The Use of Magnetic Nanocomposites in Fenton Reaction for Catalytic Degradation of Methylene Blue

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Abstract: Oxidation by Fenton-like reactions is proven and economically feasible process for destruction of a variety of hazardous pollutants in wastewater. MNPs were synthesis via a thermal decomposition method and Au@FexOy via electrooxidation procedure. The synthesis of MNPs and Au@FexOy was characterized by several techniques, Ultraviolet-visible spectroscopy (UV-Vis), and Transmission Electron Microscopy (TEM). The concentrations of dye degradation were determined spectrophotometrically using Plate Readers at 665 nm, the absorption maxima of the dye. Moreover, in order to apply using magnetic nanocomposites in Fenton reaction for degradation of methylene blue, concentration of iron ion and hydrogen peroxide must be optimized.

The magnetic nanocomposites showed good catalytic performance for MB organic dye oxidation by H2O2 after 5 hours of reaction. The reaction was able to proceed at pH neutral in room temperature. Finally, some future trends and prospective in this research areas are also discussed.

1. Introduction

Chemical industries, such as oil refineries, petrochemical units, dye and dye intermediate manufacturing industries, textile units, industries making paper, pharmaceuticals, cosmetics and synthetic deters, and tanners are the typical industries that discharge toxic organic compounds at low concentrations, thus making the water polluted (Kabita et al., 2001)[5]. A new process for wastewater treatment in order to degrade or removing these compounds in textile industry effluents is an important issue. An extensively studied is the use of advanced oxidation processes (AOP). Fenton’s chemistry is very well known and it is one of the high potential oxidation technologies because it produces a highly reactive species [OH•] (Andre et al., 2014). Previous researches indicated the catalytic capacity of the magnetic nanocomposite preform good in Fenton reaction (Cheng and Wei, 2011)[2]. The aim in this study was about to using the magnetic nanocomposite to demonstrate the degradation of organic pollutants, a study: “The use of magnetic nanocomposites in Fenton reaction for catalytic degradation of methylene blue” was conducted.

2. Aims of study

* Determine the optimum concentration of iron ion and hydrogen peroxide on degradation of methylene blue.
* Determine optimum of H2O2 concentration on degradation of methylene blue by magnetic nanocomposite for degradation of dye in textiles industry.
* Assessment the efficiency of use magnetic nanocomposite in Fenton’s reaction to orientate the application in wastewater treatment technology.

3. Methods and materials research

3.1 Determine the optimum concentration of Fe2+

* Treatment

To determine the optimum iron (II) concentration we used 4 different iron (II) concentrations as following:

- Treatment 1: Fe 0x, 0 M
- Treatment 2: Fe 1x, 3.58×10−5 M
- Treatment 3: Fe 4x, 1.43×10−4 M
- Treatment 4: Fe 8x, 2.86×10−4 M

* Procedure

All plastic tubes were covered by foil paper in order to prevent the light entering inside solutions.

1) Plastic tubes containing obtained MB solutions were placed on a magnetic stirrer for continuous stirring.
2) Adding 10µL H2SO4 0.97 M for adjust pH from 2-3. All of the experiments were carried out at room temperate.
3) The required amount of Fe2+, H2O2 was added simultaneously into the MB solution.
4) Using UV-Vis spectroscopy to determine the spectrophotometrically of MB concentration at 0, 30, 60 minutes.
5) Analyzing the degradation capacity by using Excel based on data collected form UV-Vis.
3.2 Determine the optimum concentration of H2O2

The optimum concentration of Fe2+ was used as base in this experiment.

* Treatment

To determine the optimum H2O2 concentration, we used 5 different H2O2 concentrations following:
- Treatment 1: H2O2 0.5x, 0 M
- Treatment 2: H2O2 1x, 4.41×10−4 M
- Treatment 3: H2O2 2x, 8.82×10−4 M
- Treatment 4: H2O2 4x, 1.76×10−3 M
- Treatment 5: H2O2 8x, 3.52×10−3 M

* Procedure
- Plastic tubes containing 3.13×10−5 M MB solutions were placed on a magnetic stirrer for continuous stirring.
- Using foil paper in order to cover the tubes and prevent the light entering inside solutions.
- Adding 10µL H2SO4 0.97 M for adjust pH from 2-3.
- All of the experiments were carried out at room temperate.

3.3 Effect of pH value on conversion efficiency of MB

The optimum concentration of Fe2+, H2O2 was used as base in this experiment.

* Treatment

To determine the effect of pH value on degradation of MB, experiments were conducted with 3 treatments by base of [Fe2+], Fe 8x and [H2O2], H2O2 4x:
- Treatment 1: adding 10µL H2SO4 0.97 M for adjust pH from 2.5 – 3.5.
- Treatment 2: adding 1µL H2SO4 0.97 M for adjust pH from 4.5 – 5.
- Treatment 3: adding 5µL NaOH 0.4 M for adjust pH 7.

