Application of Different Magnetic Nanoparticles in Water Treatment: Methyl Orange Adsorption Evaluation

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Abstract
In this paper, two magnetic Fe_3O_4 and $MgFe_2O_4$ samples were successfully synthesized by coprecipitation and combustion methods respectively to be used for adsorption of methyl orange dye from aqueous solution. The characteristics of the synthesized samples were evaluated using various analyses. The results of XRD assessment confirmed the successful synthesis of both samples with appropriate structure. The surface morphology of the samples proved the results of other analyses about the formation of the particles in nanosize. However, use of these samples in the methyl orange adsorption process showed that although Fe_3O_4 presented better physicochemical properties compared to $MgFe_2O_4$, the maximum adsorption capacity on the surface of these adsorbent was 20 mg/g and 56.54 mg/g, respectivly. Then, the isotherms of process were studied to obtain an adequate understanding of the adsorption process. By thorough study of these magnetic adsorbents, $MgFe_2O_4$ sample can be suggested for removal of dyes and water pollutants.

Keywords: Fe_3O_4, Mg-Fe Spinel, Magnetic Particles, Adsorbent, Methyl Orange (MO), Isotherms.

Introduction
Water as the most abundant constituent of the human body and the earth is one of the essential substances in the future of humans [1]. Nowadays, various pollutants such as heavy metals, biological, and dyes are brought into the water from various industries, which can have very devastating effects on human life and the environment [2].
As mentioned, one of the most critical pollutants coming from different industries is waterborne dyes [2]. These dyes contain toxic and carcinogenic substances that directly affect human health [3]. The importance of these problems has led scientist in recent years to research the possible ways of removing colored substances from water. Among these methods, the use of adsorbents is more attractive for industrial applications due to its convenience and economics [4].
The wide range of adsorbents has been used in recent years with unique advantages and disadvantages. Typical adsorbents used in the adsorption process have the same problem with difficulty in separation and filtration steps that will increase the cost of the process [5].

Therefore, one of the suggested methods to overcome this problem is the use of magnetic adsorbents to facilitate the adsorbent separation step.
Recently, spinels ($MgAl_2O_4$, $MgFe_2O_4$, $CuAl_2O_4$, etc.), which belong to the ceramics family, have been widely used in many industries due to their excellent properties such as chemical and thermal stability and mechanical strength [6]. Various methods for spinel synthesis have been reported in the literature, but one of the simplest and least expensive ways reported for spinel synthesis is the combustion method.
In this paper, the magnetic spinel $MgFe_2O_4$ is synthesized using a simple and inexpensive combustion method and its physicochemical properties, as well as its ability to be used as adsorbent of MO, are compared with magnetic Fe_3O_4 synthesized by co-precipitation method. After choosing the best sample for reducing the concentration of MO from water, the adsorption isotherms were precisely discussed.

Experimental

Nano Adsorbents Preparation and Procedure

To synthesis of Fe_3O_4, Iron (III) chloride nonahydrate and Iron (II) sulfate heptahydrate with a molar ratio of 2 to 1 were stirred in a certain amount of deionized water under nitrogen atmosphere to give a uniform solution for the synthesis of Fe_3O_4. Subsequently, the NH_4OH aqueous (1.5 M) solution was added dropwise to precipitation the powder and maintained the pH of the solution at 10 constant which was performed at 80°C. After ensuring complete deposition, the precipitate was separated by a magnet and washed several times with deionized water until the pH of the wash solution reached to 7. Finally, the powder was dried at 50°C for 4 hours to synthesize the Fe_3O_4 adsorbent.
The $MgFe_2O_4$ adsorbent was synthesized as follows. The precursors of iron (III) nitrate nonahydrate and magnesium nitrate hexahydrate were first dissolved in a certain amount of deionized water with a molar ratio of 0.5 Mg/Fe. Then, urea fuel was added to the solution at 1.5 times the stoichiometric ratio. After 30 minutes of stirring on the hot plate at ambient temperature, the solution temperature was brought to 70°C to form a brown gel by evaporating the water. Then the brown viscose gel was placed in the oven at 350°C, and after a few minutes, the gel began to combust vigorously; finally, $MgFe_2O_4$ brown powder was obtained.

