Removing of Methylene Blue Dye from its Aqueous Solutions Using Polyacrylonitrile/Iron Oxide/Graphene Oxide

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Received: 27/7/2021 Accepted: 11/10/2021 Published: 30/6/2022

Abstract
Organic contaminants are used to be found in industrial wastewater treatment procedures, and heavy metal ion removal is difficult. Photo Fenton reaction activity was exploited in this study to decompose organic contaminants using a functional composite hydrogel. Polyacrylonitrile (PAN), Fe₃O₄ particles, and graphene oxide make up the hydrogel (GO). It is made from GO/Fe₃O₄ and is made using the precipitation technique. GO is made from graphite using the Hummers process. And it has exceptional mechanical strength and Photo-Fenton activity as a result of various breakdown data that were influenced differently, such as H₂O₂ concentration, dye concentration, temperature, and irradiation duration. Atomic Force Microscopy (AFM) was used to examine the composite's shape and average diameter. Under UV irradiation, the degradation of Methylene Blue dye (M.B) by the PAN/Fe₃O₄/GO hydrogel composite reached 100% after 90 min. Meanwhile, after 90 min of visible irradiation, COD (Chemical Oxygen Demand) dropped to 9 mg/L and dropped to low (sub range) after two and a half hours. This research proposes a new method for processing high-consistency industrial effluent that is difficult to decompose.

Keywords: Photo- Fenton reaction, PAN/Fe₃O₄/GO composite, Methylene Blue, COD.

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1. Introduction

Because of the ease with which wastewater may be disposed of, surface water ways are the most vulnerable to pollution[1]. The Fenton reaction, which is used for wastewater treatment, includes a combination of ferrous iron (Fe²⁺) and hydrogen peroxide (H₂O₂) in an acidic solution to form the hydroxyl radical (•OH) [2]. Homogeneous Fenton reactions have various drawbacks, including an acidic pH, poor H₂O₂ consumption efficiency, and sludge production[3,4]. Its usefulness is limited due to these flaws. Furthermore, a high (H₂O₂) (Fe²⁺) molar ratio necessitates a large amount of Fe²⁺ [5,6]. This increases the amount of reagents used. Solid, iron-containing compounds or solid materials rich in iron, such as Fe₃O₄[7,8], Fe₆O₄[9], FeOOH [10], and clay [11], as well as mesoporous silica[12], are used in the heterogeneous Fenton reaction. For the breakdown of organic contaminants, iron-containing compounds were promoted. In comparison, heterogeneous Fenton reactions are an effective oxidative technology for degrading organic pollutants because they efficiently promote H₂O₂ conversion with minimal decomposition, and easy separation from solution for cyclic utilization, all of which are advantageous for practical applications. However, because of the poor contact between the iron catalyst and the carrier materials, most iron-containing catalysts are not practical and increase iron leaching after cyclic use numerous times, resulting in catalytic stability and decreased activity.[13–15] The carbon atom is one of the most abundant atoms on Earth, appearing naturally in a variety of forms and as a component in a large number of compounds known as allotropes of carbon[16]. These potential characteristics have been used in a variety of applications, including electronics, batteries, sensors, and composite materials. The preparation of hydrogels with exceptional mechanical characteristics drew a large number of people.[17]. There are three common recipes for making high-strength hydrogels: topological gels [18], double network gels [19], and composite gels[20]. Composite gels are thought to improve the mechanical properties of hydrogels, for example, composite gels with a unique organic inorganic network structure would have extraordinary mechanical properties [21].

Graphene oxide (GO) is now one of the most popular study topics among chemists, owing to its inexpensive cost of mass manufacturing and excellent water dispersibility [22–24].