* Procedure
- Plastic tubes containing 3.13×10−5 M MB solutions were placed on a magnetic stirrer for continuous stirring.
- Using foil paper in order to cover the tubes and prevent the light entering inside solutions.
- Adding 10µL H2SO4 0.97 M for adjust pH from 2-3.

3.4 Degradation of MB by Iron (II), Iron (III)

* Treatment

Experiments were conducted with 3 treatments at the same concentration of Iron ion, 2.86×10−4 M and H2O2, 1.76×10−3 M, following:
- Treatment 1: Fe2+, H2O2 0.5x, 0 M
- Treatment 2: Fe3+ + Fe2+, ratio: 0.5
- Treatment 3: Fe3+

* Procedure
- Plastic tubes containing 3.13×10−5 M MB solutions were placed on a magnetic stirrer for continuous stirring.
- Using foil paper in order to cover the tubes and prevent the light entering inside solutions.
- Adding 10µL H2SO4 0.97 M for adjust pH from 2-3.
- All of the experiments were carried out at room temperate.

3.5 The use of MNC, Au@FeOy in degradation of MB

* Treatment

Experiments were conducted with 3 treatments as following:
- Treatment 1: H2O2 4x
- Treatment 2: H2O2 200x
- Treatment 3: H2O2 2000x

* Procedure
- Plastic tubes containing 3.13×10−5 M MB solutions were placed on a magnetic stirrer for continuous stirring.
- Using foil paper in order to cover the tubes and prevent the light entering inside solutions.
- Adding 5µL NaOH 0.4 M for adjust pH 7.
- All of the experiments were carried out at room temperate.

- The required amount of Fe2+ and H2O2 were added simultaneously into the MB solution.

* Method to determine degradation capacity
- Determine spectrophotometrically of MB concentration at 0 minutes, 30 minutes and 60 minutes using UV-Vis spectroscopy.
- Based on absorption maxima of MB, analyzing the degradation capacity by using Excel.

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* Procedure
- Plastic tubes containing 3.13×10−5 M MB solutions were placed on a magnetic stirrer for continuous stirring.
- Using foil paper in order to cover the tubes and prevent the light entering inside solutions.
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- All of the experiments were carried out at room temperate.

- The required amount of Fe2+ and H2O2 were added simultaneously into the MB solution.

* Method to determine degradation capacity
- Determine spectrophotometrically of MB concentration at 0 minutes, 30 minutes and 60 minutes using UV-Vis spectroscopy.
- Based on absorption maxima of MB, analyzing the degradation capacity by using Excel.
+) 2.86×10^−4 M of MNC, Au@FexOy - Before annealing, Au@FexOy - After annealing and H2O2 200x (8.82×10−2 M);
+) 2.86×10^−4 M of MNC, Au@FexOy before annealing, Au@FexOy after annealing and H2O2 2000x (8.82×10−1 M);
* Method to determine degradation capacity
  - Determine spectrophotometrically of MB concentration at 0 minutes, 30 minutes and 60 minutes using UV-Vis spectroscopy.
  - Based on absorption maxima of MB, analyzing the degradation capacity by using Excel.

4. Results and discussion

4.1. Determination the optimum the concentration of Iron (II) for degradation of MB

To determine the optimum Iron (II) concentration we used 4 different Iron (II) concentrations as following: treatment 1(Fe 0x, 0 M), treatment 2 (3.58×10^-5 M), treatment 3 (1.43×10^-4 M), and treatment 4 (2.86×10^-4 M).

Those 4 concentration have the same concentration base with MB, 3.13×10^-5 M and Fe2+ 2.86×10^-4 M, respectively. The pH was adjusted from 2-3.5 by adding 10 µL H2SO4 0.97%.

The graph (Figure 4.1) showed the degradation of MB by different Fe2+ concentration in 60 minutes. With the increase concentration of Fe2+, the conversion efficiency increased. It also increased with a rise of time, from 0 to 60 minutes. Within 60 minutes, conversion efficiency of MB was highest at 60 minutes and Fe 8x was highest conversion efficiency with 41% at 60 minutes and Fe 0x was lowest at 1.4%.

4.2 Determination the optimum concentration of H2O2 for degradation of MB

To determine the optimum H2O2 concentration we used 5 different H2O2 concentrations as following: treatment 1 (H2O2 0.5x, 0 M), treatment 2 (H2O2 1x, 4.41×10^-4 M), treatment 3 (H2O2 2x, 8.82×10^-4 M), treatment 4 (H2O2 4x, 1.76×10^-3 M), and treatment 5 (H2O2 8x, 3.52×10^-3 M).

