TOXICITY REDUCTION OF REACTIVE METHYL ORANGE DYE FROM WASTE WATER BY USING AOP

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ABSTRACT:

By using a simple situ way TiFeGO nanocomposite was prepared from various limited of Graphene oxide nanosheets, Titanium (IV) oxide(Titania) and Iron oxide nanoparticles. The performance of TiFeGO nanocomposite as photocatalyst agent was inspected by using it in photodegradation processes (AOP advanced oxidation processes), to decolorization of Methyl Orange dye (MO) under sun radiation. A removal activity of MO dye experiments at different temperatures and the increases with increasing of temperatures, it could be gained 82% at 309 K within 600 min. Antibacterial activities of TiFeGO nanocomposite, the positive and negative control were tested versus three human pathogenic bacterial strains, (Staphylococcus aureus, Bacillus spp and Pseudomonas aeruginosa).

Keywords: Nanocomposite as photocatalyst, AOP, MO dye decolorization, Antibacterial activities.

1. INTRODUCTION

The pollutants are most present in waste water from Dyes, petrochemicals and pesticides industries. They can be transfer to the environment that may cause healthy problems for humans. There are many classical ways for removing dyes like oxidation [1], adsorption[2,3], coagulation[4], flocculation, as well as membrane separation [5,6], and advanced oxidation processes (AOP) or photocatalysis method [7].

lately, several articles have reported Effectively eliminate these organic pollutants by using photocatalysts. (8). Therefore, it is more desirable to manufacture photocatalysts. It can work efficiently under sun light.

photocatalysis processes (advanced oxidation processes AOP) have been designed for the removal of organic pollutants, which have lower biodegradable, [9], they involve in situ reproduction of potent chemical oxidants with presence of UV light. The generated radicals (·OH) are highly strong oxidants that are able to oxidize organic pollutants. AOP exhibit many features as: (i) removing of the toxicity of organic, (ii) fast degradation rate (iii) work under normal conditions and (iv) convert organic pollutants materials to green materials [10]. Between different Semiconducting metal oxides, TiO₂ and ZnO have been most used to degenerate the polluted dyes due to their special properties [11]. Titania (TiO₂) is the most great using as photocatalyst because of its efficacy, chemical stability and low cost, it has a high band gap (3.03V) [12]. TiO₂ engaged considerable interest for their novel properties, which are suitable for a widely of applications. Titania has three polymorphs, anatase, rutile as well as brookite. through these three types, the first one is the most using as photocatalyst, which is evolved by many factors as its large surface area and high crystallinity[13].

The efficiency can be increased by doping with metals and nonmetals and carbon materials (14). presently, many scientists report improvement to perform the photocatalysis via hybridization with different carbon materials. As a increasing carbon star materials, graphene oxide attract high attention because special properties like high surface area, high transparency and high electronic conductivity, Mobility [15]. Her many attempts It was synthesized to combine GO with the photocatalyst to increase its photocatalytic efficiency[16].

Magnetic nanoparticles MNPs have drawn a big interest in various applications during the latter years due to their unique properties, specially highly magnetism, easy surface modification and the large ratio of surface area to volume. The high magnetic properties of Fe₃O₄ nanoparticles canable the manipulation of these materials by using an external magnetic field[17-19].
the aim of this work determining the potentiality of a (TiFeGO) nanocomposite as a photocatalyst (which were acquired by a simple situ approach depending on the previous research[20], for decolorization of Methyl Orange dye (MO) from a water. MO dye is a pH indicator which used in titration processes due to its clear and apparent color difference at various pH ranges. MO exhibits yellow color and red color in basic medium and acidic medium, respectively[21]. Table 1 contain some properties of Methyl orange dye and figure 1a shows the chemical structure.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C₁₄H₁₄N₃NaO₃S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>327.33 g/mol</td>
</tr>
<tr>
<td>Color and appearance</td>
<td>Orange or yellow solid</td>
</tr>
<tr>
<td>Density</td>
<td>1.28 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>&gt; 300 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>Decomposes</td>
</tr>
<tr>
<td>Solubility</td>
<td>5 g/L (20 °C)</td>
</tr>
</tbody>
</table>

II. EXPERIMENTAL

2.1 Synthesis

concentrated Sulphoric acid (H₂SO₄), graphite, KMnO₄ and NaNO₃ from (Sigma Aldrich). Titanium (IV) oxide (Titania) TiO₂ nanoparticles from (Hongwu International Group Ltd company, China), Iron chloride (FeCl₃ 98%) and iron sulphate (FeSO₄·7H₂O 97%) from (Sinopharm Chemical), Hydrochloric acid (HCl) (37%) from (ROMIL-SA) company, Sodium hydroxide (NaOH) (98%) (Applichem GmbH, Germany), The materials used here without any purification.

