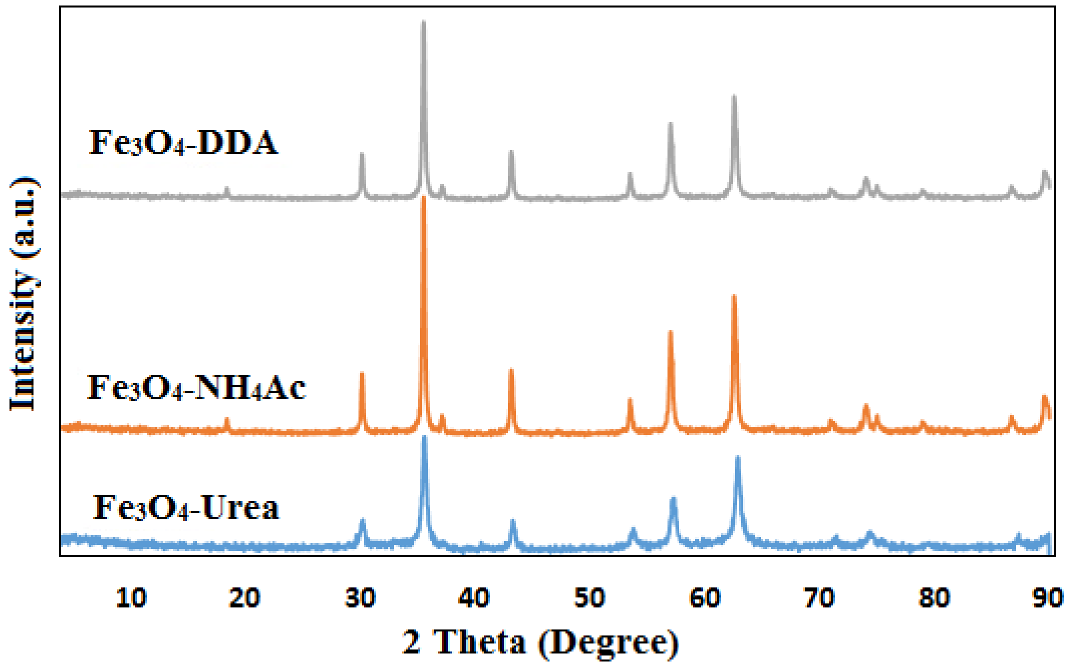

Fig. 1. The XRD pattern of Fe_3O_4 nanostructures.

3.2. Morphology study

The SEM images of Fe_3O_4 nanostructures synthesized by three methods are shown on Fig 2. For Fe_3O_4 prepared by methods 1 and 3, the sizes of particles were smaller than Fe3O4 prepared by method 2.

