Photodegradation of lauth's violet dye using GO-Fe₃O₄-TiO₂ nanocomposite under solar light

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Abstract. TFGO nanocomposite was synthesized from limited amounts of Titanium dioxide nanoparticles and Iron oxide nanoparticles as well as Graphene oxide nanosheets, by a situ method preparation. The producing materials were identify by (FTIR) and (AFM). The photocatalysis activity of TFGO nanocomposite was investigated by applying it in advanced oxidation processes (AOP) to degradation of Lauth's violet or Thionine acetate (LV) dye under solar light. The photodegradation efficiency of LV dye could be gained 98% at existance of TFGO nanocomposite as photocatalyst within 320 min. Photocatalytic processes experiments were happen at different effects like temperatures and existence of light.

Keywords: photocatalysts, AOP, TFGO nanocomposite, Thionine acetate, Lau th's violet.

1. Introduction

Organic pollutants are widely found in the effluents from the different industries like petrochemical, dyestuff, leather, cosmetics, papers, food and pesticide industries[1], which are caused clear hazards and serious health problems[2]. Recently, many studies have reported the efficient elimination of these organic contaminants using classical methods of removing these pollutants such as coagulation[3], adsorption[4,5], flocculation, oxidation [6], membrane separation [7,8], as well as photocatalysts [9]. Photocatalysis is an advanced oxidation (AOP) process which is applied for degradation of diverse pollutant under solar light. So, it is more desired to prepare photocatalysts that can worked efficaciency under natural light.

Among several photocatalysts, titanium dioxide (TiO₂) is a semiconductor, and it is the particularly suitable material for common applications such as energy storage, photocatalysis and wide range of environmental applications[10].TiO₂ is an environmental-friendly material, non-toxic, stable in aqueous solutions, relatively inexpensive, strong oxidizing power, having high chemical inertness, high thermal stability and photostability [11,12].

However the widely energy gap, the slow transfer rate of electrons to oxygen and the high recombination rate of the generated charge carriers, that lead to limited the efficiency of TiO₂ as photocatalyst[13].

The efficiency of TiO₂ as photocatalyst can be often enhanced by coupling TiO₂ nanoparticles with any other semiconductor and merged with the materials which accepting the electrons, like carbon nanostructures[14].

In this research, (TFGO) nanocomposite (consist of different amounts of GO nanosheets, Fe₃O₄, and TiO₂ nanoparticles) was prepared by using a self-assembly way at normal conditions. The efficiency of the TFGO composite for the Lauth's violet LV dye degradation is studied and the related photo-
Fenton degradation and mineralization mechanisms are discussed. Having removed the dye, (TFGO) nanocomposite was removed by the magnetic separation.

2. Experimental

2.1 Fabrication of TFGO nanocomposite

The chemicals which used in our study from Sigma Aldrich and without any purification. The anatase TiO2 nanoparticles were purchased from Hongwu International Group Ltd- China, and their size are about 30 nm-50 nm. The graphene oxide (GO) nanosheets were prepared by using a modified Hummers way as illustrated in Scheme 1 [15], and the FGO nanocomposite was obtained by self-assembly way according to the literature [9]. The synthetic procedure for the FGO nanocomposite nanocomposite is illustrated in Scheme 2, while TFGO nanocomposite which consist of limited amounts of FGO nanocomposite and titanium dioxide nanoparticles.

Thionine acetate (thionine chloride) or Lauth's violet [16], IUPAC name is 3,7-Diaminophenothiazin-5-ium (A molecular formula C_{12}H_{10}N$_3$S, molecular structure as in figure 1, and the molar mass is 228.29 g·mol$^{-1}$), which used in our research were obtained from BHD.

