Mo-goethite as new composite for the degradation of methylene blue from the water with H_2O_2

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ABSTRACT

In this study, a new structure of molybdenum (Mo) doped goethite (Mo-goethite) was synthesized by the precipitation method. Next, the morphology of the Mo-goethite surface was characterized by scanning electron microscopy, the energy-dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy, which indicates the presence of Mo in the structure. Moreover, X-ray diffraction indicated the structure and the particle diameter, which was estimated at 20 nm at 35° by Scherrer equation. The catalytic activity of Mo-goethite structure was investigated in methylene blue (MB) degradation in the presence of hydrogen peroxide. The factors studied in the evaluation of MB degradation using the catalyst include Mo/goethite molar ratio, initial H_2O_2 concentration, initial pH, and Mo-goethite dosage. The results indicate that the catalyst (Mo-goethite) has a high ability to degradation of MB in the presence of H_2O_2 in a short time. The results show that the optimum conditions for 20 mg L⁻¹ MB solution were pH = 7, 0.1 g L⁻¹ of Mo-goethite, and 21.2 mM of H_2O_2 in 30 min.

Keywords: Degradation; Goethite; Mo-goethite; H_2O_2; Removal

1. Introduction

In recent years, due to the abundant production and the high use of dyes in modern industries, the issue of contaminating drinking water with these products has been the subject of intense research [1]. Many of these dyes are considered aquatic ecosystems and humans and are a very serious threat due to their toxicity and carcinogenicity and non-biodegradability [2,3]. Therefore, the development of new technology for removing dyes from wastewater is very important. In this regard, the advanced oxidation processes (AOPs) are among the attractive methods for removing dyes from wastewater [4]. Using a wide range of pH and the loss of the reduced catalyst are two major advantages of the AOPs or the heterogeneous Fenton-like processes. Metal nanoparticles are widely used as catalysts owing to their special properties,

such as volume-to-surface. For example, the iron-based heterogeneous nanoparticles are used as Fenton-like catalysts, mainly because of their low toxicity and low cost [5].

Goethite (a-FeOOH) is one of the compounds with an iron oxide structure that is used as an adsorbent in many toxic anions and cations caused by chemical reaction and also as a catalyst for the degradation of dyes because of its special structure [6]. Consequently, many of the recent researches have focused on the modification of iron oxide's structure to improve their performances over several applications. Therefore, several recent studies have been conducted on the adsorption capacity of iron oxides in the presence of iron oxide in various compounds such as silicon, alumina, activated carbon, and clays [7–10].

Modifying the surface of iron oxide structures by the transition metals has been of great interest to the researchers [11–13]. So, incorporation of foreign di-, tri-, and metal species as Al, V, Cu, Co, Cr, Ni, Pb, Mn, and Cd in the structures

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of goethite through isomorphous substitution can modify their properties such as crystal size, morphology, stability, and dissolution behavior [14–20]. Especially in the Fenton process, the •OH radicals are produced from the decomposition of H_2O_2, which has a high ability to oxidize organic compounds in water [21]. The decomposition of hydrogen peroxide and the production of low hydroxyl radicals are due to the low efficiency of Fe(III)/Fe(II) cycle reaction. Hence, considering the high need for Fe(II) and H_2O_2 in the generation of hydroxyl radicals (•OH) [22], the use of second metal along with iron is very much considered [5,23]. Mo is used as a co-catalyst for Fe(II) to facilitate the conversion of Fe(III) to Fe(II) due to the presence of Mo(IV) in the structure, which significantly improves the decomposition efficiency of H_2O_2. In the present study, the structure of Mo-goethite is introduced as a Fenton-like catalyst with a high potential for methylene blue (MB) degradation. The morphological and structural of the Mo-goethite were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), mapping, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). Next, the effects of different factors, including Mo/goethite molar ratio, initial H_2O_2 concentration, pH solution, and Mo-goethite dosage on the removal of MB were investigated. Regarding the excellent oxidation, high efficiency, low toxicity, low cost, and strong practicality, the Mo-goethite catalytic Fenton system is can be applied in the real wastewater disinfection.

2. Experimental setup

2.1. Materials

Fe(NO$_3$)$_3$·9H$_2$O 99%), sodium hydroxide 99.99%. And also other materials such as MB, hydrochloric acid, nitric acid and hydrogen peroxide (H_2O_2) were bought from Merck Company (Germany).