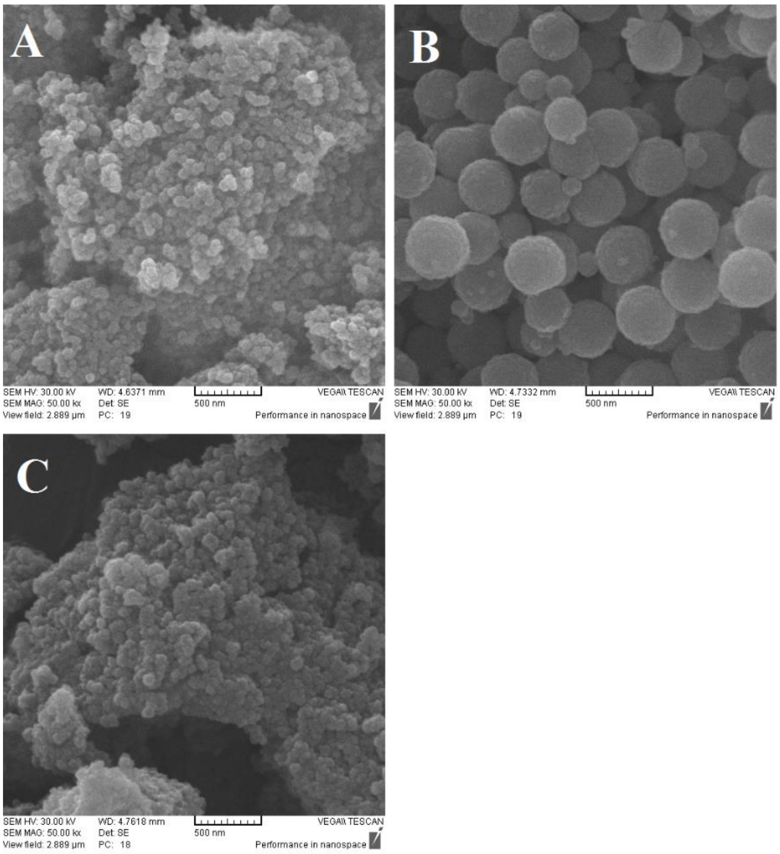

Fig. 2. The SEM images of Fe_3O_4 nanostructures prepared by (A) method 1, (B) method2 and (C) method 3.

3.3. FT-IR spectra

FT-IR spectra of Fe_3O_4 nanostructures prepared three methods indicated in Fig. 3 in the range 400-4000 cm^{-1}. In the spectra of Fe_3O_4 synthesized by method 1, the strong and the sharp absorption band appeared at 578.60 cm^{-1} is in good agreement with vibration band of Fe-O as typical band of reverse spinel iron oxide. In the spectra of Fe_3O_4 synthesized by method 2, the strong and the sharp absorption band appeared at 580.53 cm^{-1} is in good agreement with vibration band of Fe-O as typical band of reverse spinel iron oxide. In the spectra Fe_3O_4 synthesized by method 3, the strong and the sharp absorption band appeared at 570.89 cm^{-1} is in good agreement with vibration band of Fe-O as typical band of reverse spinel iron oxide. The observed peaks at 1039.56-

1081.99 cm^{-1} that related to C-O bonding on citric acid, the peaks 1278.72 and 1344.29 cm^{-1} to attributed to the stretching bond of C=O the carboxylic acid. On the other hand, the peaks at 1454.23-1650.95 cm^{-1} attributed to the symmetric and asymmetric stretching COO^{-}. The appearance of N-C-N stretching modes of the urea functionality in the (1454.23 cm^{-1}. The peaks in the range 3298.05-3444.63 cm^{-1} to attributed to the symmetric and asymmetric stretching of N-H on urea. The peaks at 2883.38-2864.09 cm^{-1} that related to C-H bonding on citric acid. One of absorption at 3164.97 cm^{-1} associated to O-H acidic vibration. These peaks showed that citric acid and urea have not been completely removed from Fe_3O_4 nanostructures synthesized by method 3.

