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Preliminary Study of Photocatalytic Degradation of Methylene Blue Dye using Magnetic Alginate/Fe_3O_4 (Alg/Fe_3O_4) Nanocomposites

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Abstract

Magnetic compound, Fe_3O_4, is one of the compounds that is easily hydrolyzed and oxidized. A coating method was presented in this study to prevent the process. The modifications of Fe_3O_4 were carried out by supporting alginate as natural polymers on the surface of Fe_3O_4. Preparation of magnetic alginate/Fe_3O_4 (Alg/Fe_3O_4) nanocomposite has been successfully synthesized. Alg/Fe_3O_4 material was synthesized using the coprecipitation method with Fe^{2+}; Fe^{3+} (with molar ratio 1:2) and alginate 1% as precursors. Synthesized Alg/Fe_3O_4 nanoparticles were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Delsa™ Nano C Particle Analyzer, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS). The Alg/Fe_3O_4 has an average diameter of 13.70 nm. Photodegradation test of synthetic methylene blue (MB) dye was found at pH 5.0 and irradiation time under UV_{245} for 60 minutes. The degradation results showed that the percentage of MB dye removal reached more than 90%.

Keywords: Alginate, Fe_3O_4, Methylene blue, Nanocomposites, Photocatalytic

Abstrak

Senyawa magnetik, Fe_3O_4, merupakan salah satu senyawa yang mudah mengalami hidrolsis dan oksidasi. Salah satu cara untuk mencegah proses tersebut dengan melakukan pelapisan bahan pendukung dipermukaannya. Pada penelitian ini, modifikasi dilakukan dengan menambahkan polimer alami yaitu alginat. Preparasi material nanokomposit magnetik alginat/Fe_3O_4 (Alg/Fe_3O_4) telah berhasil disintesis. Material Alg/Fe_3O_4 disintesis menggunakan metode kopresipitasi dengan Fe^{2+}; Fe^{3+} (dengan perbandingan rasio mol 1:2) dan alginat 1% sebagai prekursor. Nanopartikel Alg/Fe_3O_4 yang telah disintesis dikarakterisasi *Fourier Transform Infrared Spectroscopy* (FTIR), *Delsa™ Nano C Particle Analyzer*, *Transmisission Electron Microscopy* (TEM), *Scanning Electron Microscopy* (SEM), dan *Energy Dispersive Spectroscopy* (EDS). Material Alg/Fe_3O_4 memiliki diameter rata-rata sebesar 13,70 nm. Uji fotodegradasi dari pewarna sintetik metilen biru (MB) optimum pada pH larutan 5 dan waktu iradiasi sinar UV_{254} selama 60 menit. Hasil uji degradasi menunjukan persentasi penghilangan zat warna dari MB mencapai lebih dari 90%.

Kata-kata Kunci: Alginat, Fe_3O_4, Metilen biru, Nanokomposit, Fotokatalitik

Introduction

Methylene blue (MB) is one of the cationic dyes which are widely used in industry such as leather factories, metal plating plants, food companies, paint industries, pulp, and especially the textile industry. The organic dye such as MB has a large benzene ring structure which makes it difficult to degrade using conventional methods such as adsorption (Fadillah *et al*., 2018; Zhang *et al*., 2013), and biological treatments (Al-Baldawi *et al*., 2018). Therefore, several decades have developed the other methods such as photodegradation for removing MB dye in aqueous solution. Some materials that have been developed for the photodegradation process of methylene blue, i.e. GO/ZnO (Munawaroh *et al*., 2018), TiO_2 (Matsunami *et al*., 2019), Co-doped ZnS (Wang *et al*., 2016) and natural material such as clay and zeolite (Fatimah *et al*., 2015; Nugraha and Fatimah, 2013). However, the separation of material from the solution after the degradation process is still considered difficult so it is necessary to develop materials that are easier to use during the separation process after the degradation.