A GO fabricated by used Hummers approach [22]. FeGO and TiFeGO nanocomposites were syntheses according to the way in a previous studied [23,24].

2.2 Photocatalytic processes

Photocatalytic processes were done with UV radiation. Through all tests of (MO) dye degradate processes, the temperature was (289-309K). Six volumetric flasks which contain (50 mg) of TiFeGO was mixed with (50ml) of 10ppm Methyl Orange (MO) dye solution, then was shaking at about 100 rpm in the dark for 60 minutes (from figure 1c) to reach the equilibrium before the Photocatalytic experiments. During the degradate processes, flasks were withdrawn at periodic time then the photocatalyst molecules were separated by using the applied magnetic field, the residue Methyl Orange dye (MO) amount was calculated by used UV- Visible instrumental at 480nm (figure 1b), while figure 1d shows the calibration curve of (MO) dye solution.
2.3 Antibacterial activity (Agar well diffusion way)

Antibacterial activities of TiFeGO nanocomposite as well as the positive and negative control were tested against three human pathogenic bacterial strains, contain of (Staphylococcus aureus) Gram positive as well as (Bacillus spp and Pseudomonas aeruginosa) Gram negative by using disc diffusion way according to the following procedure [25], the suspension of the tested microorganism containing 10^8 CFU/ml was fabricated as well as spear ed on Mueller Hilton agar, filter paper discs (the diameter is 6 mm) were impregnated with 10 μl of samples and putted on the inoculated plates at 37°C for 24 hours. Active nanomaterial (about 10μg/disc) was used as a positive control P. control and water as a negative control N. control. The activity of antibacterial of TiFeGO nanocomposite was calculated by measuring the inhibition zone diameters of including disc (mm), then the result of the inhibition zones was compared with these of the controls.

III. RESULTS AND DISCUSSION

3.1 Photo Degradation of Methyl Orange (MO) dye

The heterogeneous photocatalytic oxidation contain several steps: The pollutant materials prevail on the surface of photocatalyst, then adsorption of pollutants on this surface, following steps is oxidation and reduction in the adsorbed surface. Desorption and removal of the products from the interface bond.

The degradation of Methyl Orange (MO) dye at presence of TiFeGO nanocomposite as photocatalyst was studied. The mechanism of the (MO) dye degrade process at presence of TiFeGO nanocomposite and sun light is proposed in the several steps [26,27]:

\[
\begin{align*}
\text{TiO}_2 + \hnu (\text{UV}) & \rightarrow \text{TiO}_2 (e^{-_{\text{CB}}} + h^{+_{\text{VB}}}) \\
\text{TiO}_2 (h^{+_{\text{VB}}}) + \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + \text{H}^+ + *\text{OH} \\
\text{TiO}_2 (h^{+_{\text{VB}}}) + \text{OH}^{-} & \rightarrow \text{TiO}_2 + *\text{OH} \\
\text{TiO}_2 (e^{-_{\text{CB}}}) + \text{O}_2 & \rightarrow \text{TiO}_2 + \text{O}_2^{-} \\
\text{O}_2^{-} + \text{H}^+ & \rightarrow \text{HO}_2^{-} \\
\text{HO}_2^{-} + \text{HO}_2^{-} & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{TiO}_2 (e^{-_{\text{CB}}}) + \text{H}_2\text{O}_2 & \rightarrow *\text{OH} + \text{OH}^{-} \\
\text{H}_2\text{O}_2 + \text{O}_2^{-} & \rightarrow *\text{OH} + \text{OH}^{-} + \text{O}_2 \\
\text{H}_2\text{O}_2 + \hnu & \rightarrow 2*\text{OH} \\
\text{OH} + \text{R} & \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

Figure(1): (a) Chemical structure, (b) UV- Visible Spectrum, (c) Equilibrium time (d) Calibration curve of Methyl Orange (MO) dye.
The residual amounts of Methyl Orange in the solution was determined by used spectrophotometer at $\lambda_{\text{max}}$ of MO dye. The results for this process shown in Figure (2) and table 2.