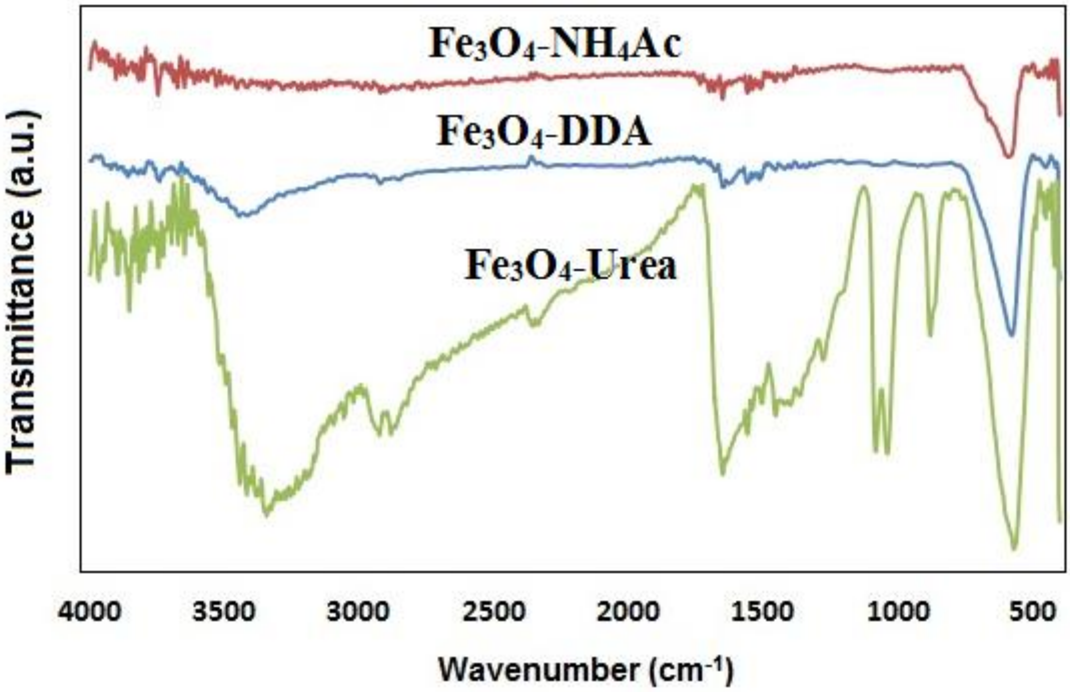

Fig. 3. FT-IR spectra of Fe_3O_4 nanostructures.

3.4. DRS-UV-Vis Spectra

The UV-Vis technique provides information including diffuse-reflectance spectra (DRS) and the band-gap energy *(E*g*)*. UV-Vis absorption spectrum of three Fe_3O_4

nanostructures is shown in Fig. 4, represents the broad absorption bands in both UV and visible regions (200–800 nm). Typically, two broad peaks were observed at about 380–400 nm on the UV absorption edge and 700 nm on the visible region which can be assigned to absorbance for Fe^{3+} and Fe^{2+} presence in prepared compound. The band-gap energy (Eg) according maxima band of absorption spectrum was evaluated by the Tauc equation as follows [39]:

$(\alpha h\nu)^n = B(h\nu - Eg)$ (2)

where $h\nu$ is the photon energy, α is the absorption coefficient, B is a constant value and Eg represents the band-gap energy. The value of n is assigned to transition which takes different values for allowed and forbidden, direct and indirect transitions [40]. By plotting of the $(\alpha h\nu)^n$ *vs*. $h\nu$ in eV with $n = 2$ for direct transitions, and then, by obtaining the extrapolation point of this curve, the band-gap energy of the products were estimated about 1.6 - 1.7 eV. These results reveal that the prepared sample can play a suitable role as a photocatalyst under light irradiation.. It is known that the photocatalytic activity is based on the generation of electron/hole pairs by means of band-gap radiation, which can lead to redox reactions with adsorbed species on the catalyst surface. The presence of holes on the surface of particles increases the surface area and so active sites. Thus these results provide large amounts of the electron/hole pairs under UV and visible irradiation and so they present a good photocatalytic performance of the as-synthesized Fe_3O_4 nanostructures.

