

## Proficient Adsorption, Photodegradation and Sonodegradation of Methylene Blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene Nanocomposite

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### Abstract

In this research, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/Graphene materials were prepared and characterized via different techniques such as X-ray diffractometer (XRD), Vibrating Sample Magnetometer (VSM), and energy-dispersive X-ray spectroscopy (EDX). The efficiency of prepared samples were investigated by elimination of methylene blue as a cationic dye from aqueous solutions via different methods such as adsorption, photodegradation and sonodegradation processes. The results indicated that the degradation rate of methylene blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite under sonocatalytic process was considerably higher than the adsorption and photocatalytic procedures. Sonocatalytic degradation of methylene blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite could be explained by the mechanisms of hot spots and sonoluminescence. The degradation pathways between sonocatalytic oxidation and methylene blue solution was described. The results showed that the conjugate structure of *nitrogen-sulfur* heterocyclic material was broken and aromatic ring was oxidized to open the ring. Methylene blue molecules were finally mineralized to H<sub>2</sub>O and CO<sub>2</sub> in the sonocatalytic degradation process. Furthermore, the figures-of-merit based on electric energy consumption (electrical energy per order (EEO)) were estimated in the degradation of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite. The results showed that less energy is consumed during the sonodegradation of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite in comparison with photodegradation procedure.

### Keywords

Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite; Methylene blue; Sonocatalytic degradation; Electric energy consumption.

### 1. INTRODUCTION

Water pollution is known as one of the most important issues worldwide because of its harmful and dangerous impact on ecosystems and human health. Dye effluent, especially, has become an important source of water pollution and is very hard to degrade because of its high toxicity and carcinogenicity [1]. Although a wide range of dye molecules are available, methylene blue, is still widely applied in the chemical and medical industries. According to a very recent investigation, the level of this mutagenic and carcinogenic dye is high in wastewater [2]. Hence, it is necessary to address this problem caused via this toxic dye molecules. Up until now, many strategies have been reported to treatment the water, such as adsorption, flocculation, extraction, ultrafiltration/nanofiltration, bioremediation, electrochemical reduction, and advanced oxidation processes (AOPs) [3]. In recent years, advanced oxidation procedures (AOPs) are recognized as the most suitable methods for the treatment of water. Among different AOPs, photocatalysis and sonocatalysis by metal oxide nanoparticles have received much attention as efficient techniques for degradation of pollutants [4]. In the case of

photodegradation, radiation with photon energy more than the band gap of nanoparticles leads to the production of electron and hole pairs, which can help in the generation of highly reactive oxygen species that eventually participate in the degradation of pollutants [5]. It is well known that the limiting factor for catalytic degradation depends upon the ability to form high numbers of reactive oxygen species. Sonocatalytic degradation of pollutants is caused by a chemical influence of ultrasonic (US) waves which arises from acoustic cavitation, i.e., production, growth, and collapse of bubbles in a liquid [6]. The transient bubble collapse generates a localized hot spot with a very high temperature. Under such conditions, thermal degradation of water takes place, resulting in the generation of highly reactive radical species, which can oxidize and degrade organic pollutants in water [7]. Sonocatalytic technique, which is a combination of solid catalyst with ultrasonic has received the most attention overcoming obstacles. Besides, the sonocatalytic performance to decompose organic dyes can be increased due to a synergistic effect of ultrasonic radiation with a catalyst [8]. Furthermore, adsorption is one of the most effective treatment processes due to its

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simplicity and low cost. The important parameter in an adsorption procedure is to select an adsorbent with high capacity and fast kinetics for pollutant elimination from wastewater.

Iron-based heterogeneous catalyst compounds (e.g.,  $\text{Fe}_3\text{O}_4$ ) have attracted increasing attention due to their high natural abundance, low price, and they could easily inhibit secondary pollution through their recovery performance [9]. However,  $\text{Fe}_3\text{O}_4$  nanoparticles usually tend to aggregate in the solution, which may decline their surface area and cause lower stability and catalytic efficiency. Taking this into consideration, it is necessary to apply a proper support that can increase their overall performance [10]. Graphene has been widely reported to be an emerging supporting compound for metal oxides because of its unique structure, chemical stability, high specific surface area, and excellent charge carrier mobility [11]. The unique physical properties could be favored to separate electron-hole pairs and inhibit agglomeration that in turn leading to the increased catalytic activity. In 2020, Pervez et.al. reported that in the presence of  $\text{Fe}_3\text{O}_4$ @GO-activated persulfate system, the degradation efficiency of Rhodamine B (RhB) was significantly increased [12]. Gong et al. [13] prepared a solvothermal-based  $\text{Fe}_3\text{O}_4$ /GO nanocomposite with a persulfate activated system for the removal of methylene blue, but this method requires a higher temperature and more time, which limits its feasibility for further uses.