2.2. Preparation of goethite and Mo-goethite

Pure goethite nanorods were synthesized based on previous methods [6]. Briefly, 10 mol L^{-1} NaOH was added dropwise to Fe(NO$_3$)$_3$·9H$_2$O (0.1 mol L^{-1}) solation until the pH 12. The resulting dark brownish suspension was placed into polyethylene bottles and aged at 60°C for 24 h. Then, filter the resulting product and rinse it with distilled water several times to remove nitrate, and the samples were dried in an air oven for 24 h at 100°C. The Mo-goethite nanoparticles were prepared by using an in situ molybdenum(IV) oxide solution during the precipitation process. Briefly, NaOH (10 mol L^{-1}) was added dropwise to a solution containing molybdenum(IV) oxide (0.1 mol L^{-1})/Fe(NO$_3$)$_3$·9H$_2$O (0.1 mol L^{-1}) with ratio 1/2 mL at pH 12. The suspension was put into polyethylene bottles and aged for 24 h at 60°C. After filtered and washed the aged suspensions, the samples were dried in an air oven for 24 h at 100°C [6].

2.3. Instruments

The UV/vis spectra were acquired by a Cary 100 UV-vis spectrometer (Varian, USA) at room temperature by a double beam. FT-IR spectra were measured on a PerkinElmer (USA) pressed into KBr pellets and is reported in wavenumbers

(cm^{-1}) and field emission scanning electron microscopy images were obtained using a HITACHI S-4160 (Japan). The crystal structures of the products were determined by X-ray diffraction PW3040/60 X'pert PRO (PANalytical, Netherlands) using CoKa radiation with l = 1.79 Å. Lattice parameters of all samples were calculated by refining the (h k l) values through Xpert Plus software. Typically, a scanning velocity of 1.5 min^{-1} was used to scan the peaks of the adsorbent diffraction pattern in the 2θ range between 5° and 80° and a Metrohm 692 pH meter (Herisau, Switzerland).

The degradation (removal %) of MB was calculated with the following equation.

$$\% \text{Removal MB} = \frac{\left(C_i - C_f\right)}{C_i} \times 100 \tag{1}$$

where C_i is initial concentration and C_f time-dependent concentration of MB.

2.4. Determination of the point of zero charge

The following procedure was determined for the point of zero charges (PZC) for the Mo-goethite: in briefly in Erlenmeyer flask, 50 mL of deionized water was added and capped with cotton than was heated until boiling for 20 min to eliminate the CO_2 dissolved in the water. After cooled water and capped, 0.5 g of Mo-goethite was added to 10 mL of CO_2-free water in a 25 mL Erlenmeyer flask. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25°C. Then the solution pH was measured and this value is the point of zero charges [24,25].

2.5. Catalytic performance tests

For the test, the Mo-goethite as a catalyst for degradation of MB, Erlenmeyer flask 50 mL was used with the shaker at a speed of 200 rpm at room temperature. First, predetermined amounts of hydrogen peroxide (30 wt.%) were added to 10 mL of MB solution (20 mg L^{-1}) in Erlenmeyer flask, and the pH of the solution was adjusted to the desired value by 0.1 M NaOH or HCl. Finally, 0.01 g of catalysts were added to the system above, and the degradation rate was evaluated using a spectrophotometer at different times up to 30 min.

3. Results and discussion

3.1. Characterization of goethite and Mo-goethite

In this study, goethite and Mo-goethite were synthesized as described in [6], with the 2:1 ratio of Fe(NO$_3$)$_3$·9H$_2$O/MoCl$_5$ at a pH of 12. Then, the structures were characterized using XRD, FT-IR, SEM, EDS, and mapping.

3.1.1. XRD analysis

Fig. 1 shows XRD patterns of pure goethite and Mo-goethite. The main diffraction peaks can be indexed to (1 2 0), (2 2 1), (1 1 1), (1 3 0), (1 4 0), (1 1 0), and (1 2 1) planes of a cubic unit cell, which correspond to a-FeOOH (JCPDS card no. 85-1326) [26]. The rest of the peaks are indexed to various low-intensity planes of goethite. As shown in Fig. 1a, the

goethite structure is seen in the studied samples. Compared to the XRD patterns of Mo-goethite, a series of peaks has been added to Fig. 1b, which indicates that the goethite structure is preserved and also the goethite structure is present in the samples. It is also possible to estimate the particle diameter at 35° for goethite and Mo-goethite at about 20 nm, respectively, with the Scherrer equation.