![Figure 1. The molecular structure of Lauth's violet dye](image-url)
Scheme 1. Illustrative procedure for synthesis the Graphene oxide (GO) by using a modified Hummers way

Graphite Powder(0.5) + H₂SO₄ (25ml) → After 15 min → NaNO₃ (0.5 gm) → Very slowly add KMnO₄ (3 gm) → Slowly add DI water (50 ml) → After 30 min → Raise the temp To 35 °C → After 72 h → Quenching with a mixture DI water (50 ml) and H₂O₂ (1.5 ml, 35%) → After 30 min → Centrifuge and washing until the pH of the solution is ~7

After 15 min

After 24 h

After 72 h

NaOH (150 ml) stirring with magnetic in temp 80°C

Scheme 2. Illustrative procedure for synthesis FGO nanocomposite

GO (0.3 g) + HCl (100 ml) → After 15 min → FeCl₃ (2.8 g) → Stirring with magnetic → After 24 h → FeSO₄·7H₂O (2.4 g) → After 72 h → Centrifuge and washing until the pH of the solution is ~7

2.2. Test of Photocatalysis Efficiency
The photocatalytic efficiency of the prepared catalyst (TFGO nanocomposite) were evaluated with sun light as UV irradiation source by photocatalytic degradation in LV aqueous solution. During all experiments of BG dye degradation, the temperature was (35°C). 8 samples contain (0.05g) of catalysts (TFGO nanocomposite) was added to the 50 ml of (10 ppm) LV solution, and they shaking at 100 cycle min⁻¹ in the dark for 70 min to reach the adsorption-desorption equilibrium (shown in Fig. S2) before the catalytic activity test. Subsequently, the heterogeneous Photocatalytic process was started when the samples was putted under sun radiation and of catalysts (TFGO nanocomposite) was added. Then, the samples were withdrawn at limited time intervals and the Photocatalysis were removed by the magnetic separation, and the residual LV dye concentration was determined by using Visible spectroscopy at 599 nm[9].
3. Results and Discussion

3.1 Characterization

The atomic force microscope (AFM) analysis measure the surface structure with high accuracy up to parts of the nanometer in addition to measuring the granular size [17-19]. AFM analysis and the particle size distribution of (GO nanosheets) are show in figure 3 with size about (3 μm), and

**Figure 2.** FTIR analysis of prepared GO nanosheets, F$_2$O$_4$, TiO$_2$ nanoparticles, and TGO, TFGO nanocomposite. a=GO Nanosheets, b=FO Nanoparticles, c=FGO Nanocomposites, d=TiO$_2$ Nanoparticles, e=TFGO Nanocomposites.
thickness of (94 nm). In a three-dimensional image of graphene oxide sheets, with a maximum height of the particles equal to (392.16 nm) and the average diameter of a Bags equal to (822.18 nm), as shown in both the table (1) and (Figure 3) the distribution of the values of the size of nanoparticles and platelets plan for the distribution of these plates respectively.

![Figure 3. shows AFM analysis for GO Nanosheets.](image)

**Table 1** A particle size distribution for GO Nanosheets

| Diameter (nm) | Volume (%) | Cumulative (n%) | Diameter (nm) | Volume (%) | Cumulative (n%) | Diameter (nm) | Volume (%) | Cumulative (n%) |
|---------------|------------|----------------|---------------|------------|----------------|---------------|------------|----------------|
| 550.00        | 9.68       | 9.68           | 750.00        | 6.45       | 38.71          | 950.00        | 3.23       | 70.97          |
| 600.00        | 3.23       | 12.90          | 800.00        | 6.45       | 45.16          | 1000.00       | 16.13      | 87.10          |
| 650.00        | 3.23       | 16.13          | 850.00        | 12.90      | 58.06          | 1100.00       | 6.45       | 93.55          |
| 700.00        | 16.13      | 32.26          | 900.00        | 9.68       | 67.74          | 1250.00       | 6.45       | 100.00         |

It is also possible to observe (AFM) examination of the iron oxide nanoparticles that were subsequently deposited on the surface of the graphene oxide as the maximum height of is (7.86 nm) as shown in Figure (4), and the prevailing diameter rate is equal to (70.63 nm), after depositing the nanoparticles of magnetic iron oxide on the surface of the graphene oxide we notice a change in the size of the particles as the maximum height of particles (34.41 nm) as shown in Figure (5), and that the dominant diameter of the nanocomposite (FGO) is equal to (80.43 nm) as shown in Figure (5).