In recent decades, adsorption, photocatalysis and sonocatalysis methods are recognized as efficient techniques for degradation of pollutants. In order to determine if  $\text{Fe}_3\text{O}_4$ /Graphene nanocomposite can act as an efficient catalyst for degradation of methylene blue, the present research focuses on the investigation and comparison of methylene blue degrading in the different techniques such as adsorption, photocatalytic, and sonocatalytic procedures. The aim of the present work was to prepare  $\text{Fe}_3\text{O}_4$ /Graphene nanocomposite and investigate its adsorption property and catalytic activity for degradation of methylene blue. To find out which energy source is better in terms of the synergistic effect with  $\text{Fe}_3\text{O}_4$ /Graphene nanocomposite for degradation of methylene blue, UV-A light and US waves were applied as sources of energy. In addition, the degradation mechanism of methylene blue on  $\text{Fe}_3\text{O}_4$ /Graphene nanocomposite was discussed. The proposed mechanism of methylene blue sonodegradation involves the sonochemical oxidation of methylene blue via OH. in solution and methylene blue oxidation at the surface of  $\text{Fe}_3\text{O}_4$ /Graphene nanocomposite in the presence of  $\text{O}_2$  activated by the cavitation event. Furthermore, electrical energy consumption and treatment cost are estimated

during methylene blue degradation because the most important factor in selecting a waste treatment process is economics.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Ferrous sulfate hexahydrate ( $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ ), ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ammonium hydroxide (28% v/v,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), graphite powder (purity 99.999%), potassium permanganate, sodium nitrate, sulfuric acid, hydrogen peroxide and methylene blue were purchased from Merck Co (Germany) and used without further purification.

### 2.2. Preparation of $\text{Fe}_3\text{O}_4$ nanoparticles

0.02 mol  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  and 0.02 mol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in a 0.01 M aqueous solution of HCl (100 mL) under vigorous mechanical stirring to form a homogeneous solution. The resulting yellow solution was then added to a 3 M aqueous solution of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (80 mL), and the reaction mixture was heated at 75 °C for 4 h. Then, the synthesized particles were washed with distilled water, separated with the help of a strong magnet, and dried under air at 60 °C for 12 h.

### 2.3. Preparation of graphene oxide

Graphene oxide was synthesized from graphite powder by using the modified Hummer's method. First, 2 g graphite was reacted with a solution of 1 g sodium nitrate and 50 mL concentrated  $\text{H}_2\text{SO}_4$ . The temperature was kept below 5 °C after stirring the mixture for 5 min. To inhibit any sudden enhancement in temperature, potassium permanganate (7 g) was gradually added under constant stirring for 30 min. When the reaction was completed, it was treated with  $\text{H}_2\text{O}_2$  (7 g) under magnetic stirring for 2 h. The mixture was heated to 40 °C and stirred for 24 h. The reaction system was cooled and transferred into an iced solution (400 mL) containing 30% hydrogen peroxide (3 mL), which was the graphene oxide gel. The gel was stratified after 48 h of precipitation. The supernatant was discarded. The remaining solid was washed with deionized water repeatedly and saved as the graphene oxide solution for further investigation.

### 2.4. Homogeneous synthesis of the $\text{Fe}_3\text{O}_4$ /Graphene nanocomposite

The mixture was generated via adding 0.016 g of  $\text{Fe}_3\text{O}_4$  nanoparticles into 1.139 g graphene oxide solution with the concentration of 1 mg/mL. After sonicating the mixture (1 g) for 20 min, it was heated to 90 °C and maintained at this temperature for 6 h under magnetic stirring. The solution washed with ethanol and water repeatedly. After drying at 60 °C overnight, the sample was

separated with a magnet and calcined for 2 h at 700 °C.

### 2.5. Characterization of prepared samples

The crystal phase composition and the size of prepared nanocomposite was recorded via X-ray diffraction (XRD) (Siemens/D5000) with Cu K $\alpha$  radiation (0.15478 nm) in the 2 $\theta$  scan range of 10°–70°. Magnetic properties of the nanocomposite were investigated via the vibrating sample magnetometer (VSM), quantum design, 14 T PPMS. The chemical composition of the prepared sample was analyzed by an energy-dispersive X-ray spectroscopy (EDX) system.

### 2.6. Studies and analysis

The catalytic activity of synthesized materials was studied in the degradation of model compound methylene blue. The photocatalytic degradation of methylene blue was measured at ambient pressure and room temperature in a batch quartz reactor. Artificial radiation was provided via 36 W (UV-A) mercury lamp (Philips, Holland) with a wavelength peak at 365 nm positioned above the photoreactor. In each run, 400 mg L<sup>-1</sup> prepared sample and 20 mg L<sup>-1</sup> methylene blue were fed into the batch quartz reactor and placed in the dark condition for 30 min with continuous stirring for adsorption–desorption equilibrium and then exposed to black-light radiation. The zero time reading was obtained from blank solution kept in the dark. The photocatalytic reaction was then started via radiating the suspension with black light. Every 5 min as interval time, 5 mL of pollutant suspension was withdrawn and centrifuged to remove catalyst particles. The concentration of remaining methylene blue was determined by UV–Vis Perkin–Elmer 550 SE spectrophotometer at the wavelength of 668 nm. Experimental set-up for the sonodegradation of methylene blue via Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was similar to that of the photocatalytic degradation of methylene blue. The set-up was exposed to sonication at ultrasonic power of 300 W. However, for the batch adsorptive removal of methylene blue via Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite without light radiation, the setup was placed inside a fully covered box in order to inhibit any exposure toward light radiation.