3.1.2. Fourier transform infrared spectroscopy

Fig. 2b presents the FT-IR spectrum of the samples. The peaks appear in the range of 890 to 790 cm⁻¹ are related to the Fe–O–H bending vibration. The spectrum associated with Fe–O is seen in the range of 620 to 475 cm⁻¹ [27]. There is a strong band in 1,365 cm⁻¹ that is due to the contamination of the goethite with CO_3^{-2} in the environment [28]. The purpose of the research was the synthesis of Mo-goethite as catalyst molybdenum alongside iron(II) ion with the preservation of the primary structure. For this purpose, the Mo-goethite spectrum shown in Fig. 2a was studied because of the similarity of its spectrum to that of the goethite spectrum (Fig. 2b).

The only difference is the peak area at 485 cm⁻¹ range (Fig. 2a), which is due to the presence of molybdenum that causes the Fe–O at 475 cm⁻¹ shift.
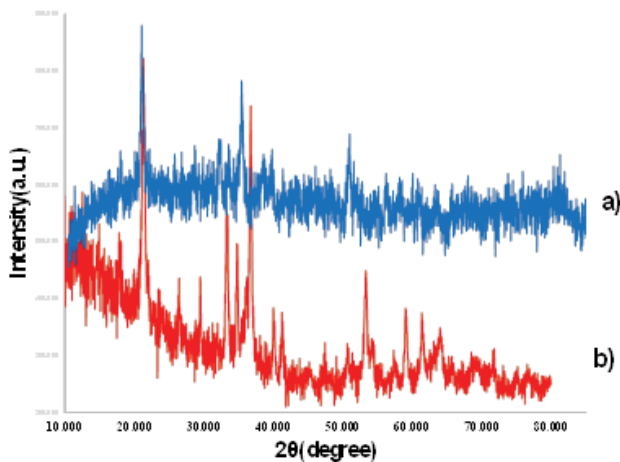
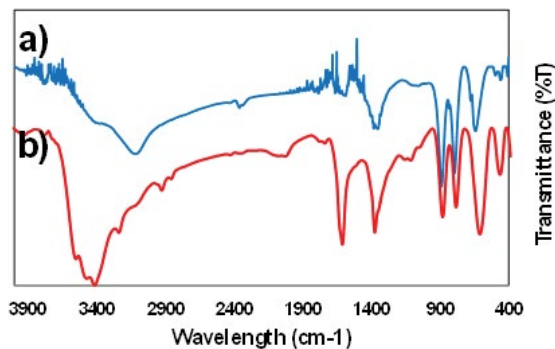

Fig. 1. XRD patterns of (a) Mo-goethite and (b) goethite.

Fig. 2. FT-IR spectrum of the (a) Mo-goethite and (b) goethite.

3.1.3. SEM and EDS-mapping analysis

The surface morphology of the Mo-goethite SEM was compared with goethite SEM. The points that can be seen belong to the structure of the Mo-goethite, which is in the form of a rod with an approximate diameter of 25 nm (Fig. 3b) that is similar to that of goethite (Fig. 3a). Next, the EDS and mapping analysis (Fig. 4) was used for illustrating Mo in the Mo-goethite structure. The EDS and mapping are powerful techniques for showing the presence of Mo in the structure. Therefore, the synthesis of the catalyst is concluded using various analyses. In the following, various catalytic parameters were investigated.

3.2. Study of catalyst performance

3.2.1. Investigation of the ratio from Mo to Fe

The ratio of the molybdenum/iron (in the synthesis of Mo-goethite) and its catalytic activity were investigated. As shown in Fig. 5, the degradation of the MB rate in the synthesis of the catalyst with the Fe/Mo molar ratio (2:1) is in the highest catalytic activity, and the efficiency of MB removal was 98.0% at 30 min. Afterward, the Mo-goethite as a catalyst with the iron to molybdenum ratio of 2:1 was selected.