The chemistry of Polyacrylonitrile (PAN) is of particular importance since it is used as a matrix in the development of carbon nanofiller-based nanocomposite for different appliances. Carbon nanotubes (CNT), graphene, and graphene oxide (GO) have all been employed in bulk composite materials and thin films[25]. Recently, there has been a surge of interest in the use of composite Nanofibers NFs in water treatment, especially for the removal of organic pollutants [26-27]. Chen et al. found that calixarene-functionalized polyacrylonitrile (PAN) composite nanofibers NFs effectively adsorb Congo red[26]. Thus, photo catalytic degradation of environmental pollutants is an interesting topic for study.
2. Experimental Part
2.1 Determination of Maximum Absorption (\(\lambda_{\text{max}}\))
The wavelength value of Methylene Blue dye (M.B) absorption is 650 nm, this was used to estimate its quantity as shown in Figure 1.

![Figure 1-UV-Visible absorption spectrum for methylene blue dye](image1)

**Figure 1-UV-Visible absorption spectrum for methylene blue dye**

2.2 Calibration curve for M.B dye
Figure 2: illustrates the calibration curve which is the linear relation between absorbance and concentration.

![Calibration curve for Methylene blue](image2)

**Figure 2- Calibration curve for Methylene blue**
2.3 Graphene oxide (GO) preparation
Hummer’s method was used to create GO from graphite [28]. 1.0 g of graphite was added into 23 ml of concentrated sulphuric acid (H₂SO₄) under stirring at room temperature, then, 0.5 g of sodium nitrate was added, and the mixture was cooled to 0°C. Under powerful agitation, 3.0 g of potassium permanganate was added slowly while the temperature of the suspension was kept near 2°C. The reaction mixture was transferred to a water bath at a temperature of 35°C and stirred for 30 min. Then, 50 ml of deionized water (DI) was added, and the solution was stirred for 15 min at 90°C. Additional 166 ml of water was added and followed by a slow addition of 5 ml of 30% hydrogen peroxide (H₂O₂), turning the color of the solution from yellow to dark brown. The mixture was filtered and rinsed with 85 ml of 4% HCl aqueous solution which followed by washing with 65 ml of distilled water to remove the acid, then oxidation product washed until the pH reached 6, then filtered and dried.

In Figure 3, FTIR spectrum of GO showed characteristic bands transmission bands of 3425, 1708, 1625, 1363,1218,1071 cm⁻¹ belongs to stretching of (O-H) and (C=O of carbonyl groups), (C=C formative vibrations of aromatic), (C‒O belong to the group of carboxylic) and epoxy and alkoxy group, respectively, this confirms the presence of successful oxidation on graphite by using the FTIR spectrum [29].

2.4 GO/Fe₃O₄ composite preparation
Hummer’s approach was used to make graphene oxide. To make the GO/ Fe₃O₄ composite, sonication was used to disperse 0.2 g of as-prepared graphene oxide in 150 ml of distilled water in the first stage. FeCl₃ and FeCl₂ in an aqueous solution comprising 0.140 g FeCl₃ and 0.0855 g FeCl₂.4H₂O was added into the graphene oxide dispersion and stirred constantly. After 2 hours of stirring, ethylamine C₂H₅NH₂ was dropped into the dispersion at a rate of around 1 ml per minute to precipitate Fe₃O₄ nanoparticles on the graphene oxide sheet. X-ray diagrams are shown in Figure 4 for GO/Fe₃O₄. XRD pattern of graphene oxide at 2θ = 11.2408° indicates an intercalation of water molecules and a generation of oxygenated functional groups such as epoxy and hydroxyl groups between the inner galleries of the graphite sheets during intense oxidation. For inner Fe₃O₄, all diffraction peaks in XRD pattern, at 2θ = 30.4917°, 35.9021°, 43.5521°, 53.945°, 57.3674° and 63.0043° can be easily indexed to the pure cubic spinel magnetite structure, which matches well with the reported
The peaks were intense and well defined and this indicates the optimum degree with respect to the structural arrangement in the long bands. Due to the combinations between two components, the spectrum of GO/Fe$_3$O$_4$ appears to have a partial reduction with respect to GO confirming the dispersion of ferric oxide on the graphene layers. This widening would overlap with most ferric oxide peaks due to lower concentrations of ferric oxide in the compound. This reaction took place at room temperature.