Pseudo-first order kinetics can be used to explain the kinetic of the degradation rate of most organic pollutants [14].

$$\frac{-dC}{dt} = k_{obs} C \quad (1)$$

In this equation,  $k_{obs}$  is the apparent rate constant which affected by pollutant concentration. The following equation will be obtained via the integrating of this equation (with the same restriction of  $C = C_0$  at  $t = 0$ ):

$$\ln \frac{C_0}{C_t} = k_{obs} t \quad (2)$$

$k_{obs}$  can be estimated from the plot of  $\ln(C_0/C_t)$  versus  $t$ . The slope of this plot is equal to  $k_{obs}$ .

## 3. RESULTS AND DISCUSSION

### 3.1. XRD Analysis of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite

The XRD pattern of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite is shown in the Fig. 1. The peaks at 2 $\theta$  values of 30.3°, 35.2°, 43.4°, 53.8°, 57.5° and 62.6° are indexed as the diffractions of (220), (311), (222), (422), (511) and (440) respectively, which resembles the standard diffraction spectrum of Fe<sub>3</sub>O<sub>4</sub> (JCPDSPDF#19-0629) with respect to its reflection peaks positions. These peaks demonstrated a strong and narrow shape, indicative of a higher crystalline nature. However, it could be seen that the diffraction peak of Graphene was absent in the Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite; the reason may be that the crystalline structures of Graphene were modified through the intercalation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the Graphene layers during preparation. The result is in accordance with the result of Xu et.al [15].

The X-Ray diffraction is not only applied for detecting the crystallographic identity of the materials phase purity, but it may be applied to quantify the proportion of crystallite size produced. The crystallite size of synthesized sample, according to the FWHM of the (311) plane reflection peak, was estimated via the Debye-Scherrer formula through equation :

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

Where  $K$  is the shape factor,  $\lambda$  is the X-ray wavelength (0.154 nm),  $\beta$  is the line broadening at half the maximum intensity (FWHM) in radian, and  $\theta$  is the Bragg angle [16].  $D$  (in nm) is the mean size of the ordered (crystalline) domains that may be smaller or equal to the grain size. The crystallite size thus obtained from this equation was found to be about 14.9 nm.

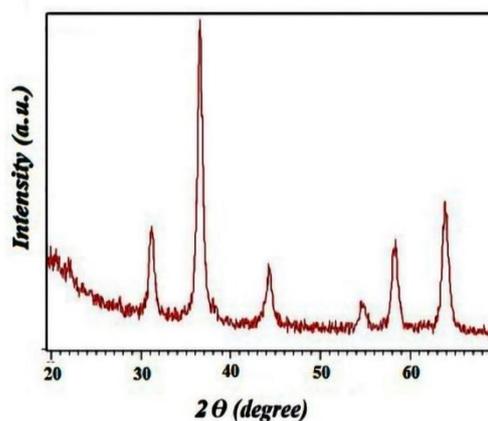
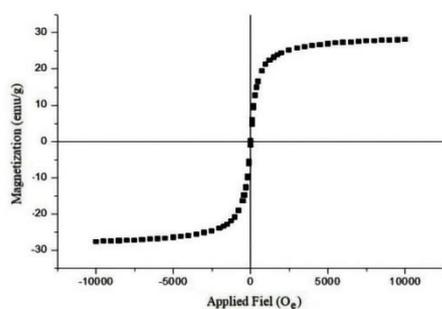


Fig. 1. XRD pattern of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite.

### 3.2. Vibrating Sample Magnetometer (VSM) Analysis

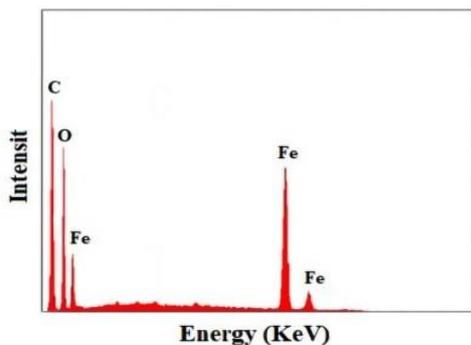
The magnetic properties of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite were studied via a vibrating sample magnetometer at room temperature, and the magnetization curves of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was shown in Fig 2. The roughly coincident hysteresis curves show that Fe<sub>3</sub>O<sub>4</sub>/Graphene is a super paramagnetic material. The saturation magnetization value of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was calculated as 28.1 emu.g<sup>-1</sup> from the magnetization curves. This magnetic property is high enough that Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite can be separated from the solution by an external magnet and redistributed into the solution after the magnetic field is disconnected. This will be an advantage for the separation, recovery, and reuse of the catalyst.