3.2.2. MB removal in different systems

At a constant time, various systems containing sole H_2O_2, goethite, Mo-goethite, and goethite in the presence of H_2O_2, and Mo-goethite with H_2O_2 in the removal of MB were investigated. As shown in Fig. 6, the hydrogen peroxide system used alone and without a catalyst did not remove any MB. For the systems of goethite and Mo-goethite without H_2O_2, the degradation percentage of MB reached 20.22% and 30.5% after reaction for 30 min, respectively. The percentage of MB removal can be attributed to the absorption capacity of the two compounds (goethite and Mo-goethite). In comparison, for the systems of goethite/H_2O_2 and Mo-goethite/H_2O_2, the degradation percentage of MB reached 85.5% and 98.0% after 30 min, respectively. The catalytic performance of Mo-goethite/H_2O_2 was higher than that of goethite/H_2O_2. The explanation for this mechanism investigation is that the typical mechanism for the Fenton reaction is as the following equation:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + {}^{\bullet}OH \tag{2}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + H^+ + {}^{\bullet}O_2H \tag{3}$$
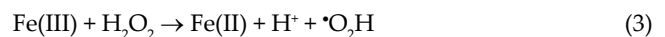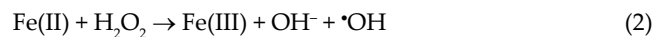
In the presence of Fe(II) as a catalyst, the H_2O_2 decomposes and to generates the $^{\bullet}OH$, which is at its highest efficiency (Eq. (2)). But, Eq. (3) shows a decrease in catalytic efficiency of conventional Fenton reaction. Therefore, the conditions that give rise to Eq. (2) increase the catalytic efficiency [29]. The key to improving the efficiency of the Fenton reaction is the conversion of Fe(II) to Fe(III), which greatly accelerates the decomposition of H_2O_2 for the generation of OH. Therefore, in the presence of Fe(III) and Mo^{4+} in goethite, Eqs. (4) and (5) will occur that causes Fe(III) convert to Fe(II). Therefore, the amount of Fe(II) is constantly existent, leading to an improvement in catalyst performance [23].
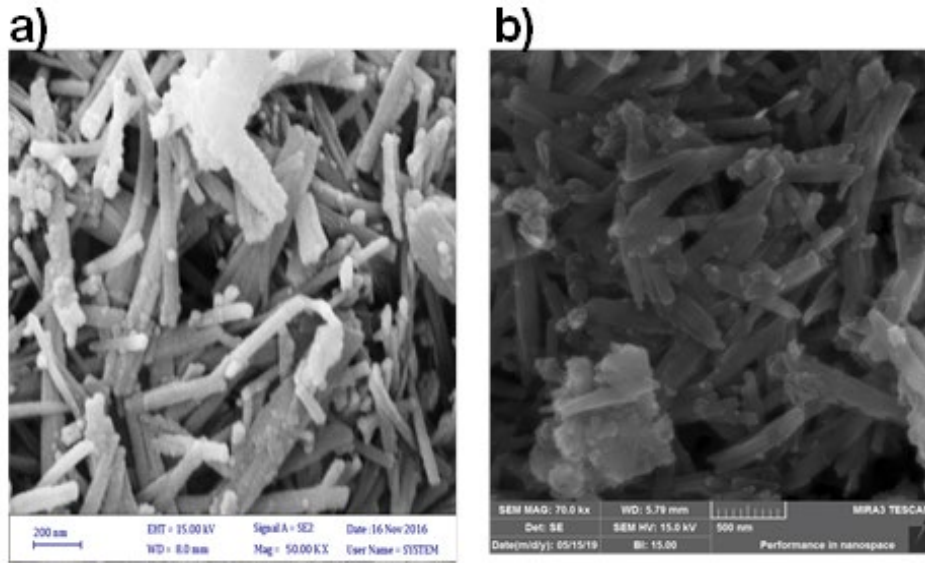
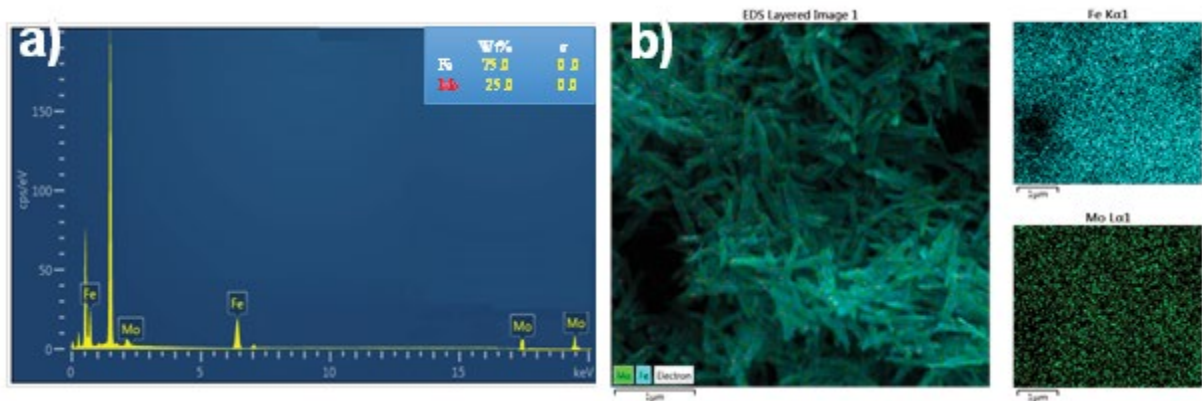Fig. 3. SEM images of (a) goethite and (b) Mo-goethite.