Table 2: MO Photocatalytic Data

<table>
<thead>
<tr>
<th>t/min</th>
<th>289K</th>
<th>299K</th>
<th>309K</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$C_t$</td>
<td>$C_t/C_0$</td>
<td>$R%$</td>
</tr>
<tr>
<td>-60</td>
<td>10.550</td>
<td>1.000</td>
<td>000</td>
</tr>
<tr>
<td>0</td>
<td>10.240</td>
<td>0.971</td>
<td>2.887</td>
</tr>
<tr>
<td>120</td>
<td>8.735</td>
<td>0.828</td>
<td>17.200</td>
</tr>
<tr>
<td>240</td>
<td>7.999</td>
<td>0.758</td>
<td>24.18</td>
</tr>
<tr>
<td>360</td>
<td>6.565</td>
<td>0.622</td>
<td>37.770</td>
</tr>
<tr>
<td>480</td>
<td>4.877</td>
<td>0.462</td>
<td>53.770</td>
</tr>
<tr>
<td>600</td>
<td>4.039</td>
<td>0.383</td>
<td>61.710</td>
</tr>
</tbody>
</table>

Figure 2 observed that TiFeGO nanocomposite exhibit so high photocatalytic efficiency to removing Methyl Orange (MO) dye from its solutions , this may be returned to raised surface area due to which increasing active sites are available for photocatalytic processes to happen. The is raising with time due to the produce of free radical increases with time by display the UV light on the surface of photocatalyst. The photodegradation of Methyl Orange was pointed in 600 minutes at existence of nanocomposites. TiFeGO nanocomposite is the more elevated photocatalytic active because the delocalization of pi electrons of GO and iron oxide, which is transfer into the conduction band of TiO2 nanoparticles. The decolorization of Methyl Orange solution at existance of TiFeGO was carried out under several temperatures (289-309K). The percentage of removal efficiency was found low at 289k and raising with the temperature of Methyl Orange solution, the Photodegradation efficiency is increased at 299k, then at 309k, which is caused by the increasing of the speed of the reaction with temperatures.

3.2 TiFeGO Antibacterial Efficacy

Antibacterial activities of TiFeGO nanocomposite , the positive and negative control were tested versus three human pathogenic bacterial strains, (Staphylococcus aureus ,Bacillus spp and Pseudomonas aeruginosa ), and antibacterial effect results were estimated in terms of zone of inhibition (table 2 and figure 3). Results which obtained from TiFeGO antibacterial efficacy appeared that the TiFeGO nanocomposite displayed a low bactericidal effect against all the bacterial strains which used in this study.

![Figure 2](image-url)
Table 3: Antibacterial activities of TiFeGO nanocomposite.

<table>
<thead>
<tr>
<th>Bacterial species</th>
<th>P. control 10mg/ml</th>
<th>N.control 10mg/ml</th>
<th>TiFeGO 120mg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Staphylococcus aureus</em></td>
<td>11mm</td>
<td>-ve</td>
<td>3mm</td>
</tr>
<tr>
<td><em>Bacillus spp</em></td>
<td>14mm</td>
<td>-ve</td>
<td>5mm</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>8mm</td>
<td>-ve</td>
<td>1mm</td>
</tr>
</tbody>
</table>
The performance of TiFeGO nanocomposite (which prepared from limited amount of GO nanosheets, TiO2 and F3O4 nanoparticles), as photocatalyst in to removing the Methyl Orange dye (MO) under sun light is assessed in this study. The tests happened at several temperatures The percentage of removal efficiency was found low at 289k and araising with the temperature of Methyl Orange solution, the Photodegradation efficiency is increased at 299k, then at 309 k, which is caused by the increasing of the speed of the reaction with temperatures. The efficiency of MO photodegradation could be obtained 82% at existence of TiFeGO as photocatalyst within 600 minutes at 309k. Results which obtained from TiFeGO antibacterial efficacy appeared that the TiFeGO nanocomposite displayed a low bactericidal effect against all the bacterial strains which used in this study.

**REFERENCES**