**Fig. 2.** Magnetization vs. applied magnetic field for Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite.

### 3.3. Elemental analysis with EDX spectroscopy

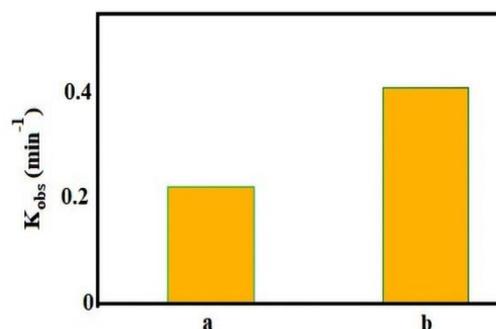
The chemical composition of the prepared Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was assessed by EDX spectroscopy. The corresponding spectrum are displayed in Fig. 3. C, O, and Fe peaks can be clearly seen from this Figure. The prepared Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was found to be free from additional elemental impurities, indicating that high purity nanocomposite was obtained through this synthesis method. Our results are in agreement with those of other authors [17].



**Fig. 3.** EDX pattern of Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide nanocomposite.

### 3.4. Adsorption of methylene blue via Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite

Since methylene blue is inevitably adsorbed upon the negatively charged Fe<sub>3</sub>O<sub>4</sub>/Graphene surface during the photodegradation and sonodegradation procedures, we first studied the adsorption behaviors with respect to methylene blue upon Fe<sub>3</sub>O<sub>4</sub>/Graphene without ultrasonication. The spectrum of blank sample that contain individual methylene blue dye shows absorption peak in the visible region located at wavelength of 668 nm. Fig. 4 demonstrates the adsorptive removal of methylene blue from aqueous solution using Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/Graphene materials. It could be observed that Fe<sub>3</sub>O<sub>4</sub>/Graphene showed excellent performance for methylene blue. Accumulation of a matter between the liquid–solid interface or gas–solid interface due to physical or chemical associations is called an adsorption process. Adsorption procedure can be controlled by physical factors on most of the adsorbents such as polarity, Van der Waals forces, H-bonding, dipole–dipole interaction,  $\pi$ – $\pi$  interaction, etc. [18]. The design of an adsorbent usually depends on the type of matter to be adsorbed or removed. Methylene blue is a cationic dye that can be eliminated via an adsorbent showing strong affinity toward positively charged molecules. Due to the dissociation of carboxyl groups, Graphene-based catalyst was negatively charged and demonstrated strong electrostatic interactions to positively charged species [19]. Based on results, the presence of Graphene in synthesized nanocomposite plays a crucial role in the degradation of cationic dyes. Almost similar type of discussion has been reported by Seo. et al [20].

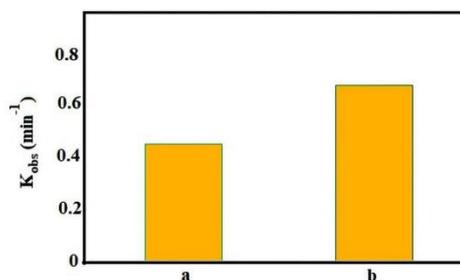
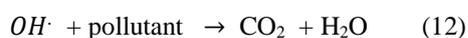
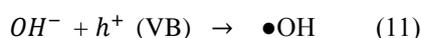
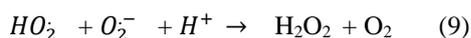
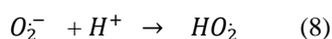
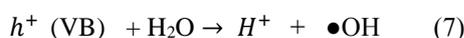
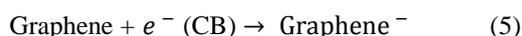
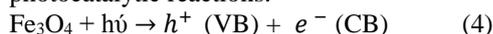


**Fig. 4.** Adsorptive removal of methylene blue from aqueous solution in the presence of (a) Fe<sub>3</sub>O<sub>4</sub>, and (b)