The development of nanocomposite-based hybrid materials (organic-inorganic) is currently a very interesting topic. Some literature showed that hybrid nanomaterials have many advantages such as good stability, physical, and thermal resistance and others. In the present study, we tried to develop the material, namely Alg/Fe_3O_4. Magnetic nanoparticles, Fe_3O_4, have been widely used for the photocatalytic process (Wang *et al*., 2018). However, Fe_3O_4 nanoparticles has limitations in its working area, especially pH (Talbot *et al*., 2018). Fe is one of the materials that is easily hydrolyzed and oxidized so that it will reduce the performance of photocatalyst.

Composite based on natural polymer such as alginate is one of the alternative to protect the surface of Fe so the material can be used at widely various pH. The use of material because the material has good stability performances and the separation of material after the process will be easier. In addition, there is no need of filtration or centrifugation steps due to the magnetic properties of the materials used.

In this research, we demonstrated synthesis of Alg/Fe_3O_4 as effective materials for photodegradation of MB dye and easy to remove from the system. These results exhibit that the prepared material has a good photocatalytic performance under UV_{254} irradiation.

Materials and Methods

Materials and Instrumentation

Alginate was purchased from Sigma Aldrich Singapore, ammonium hydroxide 25% (Merck), $FeCl_3 \cdot 6H_2O$ (Aldrich), $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Aldrich), methylene blue powder, CH_3COOH (Aldrich) and CH_3COONa (Aldrich). All reagents were used in analytical grade and without purification.

The prepared Alg/Fe_3O_4 materials were characterized by UV-Vis spectrophotometer (Agilent 8453), FTIR (Shimadzu IR prestige-21), Delsa™ Nano C Particle Analyzer (Beckman Coulter), SEM-EDS (JEOL JSM-6510A), and TEM (Hitachi H-7100).

Synthesis of magnetic Alg/Fe_3O_4 nanocomposites

Alg/Fe_3O_4 was synthesized using the coprecipitation method as shown in Figure 1 with a mole ratio 1:2 for Fe^{2+} and Fe^{3+} of 1:2 in 50 mL aqua demineralization. Then 20 mL of alginate 1% (b/v) was added into the solution and stirred at room temperature for 1 hour. 50 mL of ammonium hydroxide solution was slowly dropped into the solution at temperature 60 °C for 70 minutes. Then the precipitate was separated using magnet fields and washed using deionized aqua until reached pH 7.0 then dried at 60 °C for 24 hours.

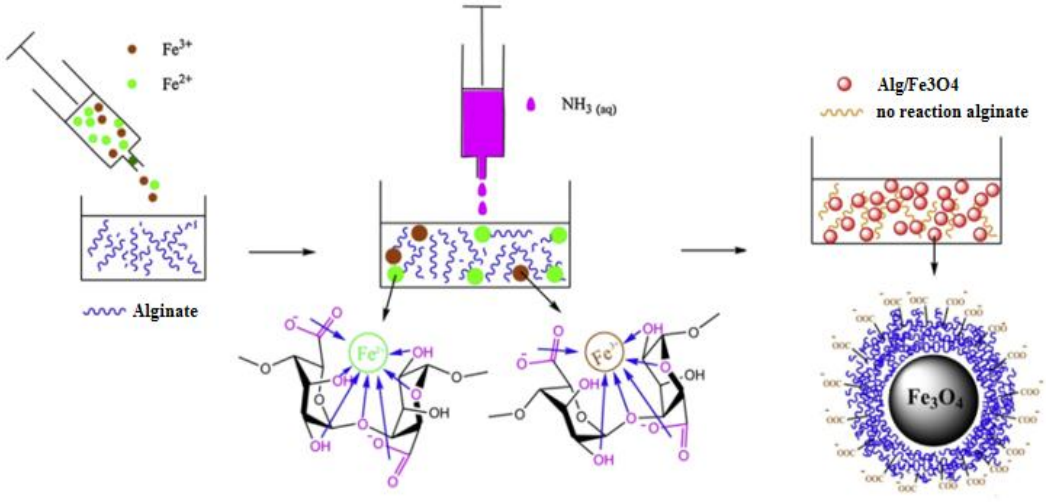

Figure 1. Illustration of synthesis of magentic Alg/Fe_3O_4 nanocomposite

Photocatalytic study

Photocatalytic degradation test was carried out in batch systems under UV_{254} radiation. 50 mg L^{-1} of MB as synthetic dye was photocatalytically treated using 100 mg of the synthesized Alg/Fe_3O_4 with variations of pH and irradiation time. The percentage of degradation was calculated using Eq.1.