![Figure 4-XRD pattern of GO/Fe$_3$O$_4$](image)

2.5 PAN/ Fe$_3$O$_4$/GO composite preparation

A simple solvothermal approach was used to make PAN/ Fe$_3$O$_4$/GO to make a heterogeneous solution. 0.05g of Polyacrylonitrile PAM was sonicated for 1 hour in 50 ml distill water. 1g GO/Fe$_3$O$_4$ was dissolved in the dispersion and agitated for 2 hours at room temperature. Following that, the compound was dried at room temperature for 24 hours.

2.6 Preparation of photocell

A copper coil encircled by the external cell by drop surface and coupled to them water bath was provided with a stainless steel pipe with a 1cm diameter and 15 cm length, see Figure 5. The temperature of the reactor and the lamp solution should be kept under control. The inner cellular surface was first treated with strong HF acid to make it rough and capable of capturing the casing, and then, the cell was entirely coated with PAN/Fe$_3$O$_4$/GO composite for 10 minutes to allow the production of a stable layer, and then the suspension was released from the reactor. To make the catalytic layer more stable as a coating, the photo reactor displays to 500ºC in the inner reactor surface.
3. Results and Discussion

3.1 Atomic Force Microscope (AFM)

AFM analysis provides the measurements of average grain size and the granularity cumulating distribution for GO/ Fe$_3$O$_4$ and PAN/ Fe$_3$O$_4$ /GO composites. The average diameter is 182.97 nm and 203.85 nm for GO/ Fe$_3$O$_4$ and PAN / Fe$_3$O$_4$ /GO composites, respectively. Figure 6 shows the atomic force microscopy image for: A) GO/ Fe$_3$O$_4$ composite and B) PAN/ Fe$_3$O$_4$ /GO composites.

![Atomic force microscopy image of: A) GO/ Fe$_3$O$_4$ and B) PAN/Fe$_3$O$_4$/GO](image)

3.2 Effect of Initial Concentration

To study the effect of initial concentration of dye on the degradation efficiency, the experiments were conducted with different initial concentrations of (3-21) ppm at pH=7, at a temperature of 298K and 5×10$^{-3}$ M of H$_2$O$_2$ + catalyst PAN/ Fe$_3$O$_4$/ GO composites (which
was used after 60 min). The increase of degradation percentage in each time with the decrease of M.B concentration and reach the highest value of 99.3% for 3 ppm M.B dye concentration. This phenomenon can be explained according to the indication that the number of the dye molecules will be increased with constant number regarding •OH. Also, with the increase in dye’s initial concentrations, extra molecules have been adsorbed onto catalyst’s surface [31], leading to decreasing in oxidation process, as shown in Figure 7.

![Figure 7](image-url)

**Figure 7**- variation of (% deg) with time for different M.B concentration at 298K, pH=7 and H$_2$O$_2$ 5*10$^{-3}$ M by PAN/Fe$_3$O$_4$/GO catalyst

### 3.3 Effect of H$_2$O$_2$ Concentration

The effect of H$_2$O$_2$ concentration on M.B dye degradation at temperature of 289K, pH=7, after 30 min in presence of catalyst PAN/Fe$_3$O$_4$/GO composite were studied, the % deg increases with H2O2 concentration increased which is shown in Figure 8.

![Figure 8](image-url)

**Figure 8**-Effect of varying H$_2$O$_2$ concentration for different M.B concentration after 30 min, at 298K, pH=7 on PAN/Fe$_3$O$_4$/GO composite catalyst
3.4 Effect of Temperature

The influence of temperature on 3 ppm M.B percent deg by PAN/Fe3O4/GO composite at four different temperature of (298, 308, 318, and 328)K at pH=7 was examined. The deterioration of M.B increased as the temperature increased, as seen in Figure 9.