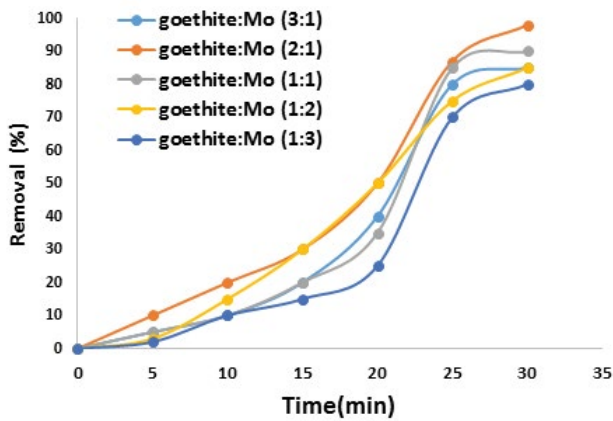Fig. 4. (a) EDS images of Mo-goethite and (b) mapping images of Mo-goethite.

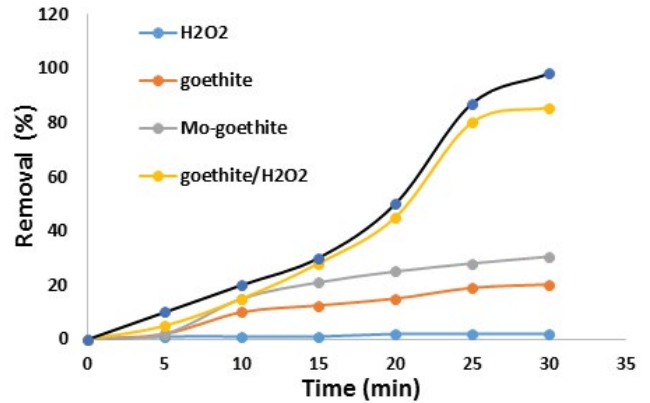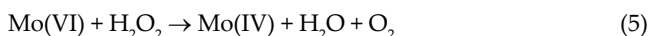Fig. 5. Effect of Fe/Mo molar ratios on the degradation of MB ([MB] = 20.0 mg L^{-1}, [H$_2$O$_2$] = 21.5 mM, Mo-goethite = 0.1 g mL^{-1}, and pH = 7.0).
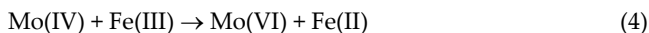

Fig. 6. Removal % of MB in different systems MB ([MB] = 20.0 mg L^{-1}, [H$_2$O$_2$] = 21.5 mM, Mo-goethite = 0.1 g mL^{-1} and pH = 7.0).