$$\text{Degradation (\%)} = 100\left(\frac{C_O - C_e}{C_o}\right) \quad (1)$$

Where Ce is equlibrium consentration after degradation process and C_o is intial concentration before degradation process.

Discussion

Synthesis and Characterization of Alg/Fe_3O_4

Magnetic Alg/Fe_3O_4 nano-composites were synthesized by coprecipitation methods with mixing Fe^{2+}, Fe^{3+} (with molar ratio 1:2) and alginate 1% as precursors. The process of synthesized nanoparticle materials has been successfully formed under base conditions. The process of synthesized Alg/Fe_3O_4 is shown in Figure 2(a). The synthesized materials can be easily observed as well through bringing the synthesized material to magnetic fields as shown in Figure 2(b).

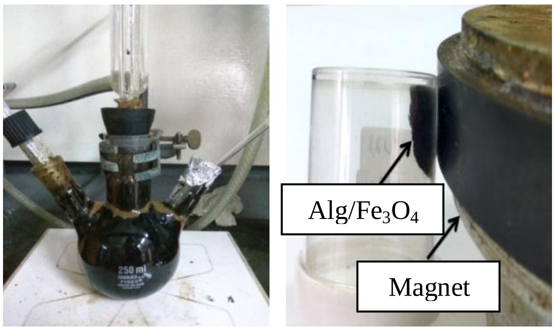

Figure 2. (a) The process of synthesized Alg/Fe_3O_4, and (b) the results of synthesized Alg/Fe_3O_4

However, to ensure that the results have been successfully synthesized, several characterizations were carried out in this study. FTIR characterization as shown in Figure 3. FTIR spectrum confirmed that there is the vibration of octahedral and tetrahedral Fe-O at wavenumber 489.91 cm^{-1} and 570.92 cm^{-1}, respectively. While at wavenumber 3385.03 cm^{-1} indicates the presence of a hydroxyl group from alginate (Platero et al., 2016). Overall, the results of FTIR characterization revealed that the Alg/Fe_3O_4 nanocomposites have been successfully formed.

The surface morphology of Alg/Fe_3O_4 materials can be seen using SEM characterization (Figure 4). Based on the EDS data, it can be seen that the main composition of Alg/Fe_3O_4 is C, O, Na derived from alginate which

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overlays on the surface of Fe_3O_4. Meanwhile, Fe and O are derived from Fe_3O_4. The percentage results displayed by EDS data are semi-quantitative analysis because testing materials only carriy out a mapping of a certain spot from composite materials, so they cannot accurately represent the percentage of each element on the materials.