### 3.5. Photocatalytic activity

The efficiency of the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles and Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite towards the photocatalytic degradation of methylene blue was assessed in aqueous conditions against black light. Fig. 5 demonstrates the photocatalytic removal of methylene blue from aqueous solution using Fe<sub>3</sub>O<sub>4</sub>

and Fe<sub>3</sub>O<sub>4</sub>/Graphene materials. It is obvious from the results that the intensity of the absorption peak of methylene blue declined upon enhancing radiation time. The prepared Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was found to be more efficient at degrading completely tested dye compared to Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Pleguezuelos et al. studied dye sensitized degradation which follows the radical mechanism [21]. It is possible that Fe<sub>3</sub>O<sub>4</sub> decorated on both sides of Graphene sheets may have enhanced their specific surface area, which resulted in increased degradation of methylene blue molecules. Furthermore, OH radicals generated during the reaction may have positively influenced the degradation procedure. The negatively charged surface of Fe<sub>3</sub>O<sub>4</sub>/Graphene can show strong electrostatic interactions to positively charged dye molecules. The high photocatalytic activity can be related to the conductive bonding of Fe<sub>3</sub>O<sub>4</sub> on the Graphene, which may lower the recombination of photocreated electron–gap pairs. This mechanism can be responsible for the increased removal efficiency of Fe<sub>3</sub>O<sub>4</sub>/Graphene compared to Fe<sub>3</sub>O<sub>4</sub>. During the photocatalytic procedure, the pollutant was transformed into reactive, unstable intermediates and mineralized to color less materials. Electron–hole pairs in the excited Fe<sub>3</sub>O<sub>4</sub> could be efficiently detached to enable an effective change into photoinduced electrons from Graphene sheet to Fe<sub>3</sub>O<sub>4</sub>. This essential electron transfer mechanism can play a major role in the removal of methylene blue [22]. As a result, the increased photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>/Graphene could play a critical role to solve pollutant related environmental problems. The following mechanism would be proffered for the photocatalytic reactions.



**Fig. 5.** Photocatalytic removal of methylene blue from aqueous solution in the presence of (a) Fe<sub>3</sub>O<sub>4</sub>, and (b) Fe<sub>3</sub>O<sub>4</sub>/Graphene samples.

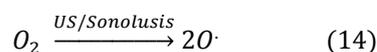
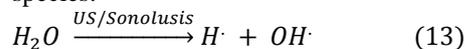
Similarly, Reszczy et al. affirmed that methylene blue was degraded into small intermediate products initially rather than directly into CO<sub>2</sub> and H<sub>2</sub>O [23].

### 3.6. Sonocatalytic removal of methylene blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene

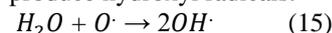
The performance of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/Graphene sonocatalysts were compared in the removal of methylene blue. From the findings presented in Fig. 6, it can be observed that the degradation rate of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene is much more than Fe<sub>3</sub>O<sub>4</sub> which represent more activity under ultrasonic illumination. In fact, the large surface area of Graphene has led to the more dispersion of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in it and hence enhancing absorption of ultrasonic illumination, which makes more electron-hole pairs for methylene blue removal [24].

Also, the fast removal of methylene blue by sonocatalytic process in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene sonocatalyst is related to the sonoluminescence mechanism. Sonoluminescence involves an intense UV-light, which promotes Fe<sub>3</sub>O<sub>4</sub>/Graphene to act as an efficient photocatalyst during ultrasonic irradiation [25]. The sonodegradation mechanism of methylene blue on Fe<sub>3</sub>O<sub>4</sub>/Graphene sonocatalyst can be explained as follows:

The chemical influences of ultrasound are due to the phenomenon of cavitation which is the nucleation, growth, and collapse of bubbles in a liquid. The collapse of the bubbles induces high-energy phenomena, i.e., high temperature and pressure (~5000 K and 500 bars), electrical discharges, and plasma influences. The consequences of these extreme conditions are the direct thermal dissociation (sonolysis) of dissolved O<sub>2</sub> and H<sub>2</sub>O molecules into highly reactive radical species:

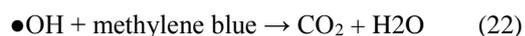
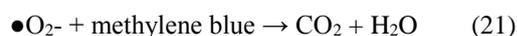
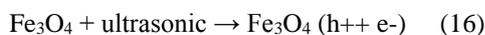


These oxygen radicals may react with H<sub>2</sub>O to produce hydroxyl radicals:



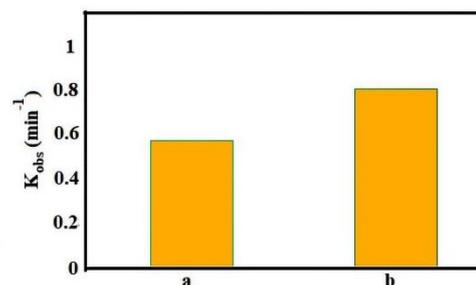
It is well known that sonochemistry also includes the emission of light energy for a short period of time. The radiation can lead to the photoexcitation of electrons from the valence band to the conduction band, thus leading to the production of electron-hole pairs in a similar manner as described above for the photocatalysis [26]. Hydroxyl radicals with high oxidizing activity can more react with pollutant and degrade it into small species.