Results and discussion

XRD Analysis

The XRD analysis of the synthesized adsorbents and the standard pattern of related materials are given in Figure 1a. The figure shows that the peaks created for the Fe_3O_4 sample are in perfect agreement with the standard JCPDS pattern of Fe_3O_4 (Cubic, 01-075-0033; 2Θ=18.3°, 30.1°, 35.5°, 37.1°, 43.1°, 53.5°, 57.0°, 62.6°, 74.1°, 89.8°). Comparing the sample peaks with the standard JCPDS pattern of Fe_2O_3 (Rhombohedral, 01-084-0306; 2Θ=24.2°, 33.2°, 35.6°, 40.9°, 49.5°, 54.1°, 57.6°, 62.4°, 64.0°, 72.0°) revealed that no Fe_2O_3 was synthesized during the synthesis of the Fe_3O_4 sample.
On the other hand, by simultaneously evaluating the sample peaks of $MgFe_2O_4$ and the reference pattern of $MgFe_2O_4$ (Cubic, 01-073-2211; 2Θ=30.2°, 35.6°, 43.2°, 53.6°, 57.2°, 62.8°, 74.3°) it can be concluded that the magnetic spinel of $MgFe_2O_4$ is correctly synthesized. The standard JCPDS pattern of MgO (Cubic, 01-077-2364; 2Θ=37.0°, 42.9°, 62.3°, 74.7°, 78.7°) is also illustrated in the figure to ensure the synthesis of $MgFe_2O_4$ due to similarity of standard JCPDS pattern of the Fe_3O_4 and $MgFe_2O_4$ to each other. The XRD

analyse of $MgFe_2O_4$ adsorbent reveals that no peak of MgO has been created, that means, magnesium nitrate precursor was used in spinel synthesis, not MgO.

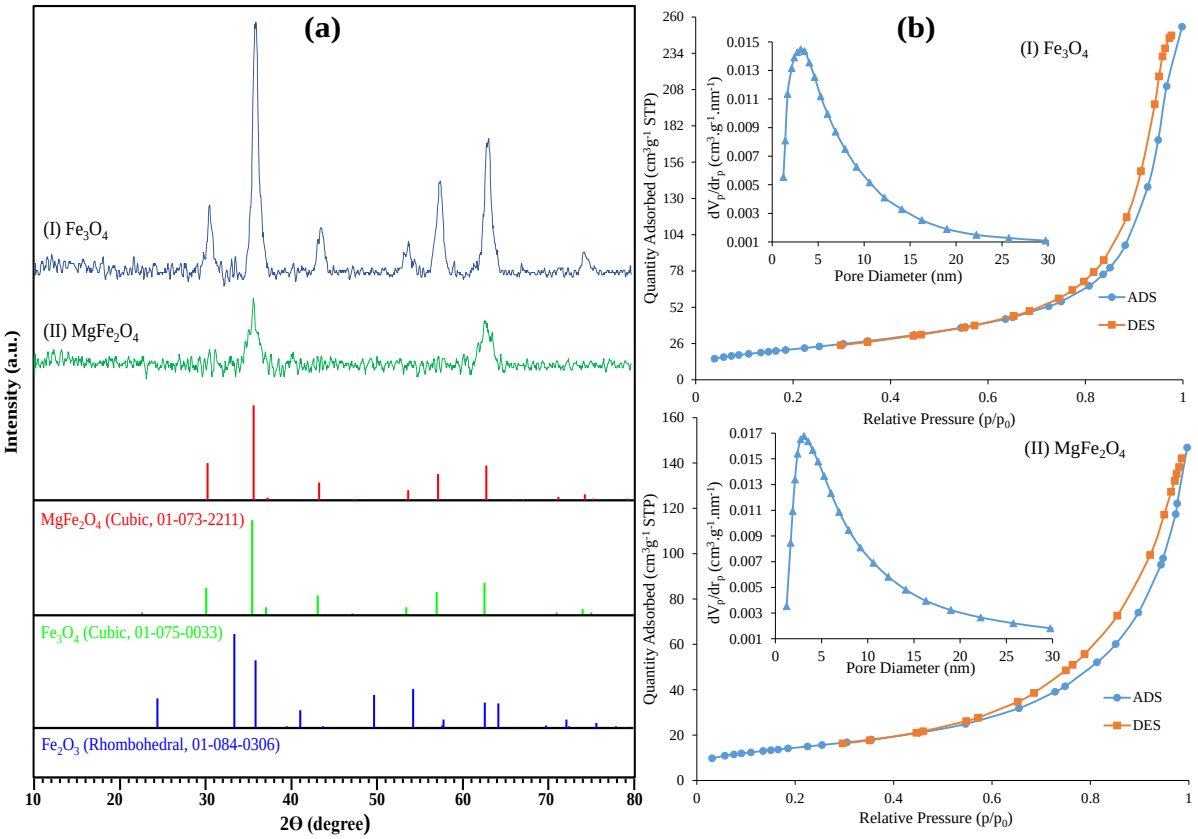

Figure 1. a) XRD patterns, b) Adsorption/Desorption isotherms and pore size distribution nano adsorbents: (I) Fe_3O_4, (II) $MgFe_2O_4$.