Those 5 concentration have the same base concentration of MB, 3.13×10^-5 M and Fe2+ 2.86×10^-4 M, respectively. The pH was adjusted from 2-3.5 by adding 10 µL H2SO4 0.97%.

The graph presented the degradation of MB by different H2O2 concentration within 60 minutes. With the increase concentration of H2O2, the conversion efficiency increased. It also increased with a rise of time, from 0 to 60 minutes. Within 60 minutes, conversion efficiency of MB was highest at 60 minutes and H2O2 4x was highest conversion efficiency with 41% at 60 minutes and H2O2 0.5x was lowest at 1.5%.

Figure 4.1. Degradation MB by different Fe2+ concentration in 60 minutes, pH = 2-3.5
4.3 Effect of pH value on degradation of MB

To determine the effect of pH value on degradation of MB, experiments were conducted with 3 treatments by base of [Fe2+], Fe 8x and [H2O2], H2O2 4x as following: treatment 1 (pH 2.5-3.5), treatment 2 (pH 4-5.5), treatment 3 (pH 7-7.5).

The graph 4.3 presented the degradation of MB by different pH value within 60 minutes. Surprisingly, with the increase pH value, the conversion efficiency increased.

But the conversion efficiency still increased with a rise time, from 0 to 60 minutes. Within 60 minutes, conversion efficiency of MB was highest at 60 minutes. The treatment 1, was adjusted pH 2-3.5, was highest conversion efficiency with 41% at 60 minutes. Treatment 3, was adjusted pH 7, was lowest the conversion efficiency at 33 %.

4.4 Degradation of MB by Iron (II), Iron (III)

Both Fe3O4 magnetic nanoclusters and Au@FexOy nanocomposites have good catalytic potential on the degradation of methylene blue (Andre, 2014). In theory, the ratio between Fe (II) and Fe (III) reactants of Fe3O4 magnetic NPs was 0.5. As a result, Fe (II); Fe (III); Fe (II) + Fe (III) solution was considered to be our positive control which compared with our magnetic nanoclusters and Au@FexOy.

According to Figure 4.4, the decomposition of H2O2 reaction was rapid at the beginning when in the Fe (II) solution whereas decomposition of H2O2 was slightly slower. Interestingly, the changed profile of the mixed Fe (II) and Fe (III) solution was similar approach to Fe (II). So, according to above observation, we assume that while the decomposition of MB start with Fe (III), other reaction may be involved during the decomposition reaction, which was shown below:

\[
\begin{align*}
\text{Fe}^{3+} + \text{HO}_2^- & = \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \\
\text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & = \text{Fe}^{3+} + \text{H}_2\text{O}_2 \\
2\text{HO}_2^- & = \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

Although, the reaction was prior to Fe (II) for the degradation, still all the three groups achieve to 90 %. The reaction was almost complete.

The results are showed in figure 4.4:
4.5 The use of MNC, Au@FexOy in degradation of dye

1) According to the optimum concentration of iron (II) and H2O2 as described in those experiments above, we apply to using magnetic nanocomposites in Fenton reaction for degradation of MB. In the treatment, we used MNC with $2.86 \times 10^{-4}$ M and H2O2, $1.76 \times 10^{-3}$ M (4x), pH 7 adjusted by adding $5 \mu$L NaOH in the solution. The conversion efficiency was presented in Figure 4.5.

From figure 4.5, degradation of MB by MNC with H2O2 4x, conversion efficiency is very low. It became constant after 30 minutes. The max conversion efficiency is 10% at 420 min. So the concentration of H2O2 here was not optimum for degradation of MB by magnetic nanoparticles.

2) To verify the conversion ability of magnetic nanocomposites on degradation of dye, we conducted experiment with concentration of H2O2 at 200 times dilute fold for 5 hours incubation. Then, we further spike 20 µL H2O2 $8.82 \times 10^{-1}$ M (200x) in solutions to realize the degradation procedure.

![Figure 4.4. Degradation of methylene blue by Fe (II); Fe (II) + Fe (III) and Fe (III) at pH 2.5-3.5](image)

![Figure 4.5 Degradation of methylene blue by MNC, H$_2$O$_2$ 4x and pH = 7](image)

![Figure 4.6 Degradation of methylene blue by MNC, H$_2$O$_2$ $8.82 \times 10^{-1}$ M (200x), pH = 7 with spike at 5 hours](image)
From the figure 4.6, when increase H2O2 concentration up to 200x, the conversion efficiency is still low and almost no reaction at 300 min. Surprisingly, after adding 20µL H2O2 8.82 M, conversion efficiency rapid increases tend to a 39% at 720 minutes. This is a base for determination of H2O2 on MB degradation, we conduct experiment following.