As exhibited in Equations (13-19), the sonocatalytic degradation of methylene blue by ultrasonic illumination began with excitation of Fe<sub>3</sub>O<sub>4</sub> and formation of electron-hole pairs. High oxidation valence-band holes can oxidize methylene blue molecules. Water degradation or reaction of h<sup>+</sup> with H<sub>2</sub>O can produce hydroxyl radicals. Meanwhile, the reaction between conduction-band electrons (e<sup>-</sup>) and proper electron acceptors (such as O<sub>2</sub>) yielded oxidative radicals. The produced hydroxyl radicals can easily degraded methylene blue molecules [24]. On the other hand, •O<sub>2</sub><sup>-</sup> and •OH play a key role in the degradation procedure of methylene blue by ultrasonic technique. Fig7, shows a proposed mechanism for the sonodegradation process of Fe<sub>3</sub>O<sub>4</sub>/Graphene for methylene blue dye.

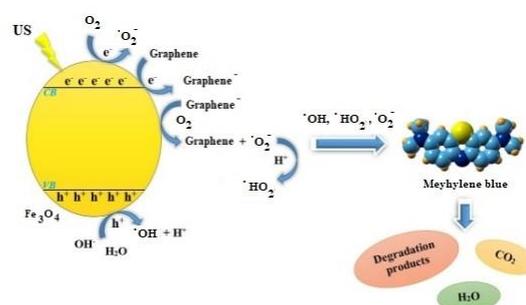


Mohammadi et al. [27] showed that the existence of heterogeneous catalysts in the ultrasonic system can enhance the oxidizing procedure. The presence of heterogeneous catalyst can provide additional cores which increase the rate of generation of cavitation bubbles, which subsequently improve

the production of •OH via growing the pyrolysis degree of H<sub>2</sub>O.



**Fig. 6.** Sonocatalytic removal of methylene blue from aqueous solution in the presence of (a) Fe<sub>3</sub>O<sub>4</sub>, and (b) Fe<sub>3</sub>O<sub>4</sub>/Graphene samples.



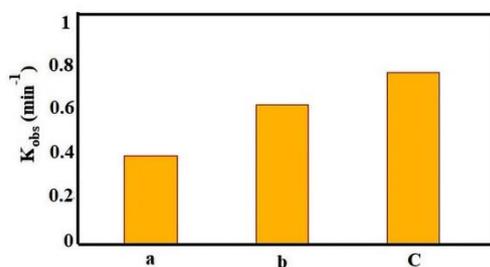
**Fig. 7.** Proposed sonodegradation mechanism for methylene blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite.

### 3.7. Comparison of adsorption, photodegradation and sonodegradation of methylene blue using Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite

The degradation rate of methylene blue by adsorption, photolysis and sonolysis procedures in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite is depicted in Fig 8. The results indicated that the degradation rate of methylene blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite under photocatalytic process was considerably higher than the adsorption procedure, indicating that the synergistic adsorption-photocatalysis had definitely occurred. This observation clearly demonstrated that during the degradation of methylene blue by Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite under light radiation, both adsorption and photocatalytic processes occurred simultaneously. During the experiment in the dark, the degradation rate of methylene blue by the adsorption process was estimated to be 0.41 min<sup>-1</sup>. However, when Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was exposed to light radiation, the the degradation rate of methylene blue jumped to 0.62 min<sup>-1</sup> indicating that both photocatalytic and adsorption processes manifested simultaneously

Also, the degradation rate of methylene blue by photolysis and sonolysis procedures in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite is shown in Fig7. It can be observed that

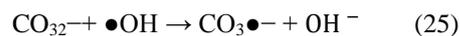
sonodegradation rate is higher than photodegradation rate. US radiation is a better source than UV-visible radiation for the removal of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite. Fe<sub>3</sub>O<sub>4</sub> nanoparticles have a lower band gap (2.2 eV). Therefore, electron-hole recombination is faster and easier [28]. So, the production of hydroxyl radicals is hard, which results in lower degradation of methylene blue in the case of photocatalysis. In the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite, the sonodegradation rate of methylene blue was increased. This is due to synergistic effects of ultrasound and solid catalyst, namely [29], (i) added compounds could provide additional nuclei for cavitation bubble production, (ii) US radiation enhances the mass transfer of methylene blue between the liquid phase and Fe<sub>3</sub>O<sub>4</sub>/Graphene surface, (iii) US radiation increases the active surface area due to ultrasound disaggregating, and (iv) the catalyst can be promoted by ultrasound-induced luminescence which has a wide wavelength. This phenomenon can increase the generation of hydroxyl radicals in the reaction mixture [30]. Therefore, sonocatalysis can enhance the removal rate of dyes.



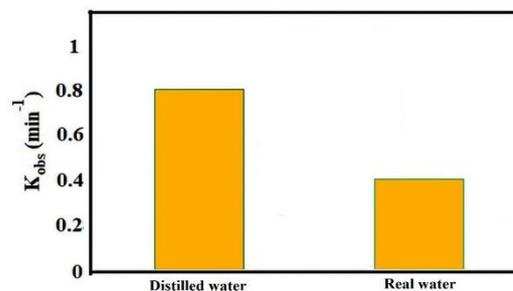
**Fig. 8.** Degradation rates of methylene blue under (a) Adsorption process, (b) UV-visible radiation, and (c) US radiation.