$$\text{Mo(IV)} + \text{Fe(III)} \rightarrow \text{Mo(VI)} + \text{Fe(II)} \tag{4}$$

$$\text{Mo(VI)} + \text{H}_2\text{O}_2 \rightarrow \text{Mo(IV)} + \text{H}_2\text{O} + \text{O}_2 \tag{5}$$

3.2.3. Effect of pH

The pH is one of the important parameters that affect the performance of the catalyst in the decolorization of dyes. Therefore, this effect in the degradation of MB in the presence of Mo-goethite and H_2O_2 is shown in Fig. 7. Based on this figure, the degradation efficiencies were strongly dependent on the pH. The MB removal rate is 30% within 30 min in pH 3.0. With increasing pH up to 7, this removal percentage also increases to 98.0%. Also, a further increase in pH to 9 resulted in a decrease in degradation efficiency to 95.0%. Therefore, pH 7 is the best condition for removing MB.

The point of zero charges (pH_{pzc}) value of Mo-goethite was determined to be 6.5. It can be deduced that the surface of the Mo-goethite was negatively charged at pH > 6.5 and positively charged at pH < 6.5. At low pH values, the electrostatic repulsion between cationic MB dye molecules and the positively charged Mo-goethite surface inhibits the adsorption of MB. Moreover, the surface of Mo-goethite was negatively charged at high pH values, which will facilitate the adsorption of MB.

Therefore, the degradation efficiency increased with the increase of pH_0 from 3.0 to 7.0. Also, it should be noted that the degradation rate decreased with increasing the pH_{pzc} from 7.0 to 9.0. The phenomenon can be explained by the fact that at alkaline condition, the oxidation potential of $^\bullet\text{OH}$ decreased and the production of OH on the surface of composite was restricted [4,30]. At pH_0 9.0, the degradation process has been limited by the relatively lower concentration of free radicals compared with pH_0 7.0, leading to a decrease in MB decolorization efficiencies.

3.2.4. Effect of H_2O_2 concentration

The effect of hydrogen peroxide on the degradation of the MB by Mo-goethite is one of the important parameters that have been studied. The results are reported in Fig. 8. As can be seen, in 30 min, approximately 30.5% of the MB
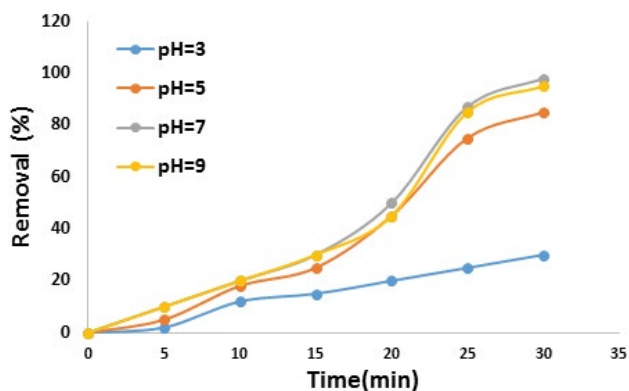

Fig. 7. Effect of initial pH on the degradation of MB ([MB] = 20.0 mg L⁻¹, [H_2O_2] = 21.5 mM, Mo-goethite = 0.1 g mL⁻¹, and pH = 7.0).
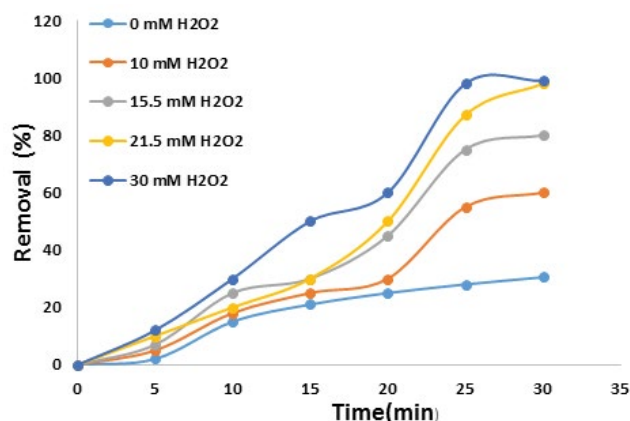
Fig. 8. Effect of initial H_2O_2 concentration on the removal % of MB ([MB] = 20.0 mg L⁻¹, [H_2O_2] = 21.5 mM, Mo-goethite = 0.1 g mL⁻¹, and pH = 7.0).
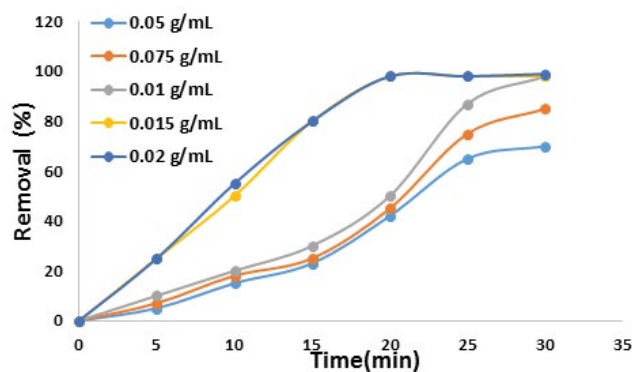