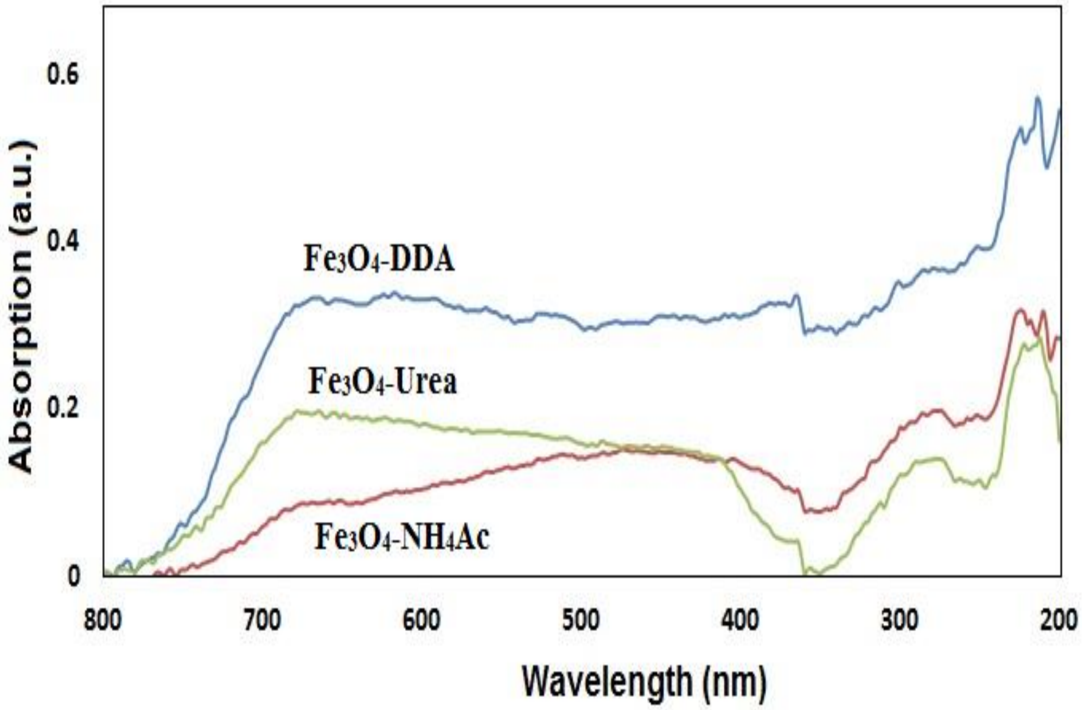

Fig. 4. UV-Vis absorption spectrum of three Fe_3O_4 nanostructures.

3.5. Photocatalytic degradation of MB

The photocatalytic activity of Fe_3O_4 nanostructures photocatalysts under visible LED light irradiation was defined by measuring the photodegradation of MB aqueous solutions. Methylene blue is a cationic dye with a methyl nitride group $[(CH_3)_2N^+]$.

The photocatalytic activity of as-synthesised Fe_3O_4 nanostructures synthesized by different methods were tested Fig. 5 exhibits the photodegradation of MB in presence of Fe_3O_4 nanostructures synthesized by different methods under visible light irradiation. It was demonstrated that the photocatalyst prepared by method 3 (Fe_3O_4-Urea) has the highest photocatalytic activity.

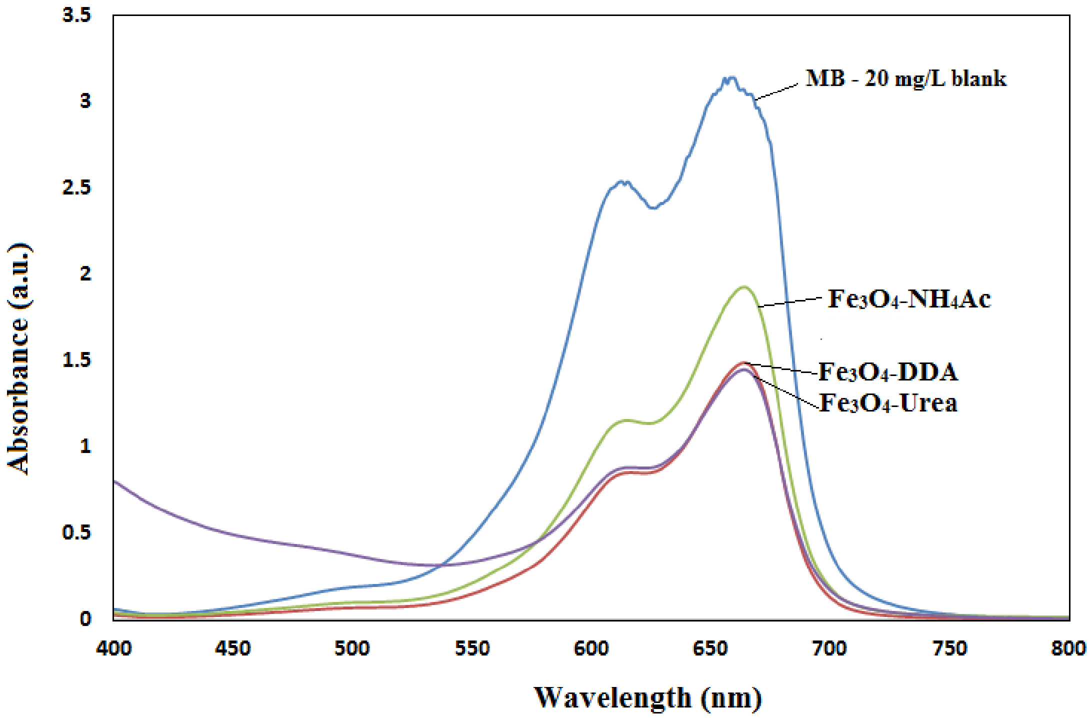

Fig. 5. The photodegradation of MB at 25 °C using Fe_3O_4 nanostructures (0.02 g catalyst, 20 mL MB, 20 mg/L, 180 min).