BET/BJH Analysis

One of the most important parameters in the adsorption process is the surface area and pore volume and diameter of the adsorbent. These specifications were obtained for both studied samples by BET-BJH analysis, in which the results are presented in and Figure 1b. The results shown that the specific surface area of Fe_3O_4 is about 1.5 times the magnetic spinel of $MgFe_2O_4$, 80.3 m^2/g and 52.1 m^2/g, respectively. The difference in surface area can be due to the different nature of the two materials as well as the various synthesis methods [7]. Also, by comparing the pore volume and diameters, it is found that the Fe_3O_4 adsorbent has higher pore volume but lower pore diameter than the magnetic spinel. Due to the large size of the methyl orange molecules, the used adsorbent must have a large pore diameter to allow better adsorption process. Therefore, the $MgFe_2O_4$ sample with average pore diameter of 6.9 nm compared to Fe_3O_4 with average pore diameter of 5.4 nm can be better adsorbent for coarse methyl orange molecules [8]. The adsorption-desorption hysteresis of both adsorbents is also very similar to the H1 type, which indicates the formation of cylindrical holes in the adsorbents. The created cylindrical pores in the samples can facilitate the entry of large methyl orange molecules into the adsorbent pores and thus increase access to the internal adsorbent surface [9]. As seen in Figure 1b**Error! Reference source not found.**, the maximum size distribution of the pore diameters of both adsorbents is in the range of 2 to 30 nm, which proves that the adsorbents are mesopore (2–50 nm).

FESEM Analysis

The FESEM analysis of both synthesized samples was performed that the results are visible in Figure 2. The study of both adsorbents reveals that the samples have nano dimensions which are in good agreement with the XRD analysis results. Both Fe_3O_4 and $MgFe_2O_4$ seem to have the same morphology; however, more uniformity is observed in the structure of the Fe_3O_4 adsorbent. The reason for this uniformity may be due to differences in synthesis methods. The sample synthesized by the combustion method due to the uncontrollable nature of the combustion process has more agglomerated particles than the sample synthesized by the co-precipitation method.

On the other hand, the use of the combustion method has resulted in the formation of more cavities in the $MgFe_2O_4$ spinel, which may be due to the combustion gases removed from the original gel composition [10]. More porosity with a larger pore diameter caused by the combustion synthesis method can have a significant effect on the absorption of large molecules (such as methyl orange). It makes more accessible the internal surface area of the materials (inside the pores) for dye molecules to easier diffusion/permission [11].

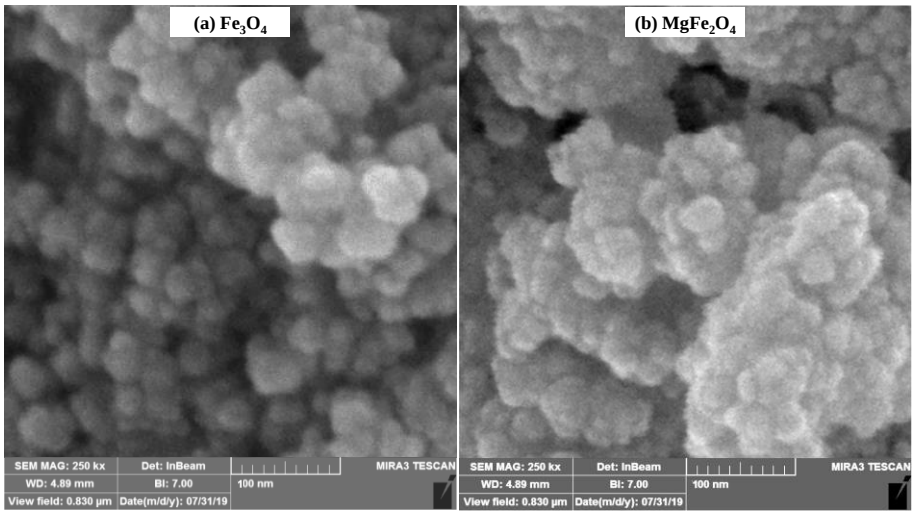

Figure 2. FESEM images of nano magnetic adsorbents: (a) Fe_3O_4, (b) $MgFe_2O_4$.

Performance Study toward Removal of Methyl Orange

Despite all the good or bad properties of the synthesized samples, the most important characteristic is their ability to absorb dye from water. For this purpose, 0.05 g of the adsorbent was poured into 50 ml of methyl orange solution in water (100 mg MO/L) at pH 6. The solution with the adsorbent was placed on a shaker at 200 rpm, and the mixing temperature was adjusted to 25°C. After one hour of the adsorption process, some samples were taken from both test vessels. Then spectrophotometer analysis in the range of 350 to 600 cm^{-1} was used to obtain methyl orange absorption. The results showed that the maximum capacity adsorption of MO on the surface of Fe_3O_4 and $MgFe_2O_4$ adsorbents was 20 mg/g amd 56.54 mg/g, respectively. Thus, it was found that the $MgFe_2O_4$ sample had stronger adsorption on methyl orange. Therefore, the adsorption isotherms of this sample will be examined below.