Fig. 9. Effect of Mo-goethite dosage on the removal % of MB ([MB] = 20.0 mg L⁻¹, [H_2O_2] = 21.5 mM, Mo-goethite = 0.1 g mL⁻¹, and pH = 7.0).

is removable is a system not having H_2O_2. By increasing the amount of hydrogen peroxide, the amount of removable is increased by about 98% to increase the concentration of H_2O_2 by 21.5 mM. Increasing the amount of MB removal was associated with increased hydrogen peroxide levels due to the generation of $^\bullet\text{OH}$ in the system. Increasing the concentration of H_2O_2 does not affect the percentage of MB removal due to the scavenging effect according to Eqs. (6) and (7).

$$\text{H}_2\text{O}_2 + {^\bullet\text{OH}} \rightarrow \text{H}_2\text{O} + \text{HO}_2^\bullet \tag{6}$$

$$\text{HO}_2^\bullet + {^\bullet\text{OH}} \rightarrow \text{H}_2\text{O} + \text{O}_2 \tag{7}$$

This side reaction reduces the availability of $^\bullet\text{OH}$ and reduces the degradation of organic structures [31]. Therefore, to have high performance, excess hydrogen peroxide should be avoided. The appropriate amount for this reaction is 21.5 mM.

3.2.5. Effect of Mo-goethite dosage

The degradation ratio and the catalyst (Mo-goethite) content are shown in Fig. 9. As can be seen, under optimal

conditions (pH 7, 21.2 mM of H_2O_2, and in 30 min), various catalyst amounts were examined from 0.05 to 0.2 g mL^{-1}. With increasing the catalyst content, the degradation percentage is also increased such that the MB removal is 98% in 0.1 g mL^{-1} of the Mo-goethite. As the catalyst content is increased, the degradation rate is increased and stabilized at 0.2 g mL^{-1}, which can be attributed to the presence of H_2O_2 in the environment and the amount of $^•$OH produced. Therefore, the best value for MB removal is 0.01 g mL^{-1}.

4. Conclusions

Mo-goethite can highly degrade MB. In this study, this structure developed and characterized using the XRD, SEM, and FT-IR analyses. The results showed that goethite could highly degrade the MB with molybdenum and in the presence of hydrogen peroxide. Optimal conditions for removing 98% of the MB using the Mo-goethite as a catalyst were found as follows: pH 7.0, 21.2 mM of H_2O_2, and 0.1 g mL^{-1} of Mo-goethite after 30 min. A possible mechanism for the degradation of MB in the Mo-goethite/H_2O_2 system was proposed. In this heterogeneous system, MB molecules were first adsorbed on the surface of Mo-goethite. Fe(II) on the Mo-goethite can react with H_2O_2 and form Fe(III) and $^•$OH [Eq. (2)], and the generated Fe(III) can further react with H_2O_2 to form Fe(II) [Eq. (3)]. Subsequently, Mo(IV) on the Mo-goethite can react with Fe(III) and form Mo(VI) and Fe(II) [Eq. (4)], and the generated Mo(VI) can react with H_2O_2 and produce Mo(IV) [Eq. (5)]. Finally, Mo-goethite showed good stability and the adsorbed MB was oxidized by the generated radicals to CO_2, H_2O, and other by-products. With these outstanding performances, the Mo-goethite can be used as an efficient heterogeneous catalyst for dye wastewater treatment

Acknowledgment

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