The adsorption of MB using Fe_3O_4 nanostructures have been demonstrated in Fig. 6 in dark after 3 h. The dark condition was tested to investigation of adsorbing properties of catalysts. The results show that removal efficiency of MB in presence of Fe_3O_4 nanostructures prepared by method 2 (Fe_3O_4-NH_4Ac) have the highest adsorption activity. Because the morphology of Fe_3O_4-NH_4Ac was nanohollow sphere and therefore can remove MB from solution by adsorption.

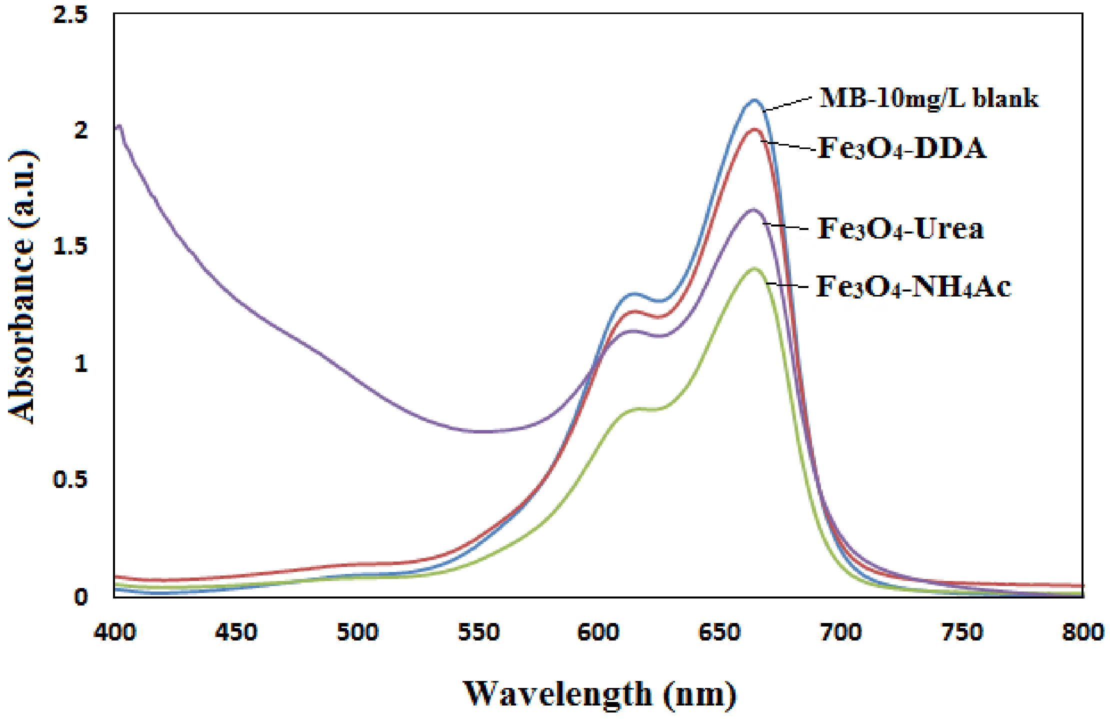

Fig. 6. The adsorption of MB at 25 °C using Fe_3O_4 nanostructures (0.02 g catalyst, 20 mL MB, 20 mg/L, 180 min).

4. Conclusions

Fe_3O_4 nanostructures were successfully synthesized through solvothermal approach by different hydrolysis factor in three methods. The results obtained from the photodegradation of methylene blue under LED light show that the Fe_3O_4 nanostructures prepared using urea and citric acid exhibits a higher photocatalytic activity than the Fe_3O_4 nanostructures synthesized using NH_4Ac or dodecyl amine as hydrolysis factors.

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