![Figure 9: Variation of 3 ppm M.B %deg by PAN/Fe3O4/GO composite with different temperature](image)

3.5 Kinetic Degradation Study

Using a PAN/Fe3O4/GO composite, the first order equation (1) was applied to a 3 ppm M.B degrading process with an H2O2 concentration of 0.005 M: When and where: C0: initial M.B concentration, Ce: M.B concentration following UV exposure at Time(t). Figure 10 depicts the linear relation between ln Ce and time for 3 ppm M.B dye degradation at four temperatures.

\[ \ln C_e = \ln C_0 - K \cdot t \] ...........(1)

![Figure-10: lnCe V.S time for the degradation of 12 ppm M.B at four temperatures by using Triple catalyst PAN/Fe3O4/GO composite.](image)
Figure 11- Arrhenius plots, relation lnk with 1/T for the 12 ppm M.B %deg. PAN/ Fe3O4/GO composite.

Arrhenius equation was applied to calculate kinetic parameter A, Ea. (Figure 11) as following [32]:

\[
\ln k = \ln A - \frac{Ea}{RT}
\]

Where T: is the absolute temperature (in kelvins), k is the rate constant, Ea is the reaction's activation energy (in kJ mol\(^{-1}\)), A is the pre-exponential factor, and R is the global gas constant.

The activation energy (also known as the minimum energy necessary to initiate a chemical reaction) of degradation is represented by Ea, while the pre-exponential factor in the rate equation is represented by A.

Table 1 shows the values of Ea and A obtained from the slope and intercept of the Ln k versus 1/T plot.

Table 1- Kinetic parameter for PAN/ Fe3O4/GO composite

<table>
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<tr>
<th>T(K)</th>
<th>k(min(^{-1})10(^{-3}))</th>
<th>ln k</th>
<th>Ea/kJ.mol(^{-1})</th>
<th>A (min(^{-1}))</th>
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<td>298</td>
<td>13.2</td>
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<tr>
<td>308</td>
<td>28.0</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>-3.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>36.9</td>
<td>-3.29</td>
<td>23.739</td>
<td>216.8</td>
</tr>
</tbody>
</table>

3.6 COD (Chemical Oxygen Demand) Test

COD is a commonly used as a metric method for measuring the contaminants in wastewater and natural waterways[33]. COD was eliminated by 9 mg/L of PAN/Fe3O4/GO composite. After 90 minutes of irradiation time for a concentration of 3 ppm M.B at pH=7, temperature 298K- and 0.005M H\(_2\)O\(_2\). Under the same settings, after two and a half hours, this result dropped to zero.

Conclusions

In conclusion, the degradation capability of Methylene Blue dye on PAN/ Fe3O4/GO composite as catalysts was studied. AFM was used to characterize the composite, including its average diameter and shape. The particle size increases after adding GO/ Fe3O4
composite to PAN, and the percent degradation efficiency for M.B increases. Using a PAN/Fe3O4/GO composite as a catalyst, the Photo-Fenton method was effectively used to remove the contaminants dye. The optimum irradiation time was determined to be 90 minutes. The pH impact revealed that pH=7 had the best degradation of M.B dye on PAN/Fe3O4/GO composite. The degradation of M.B dyes on the PAN/Fe3O4/GO composite increased with increasing temperature, according to the temperature impact data. After the dye solution has been subjected to irradiation for a longer amount of time, the color has been totally eliminated and the dye has been transformed into organic material (COD test after 2h is low or under range). M.B dye degradation on PAN/Fe3O4/GO composite was well interpreted with the first order, according to the kinetic research findings. Finally, the utilized approach (photo Fenton procedure) is suggested for the treatment of organic compound-containing wastewater.

References