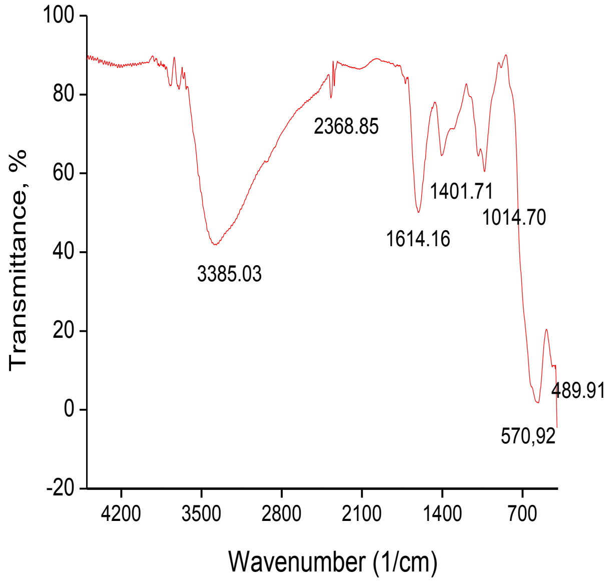

Figure 3. FTIR spectrum of Alg/Fe_3O_4 nanocomposites

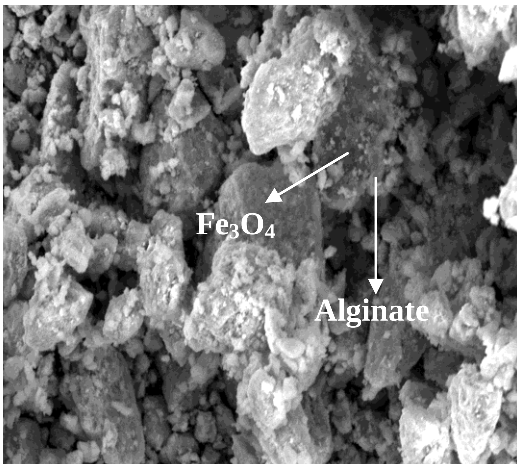

Figure 4. SEM characterization of Alg/Fe_3O_4

The size of the materials was confirmed using the Transmission Electron Microscopy (TEM) instrument. Based on Figure 5, it shows that the sodium alginate coated magnetite nanoparticles are spherical with an average size distribution of 13.7 nm. The average size distribution obtained from processing using imageJ software.

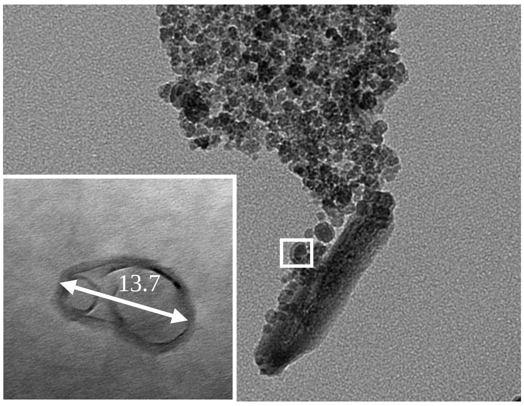

Figure 5. TEM characterization of Alg/Fe_3O_4

Surface electric charge (zeta potential) of Alg/Fe_3O_4 was measured by dispersing the materials into solution at pH 2.0 and 4.0. Then it was measured using the Delsa™ Nano C Particle Analyzer instrument. The results showed that the zeta potential of Alg/Fe_3O_4 at pH 2.0 and pH 4.0 is -5.01 and -9.46 mV, respectively. The results indicate that the coated alginate on the surface of Fe_3O_4 makes the surface charge become negative. This shows that the mechanism of interaction between the material surface and dyestuff is electrostatic interaction (Ghaedi *et al*., 2015).

MB degradation using Alg/Fe_3O_4 under UV_{254} light

Photocatalytic activity was performed in a batch system under UV_{254} light. The degradation test was conducted with the variation of pH and irradiation time of 30, 60, 90, and 120 minutes. The results were found degradation optimum at pH 5.0 and irradiation time at 60 minutes as shown in Figure 6(a) and (b).

It confirmed that at low pH especially at pH 5.0, MB dye will be protonated, so the charge of MB will be positive (Fadillah *et al*., 2018; Yanhui Li, 2013) . The process would improve in electrostatic interactions between dye molecules and Alg/Fe_3O_4 and the degradation occurred more significantly. Although at high pH, the degradation is not better than at low pH, the color of MB still decreases. This proved that Fe_3O_4 material could still work as well even at the base condition. The material could still work due to it was coated with alginate on the surface so it was not hydrolyzed.