One of the important points in the adsorption process is the investigation of adsorption isotherms, which allows investigating the type of interaction between the adsorbent and the adsorbate as well as the final adsorbent capacity. For this purpose, two important isotherms of Langmuir and Freundlich were investigated for the methyl orange adsorption process on

$MgFe_2O_4$ surface. The linear equations of these isotherms were evaluated, which the results are shown in Figure 3 and Table 1. Figure 3a shows that at low concentrations of methyl orange (up to 100 mg/L) there is a good agreement between the adsorption data and the Langmuir model (R^2 = 0.984 and maximum adsorption capacity = 243.9 mg/g), but with increase in initial concentration of adsorbate, the regression coefficient reduced to 0.841 (maximum capacity = 108.7 mg/g). Given the nature of this theory, it can be said that in the low amount of adsorbate, only one layer of dye is adsorbed on the adsorbent [12], but with the increase of methyl orange the theory is no longer true, and other adsorbed layers are likely to be adsorbed on the adsorbent surface.

The high accuracy between adsorption data with the Freundlich model Figure 3b, which expresses the multilayer adsorption of adsorbate on the heterogeneous adsorbent surface [13], can confirm the results. The results show that the adsorption process follows the Freundlich theory (R^2 = 0.949) in the range of low to high concentrations of methyl orange. The slope of the line (1/n = 1.33) in the Freundlich equation expresses the adsorption power of the dye on the heterogeneous adsorbent, and its smaller values (near zero) show more similarity of the adsorption process to the heterogeneous system and confirm the suitability of the adsorbent [14].

Table 1. Linearized equations of isotherm models for the adsorption of MO on the $MgFe_2O_4$ surface.

Isotherm Models	Linearized equations	Parameters	
Langmuir	$\frac{C_e}{q_e}=\frac{1}{K_L q_m}+\left(\frac{1}{q_m}\right)C_e$	R^2 q_m (mg/g) K_L (L/mg)	0.8415 108.69 0.019
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	R^2 n K_F (mg/g)	0.949 1.33 2.928
Experimental data		q_e (mg/g)	56.54

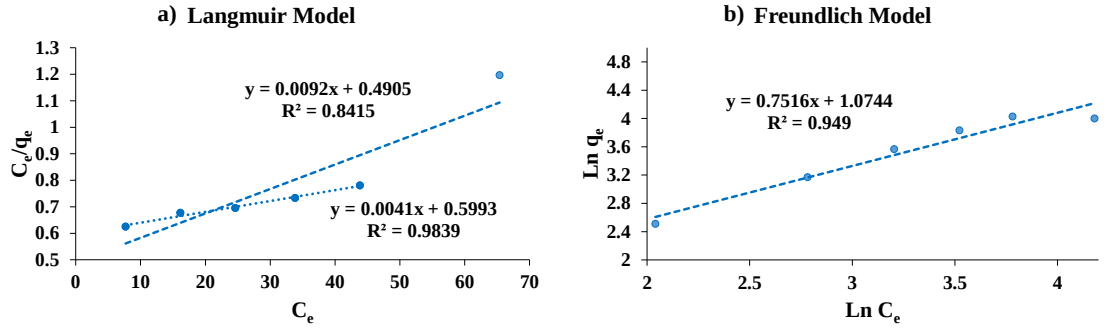

Figure 3. Curve fitting of various isotherm models for MO adsorption on $MgFe_2O_4$ surface: (a) Langmuir, (b) Freundlich models.

Conclusions

In the present study, two magnetic adsorbents Fe_3O_4 (synthesized by co-precipitation method) and $MgFe_2O_4$ (synthesized by combustion method) were investigated in the methyl orange adsorption process from aqueous solution. The results showed that the Fe_3O_4 sample had much better characteristic as an adsorbent. However, the use of the combustion method in the synthesis of the $MgFe_2O_4$ magnetic spinel resulted in larger pores in this sample, which could compensate its other bad properties for the simple diffusion of large molecules of MO into the

pores and quickly absorbed. The examination of the samples in the MO adsorption process confirmed the influence of the pore diameter on the adsorption so that the $MgFe_2O_4$ showed a higher adsorption capacity than the Fe_3O_4. Investigation of the adsorption isotherms for the $MgFe_2O_4$ sample proved that the adsorption rate is not controlled by the entry of large MO molecules into the pores as well as by creating a boundary layer on the adsorbent surface. These studies showed that the adsorption step of MO on the $MgFe_2O_4$ controls the rate of adsorption. At the end of the studies, the $MgFe_2O_4$ sample can be suggested for the removal of dyes and water pollutants after further assessment, which performed in our future works.

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