3) MNC and Au@FexOy was further investigated for MB degradation afterwards. The experiments were conducted with MNC, Au@FexOy before annealing and Au@FexOy after annealing at the same concentration 2.86×10–4 M (Figure 2.6). The concentrations of H2O2 were kept at 8.82 M (2000 times diluted fold).

In figure 4.7, it showed that magnetic composite has well done reaction in the presence of H2O2 in Fenton reaction. Maximum conversion efficiency of Au@FexOy after annealing, Au@FexOy before annealing and MNC are 80%, 23% and 71%, respectively.

We found that the behavior between Au@FexOy before and after through annealing process performed significantly different behaviors in degradation. Surprisingly, the reaction was achieved almost 70-80 % in magnetic particles.

4) To compare and assess the effectiveness between Iron ion and magnetic nanocomposites, experiments were conducted with 7 treatments:
- Treatment 1: H2O2 + H2O
- Treatment 2: Fe2+
- Treatment 3: Fe3+
- Treatment 4: Fe 2++Fe3+
- Treatment 5: MNC, 2.86×10–4 M.
- Treatment 6: Au@FexOy after annealing, 2.86×10–4 M.
- Treatment 7: Au@FexOy before annealing, 2.86×10–4 M.

![Figure 4.7. Degradation of MB by MNC, Au@FeOx after annealing, Au@FeOx before annealing at pH = 7, [H2O2] = 2000x](image1)

![Figure 4.8. Degradation of MB by a) H2O2 + H2O, b) Fe(II), c) Fe(III), d) Fe(II)+Fe(III), e) Au@FeOx after annealing, f) Au@FeOx before annealing and g) MNC (pH = 7)](image2)
According to Figure 4.8, degradation of MB by Iron ion (II and III) group were rapid at the beginning of reaction with 90% conversion efficiency within 60 minutes whereas groups from Au@FexOy, MNC was much slower when reaction began.

We found the precipitants from the magnetic particles in the bottom of plastic tubes after the experiments completed. In detail, as we can see from Figure 4.9 (B), there were yellow precipitants on degradation of MB by Fe (II). This is evidence that Fe (II) is converted into Fe (III) at the end of reaction. On degradation of MB by magnetic nanocomposites, there are also precipitants at the end of reaction as present on Figure 2.8 (A). However, these are magnetic nanoparticles after reaction and they still have magnetic field. This is very important indicating advantages of using magnetic composites in Fenton’s reaction. We can reuse or recycle them not only once use that presented in many studies with the benefit in reuse of magnetic nanoparticles (Han et al., 2014).

In addition, even all the experiment for degradation of MB by magnetic nanoparticles were controlled with pH neutral (pH = 7) which was more suitable in real situation, the conversion efficiency was still remain certain extent compare to Iron (II)/Iron (III). Although the best condition for fenton reaction was conducted in pH 2.5-3.5.

On the other hand, with core-shell nanostructure, probably because there was only an amount of Iron ion on surface of magnetic nanocomposites reacted with H2O2 in Fenton reaction; however, there was still iron ion inside non-react.

In fact, when using Iron (II) or Iron (III) in Fenton’s reaction occurred in real wastewater environment, totally Iron ion will take part in the reaction. However, Iron ions do not only reacting with H2O2 same as in theory, it also reacts with ions or organic compounds in wastewater, this will affect to the conversion efficiency of degradation of dye. By contrast, magnetic nanocomposites, will prevent nanoparticles and block organic compounds in wastewater react with iron ion. This indicated the conversion efficiency of MNC and Au@FexOy lower than Iron (II)/Iron (III) but more realistic in the real cases.

5. Conclusion and discussion

5.1. Conclusion
Gold@iron oxide nanoparticles and magnetic nanoparticles were successfully synthesized by a simple and inexpensive synthetic procedure with controlled size and shell thickness. Continue survey the synthesis of magnetic nanoparticles with different conditions to uniform the size of nanoparticles and optimize the synthetic procedure. It is very necessary to optimize the concentration of H2O2. Iron ions in Fenton reaction for apply using magnetic nanocomposites on degradation of MB.

5.2. Discussion
For degradation of methylene blue by iron ions, the optimum concentrations of iron ion, hydrogen peroxide were Fe 8x (2.86×10−4 M) and H2O2 4x (1.76×10−3 M) was an optimum Fe2+ concentration for the most effective degradation of 3.13 × 10−5 M MB solution, the optimum pH value range from 2-4.
For degradation of MB by magnetic nanocomposites, the optimum H2O2 concentration is 2000x (8.82×10−1 M). After 5 hours, magnetic nanocomposites performed good in Fenton reaction for degradation of methylene blue with conversion efficiency of MNC at 71%, Au@FexOy after annealing at 80% and Au@FexOy before annealing at 23%.

6. References