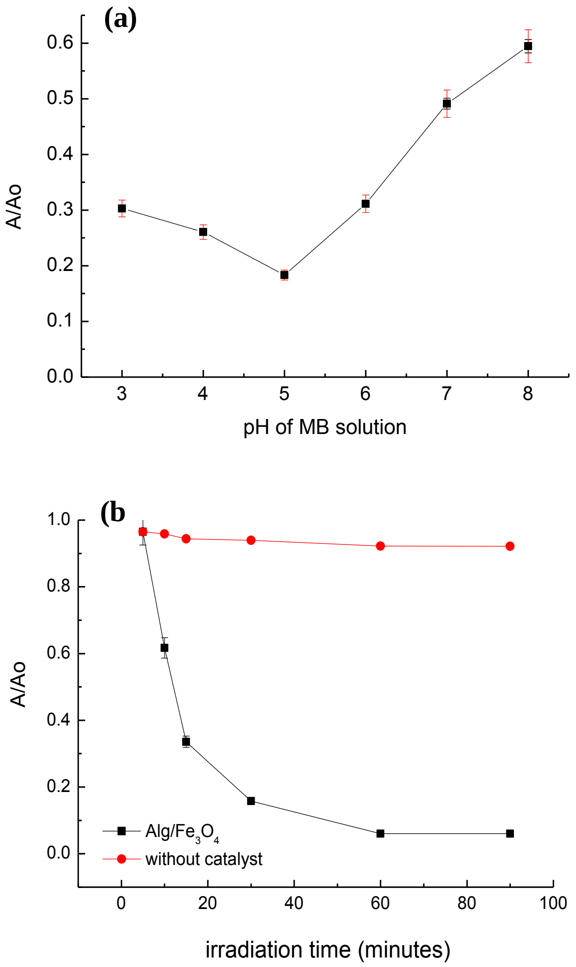

Figure 6. (a) the pH influence on degradation of 50 mg L^{-1} MB,15 minutes, (b) Effect of contact time on degradation of 50 mg L^{-1} MB at pH 5.0

A variety of photocatalyst materials has been reported by previous resechers to investigate performance of degradation of MB dye (Table 1). Fe_3O_4 has been developed by Hung *et al*. (2016), however % degradation of MB dye was still relatively low due to hydrolysis and corrosion on the surface of Fe_3O_4. Whereas, Alg/Fe_3O_4 shows better results because the surface of the material is covered with alginate. In addition, the presence of an active group on the surface of the alginate causes the material to work simultaneously between degradation and adsorption. Based on Figure 6(b), it shows that the presence of Alg/Fe_3O_4 could significantly decrease the color of MB dye. The presence of Alg/Fe_3O_4 as photocatalyst can directly degrade the MB into green compounds such as carbon dioxide (CO_2) and pure water (H_2O). The longer irradiation time will cause to be an excited electron and also makes the h^+ increases. It makes more OH radical production on the system so the degradation of the dyestuff is obtained at a maximum of 94 $\pm$ 0,14%.

Table 1. Various photocatalyst materials for degradation of MB dye

Type of Materilas	Removal efficiency (%)	T (minutes)	References
TiO_2/Fe_3O_4/GO	82.0	90 (UV)	(Nadimi *et al.*, 2019)
GO/ZnO	86.8	100 (UV)	(Zhang *et al.*, 2019)
ZrC NPs	80.0	300 (Solar)	(Singh Vig *et al.*, 2018)
Ce-TiO_2/Fe_3O_4	90.0	240 (UV)	(Shi *et al.*, 2012)
Fe_3O_4	70.0	50 (UV)	(Hung *et al.*, 2016)
Alg/Fe_3O_4	94.0	60 (UV)	This work

Conclusion

The photodegradation test reveals that the Alg/Fe_3O_4 nanocompsites can still work for the degradation of MB dye in acid-base solution. The presence of Alg/Fe_3O_4 as photocatalyst exhibit efficient activities for the degradation of MB dye. The optimal condition was observed at pH 5.0 and irradiation time at 60 minutes with the percent degradation reach more than 90% under UV_{254} radiation. This material shows good prospect as photocatalyst material. Futhermore, it still needs to be more studied, especially the influence of ionic strength in the system during photodegradation.

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