### 3.8. Treatment of Real Water Containing methylene blue

In order to investigate the efficiency of Fe<sub>3</sub>O<sub>4</sub>/Graphene in ultrasonic degradation of methylene blue in the real water, 20 mg L<sup>-1</sup> of methylene blue was added into a real water sample (carbonate hardness: 94 mg L<sup>-1</sup> CaCO<sub>3</sub>, sulphate concentration: 175.1 mg L<sup>-1</sup> SO<sub>4</sub><sup>2-</sup>) that was obtained from an irrigation well in Tabriz, Iran. Results in Figure 9 show the influence of presence of common anions such as sulphate, carbonate, and bicarbonate on the removal of methylene blue. It is clear from that, in presence of SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, the percent of removal decreases. This inhibition is undoubtedly due to their ability to act as hydroxyl radical's scavengers via the following reactions:



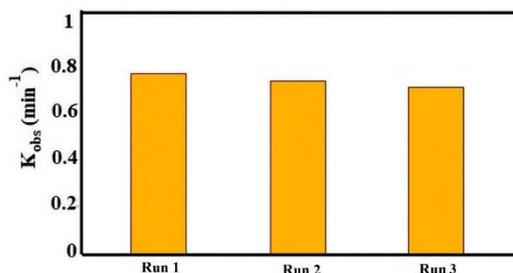
These ions can also block the active sites on the Fe<sub>3</sub>O<sub>4</sub>/Graphene surface thus deactivating the catalysts towards dye and intermediate molecules. Although the produced radical anions have been shown to be an oxidant itself, but its oxidation potential is less than that of •OH. The present result was justified according to the previous work of Xiao et al. [31]. In the AOP system, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> were used as a radical scavenger, hence these ions were involved with methylene blue molecules for quenching with reactive radicals, such as •OH, and generated SO<sub>4</sub><sup>•-</sup>, and CO<sub>3</sub><sup>•-</sup> radicals with a lower redox potential than •OH. This result is supported by the previous investigation by Bendjama et al. [32].



**Fig. 9.** Investigation of the efficiency of Fe<sub>3</sub>O<sub>4</sub>/Graphene in the removal of methylene blue from real water.

### 3.9. Catalyst reusability

As an economical perspective and green chemistry, the reusability of as-prepared Fe<sub>3</sub>O<sub>4</sub>/Graphene catalyst was investigated under the optimized reaction conditions of methylene blue sonodegradation. The catalyst was recovered by magnetic separation and washed with acetone and deionized water several times and dried at 600 °C for 8 h. The dried solid was used for future reactions. The recycled sample were applied under the same reaction conditions. From Fig10, a negligible decrease in sonodegradation efficiency was observed due to the loss of catalyst during the recycling procedure [33]. Then, the as-prepared Fe<sub>3</sub>O<sub>4</sub>/Graphene was proposed as an efficient catalyst for the removal of methylene blue with high stability and reusability.



**Fig. 10.** The reusability of Fe<sub>3</sub>O<sub>4</sub>/Graphene catalyst for removal of methylene blue.

Kara et.al. [34] prepared magnetite/nickel oxide mixed metal oxide composite (FNMMO) and applied it as an adsorbent to dispose of dye wastewater. They found that this composite can be reused for three times and no significant change was observed in its adsorption activity. However, a study focused on the degradation of methylene blue by Fe-Co bimetallic catalyst exhibited a behavior different from this trend. The cyclic test showed that the FBC- synthesized bimetallic catalyst is unstable and showed poor recyclability in the reaction system [35].

### 3.10. Electrical energy efficiency

Various factors, such as economics, regulations, effluent quality goals, and operation, are important in selecting a wastewater treatment procedure. Among these, economics has been considered as the most important parameter. In photocatalytic and sonocatalytic degradation processes, electric energy consumption is recognized as an important fraction of the operating costs. Therefore, simple figures of merit based on electric energy consumption are helpful and informative. The suitable figure of merit in the low dye concentration is the electrical energy per order (EEO). The following equations can be applied to estimate EEO (kWh/m<sup>3</sup> /order):

$$E_{E0} = \frac{P_{el} \times t \times 100}{V \times 60 \times \frac{C_0}{C}} \quad (26)$$

where P is the input power (kW) to the AOP system, t is the radiation time (min), V is the volume of water (l) in the reactor, C<sub>0</sub> and C are the initial and final dye concentrations, respectively [36]. This equation for a pseudo-first-order reaction in a batch reactor can be written as follows:

$$E_{E0} = \frac{P_{el} \times 38.4}{V \times K_{obs}} \quad (27)$$

In this equation, K<sub>obs</sub> is the pseudo-first-order reaction rate constant (min<sup>-1</sup>). The EEO quantities for photodegradation and sonodegradation of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite are 9.29 and 7.2 kWh/m<sup>3</sup>/order respectively. Sonocatalytic degradation of methylene blue requires less energy consumption in comparison with other processes. In the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite, sonocatalytic degradation of methylene blue can be achieved with upper rate. So, EEO is decreased with K<sub>obs</sub> increasing [37]. It can be seen clear from this table that EEO value for the sonodegradation of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite is less than that of photodegradation process. EEO is an important parameter in view of the evaluation of the treatment costs. By considering 0.045 US \$ per kW per h as the cost of electricity in Iran, the

contribution to operation costs of photodegradation and sonodegradation of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite will be 0.42 and 0.31 US \$ per m<sup>3</sup>, respectively. Thus, sonodegradation is more economical, due to decrease in energy required.

## 4. CONCLUSION

The present study was carried out to synthesize and investigate the efficiency of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite to adsorb, photodegrade and sonodegrade a cationic dye (methylene blue). The results of the XRD, VSM, and EDX analyses showed that the synthesis of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was carried out successfully. The synergistic effect of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite and sonocatalysis has been showed to be more effective in degrading methylene blue as compared to Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite and adsorption or photocatalysis processes. Sonocatalytic degradation of methylene blue in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite could be described by the mechanisms of hot spots and sonoluminescence. The sonodegradation mechanism of methylene blue via Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite was described. Based on results, the degradation efficiency significantly decreased in the presence of different anions such as sulfate, carbonate, and bicarbonate, confirming the role of % OH radicals in the sonodegradation process. Also, the cyclic test showed that Fe<sub>3</sub>O<sub>4</sub>/Graphene nanocomposite is stable and showed high recyclability in the reaction system. Thus, the present investigation provides an efficient, stable, economical and environmentally friendly adsorbent with potential for particle application in the treatment of dye water. The electrical energy consumption per order of magnitude for sonodegradation of methylene blue was lower than that of adsorption or photodegradation processes.

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## جذب سطحی، تخریب فتوکاتالیزوری و سونوکاتالیزوری متیلن بلو با استفاده از نانوکامپوزیت $\text{Fe}_3\text{O}_4/\text{Graphene}$

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### چکیده

در این تحقیق ترکیبات  $\text{Fe}_3\text{O}_4$  و  $\text{Fe}_3\text{O}_4/\text{Graphene}$  تهیه و با استفاده از تکنیک‌های مختلف نظیر پراش اشعه ایکس ( $XRD$ )، مغناطیس سنج ارتعاشی ( $VSM$ ) و طیف سنجی پراش انرژی پرتو ایکس ( $EDX$ ) شناسایی شدند. کارایی نمونه‌های تهیه شده در حذف متیلن بلو به عنوان یک رنگ کاتیونی از محلول‌های آبی با استفاده از روش‌های مختلف نظیر جذب سطحی، فرایندهای تخریب فتوکاتالیزوری و سونوکاتالیزوری مورد بررسی قرار گرفت. نتایج نشان داد سرعت تخریب متیلن بلو با استفاده از نانوکامپوزیت  $\text{Fe}_3\text{O}_4/\text{Graphene}$  تحت فرایند سونوکاتالیزوری بیشتر از فرایندهای جذب سطحی و تخریب فتوکاتالیزوری است. تخریب سونوکاتالیزوری متیلن بلو با استفاده از نانوکامپوزیت  $\text{Fe}_3\text{O}_4/\text{Graphene}$  از طریق مکانیسم‌های نقاط داغ و لومینسانس قابل توجه است. گذرگاه‌های تخریب بین اکسایش سونوکاتالیزوری و محلول متیلن بلو توضیح داده شد. نتایج نشان داد ساختار کنژوگه ترکیب هتروسیکل نیترژن-سولفور شکسته شده و حلقه آروماتیک اکسید شده و به حلقه باز تبدیل می‌شود. در نهایت، معدنی شدن کامل مولکول‌های متیلن بلو طی فرایند تخریب سونوکاتالیزوری رخ می‌دهد. همچنین رقم‌های شایستگی برای انرژی الکتریکی به ازای هر مرتبه ( $EEO$ ) در تخریب متیلن بلو در حضور  $\text{Fe}_3\text{O}_4/\text{Graphene}$  تخمین زده شد. نتایج نشان داد در تخریب سونوکاتالیزوری متیلن بلو با استفاده از نانوکامپوزیت  $\text{Fe}_3\text{O}_4/\text{Graphene}$ ، در مقایسه با تخریب فتوکاتالیزوری انرژی کمتری مصرف می‌شود.

### کلید واژه‌ها

نانوکامپوزیت؛ متیلن بلو؛ تخریب سونوکاتالیزوری؛ مصرف انرژی الکتریکی؛  $\text{Fe}_3\text{O}_4/\text{Graphene}$