![Figure 4. shows AFM analysis for Fe₃O₄ Nanoparticles](image)
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3.2. photo degradation efficiency

The photo degradation of LV dye in the existence of TFGO nanocomposite as photocatalyst agents was studied under solar light energy. The residue amount of LV dye in the reaction blend was calculated by using spectrophotometer. The results gained for the degradation of LV dye be seen in Figures 8, 9. The eminent degradation of LV dye was in 320 min study in the existence of TFGO.
nanocomposite in comparison to the other photocatalyst agents. Photocatalytic processes experiments were happen at different like effects of Photocatalysis, temperatures and existence of sun light. The removal efficiency of TFGO nanocomposite was calculated using equation[20]:

$$ R\% = (C_0 - C_t/C_0) \times 100 $$

(1)

$C_0, C_t$ are initial and final concentration of LV dye in the solution, then the results tabulated in table 1.

**Table 1. The Photocatalytic Data of TFGO nanocomposite as photocatalyst**

| T(min) | T(298K) | T(308K) | T(318K) | T(298K) dark |
|--------|---------|---------|---------|-------------|
|        | C_t     | C_t/C_0 | R%      | C_t        | C_t/C_0 | R% | C_t | C_t/C_0 | R% |
| -60    | 0       | 1       | 0       | 1          | 0       | 58.6 97 | 0   | 58.6 97 | 0   |
| 0      | 8.863   | 0.798   | 11.097  | 52.184     | 0.73 7  | 20.1 04 | 44.5 59 | 0.8 05 | 24.0 86 | 53.7 17 | 0.915 86 |
| 120    | 8.049   | 0.725   | 24.740  | 44.176     | 0.15 2 | 28.7 21 | 40.2 10 | 0.7 66 | 31.4 62 | 50.3 07 | 0.857 14.295 |
| 240    | 6.318   | 0.569   | 26.436  | 43.180     | 0.11 0 | 38.9 03 | 31.5 71 | 0.7 36 | 46.2 14 | 48.3 91 | 0.824 17.559 |
| 360    | 3.857   | 0.347   | 31.332  | 40.307     | 0.07 4 | 52.4 80 | 17.3 56 | 0.7 29 | 70.4 31 | 45.5 94 | 0.777 22.324 |
| 480    | 2.879   | 0.259   | 45.300  | 32.107     | 0.06 9 | 70.0 39 | 9.84 7 | 0.7 28 | 83.2 25 | 42.3 76 | 0.722 27.807 |
| 600    | 2.375   | 0.214   | 61.423  | 22.644     | 0.05 6 | 81.1 36 | 6.85 8 | 0.7 18 | 88.3 16 | 40.9 58 | 0.698 30.221 |

a. Effect of Sun Lights Presence

The photodegradation reaction of LV dye in existance of TFGO nanocomposite as photocatalyst was studied at presence of sun light or at the dark. From the results which exhibit in Figure 24 that shown the TFGO nanocomposite at the presence of sun light are proving as an more efficient photocatalyst for the degradation of LV dye compared with putting LV dye solution at dark
b. Effect of Temperatures

The photodegradation reaction of LV dye solution in existence of TFGO nanocomposite as photocatalyst was also carried out under varying temperature conditions from (298 to 318k), (Figure 9). The percentage of Photodegradation efficiency was found to very low at 298k for TFGO nanocomposite, and then increases at 308k, and then at 318k, this is due to the increase in the speed of the photodegradation reaction with increasing temperatures.
4. Conclusion: The purpose of this article was to describe that, prepared FGO and TFGO nanocomposite from limited amount of GO nanosheets, F$_3$O$_4$ nanoparticles, TiO$_2$ nanoparticles. The prepared materials and components were characterized by using many advises like (FTIR) and (AFM). The performance of prepared materials and components as photocatalyst was investigated by applying them in advanced oxidation processes (AOP) to degradation of BG dye under solar light. The photodegradation efficiency of LV dye could be gained 98% at existence of TFGO nanocomposite as photocatalyst within 320 min. Photocatalytic processes experiments were happen at different effects like Photocatalysis, temperatures and existence of sun light.

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Figure 9. The photo degradation of LV dye in existance of TFGO nanocomposite as photocatalyst at different temperatures.

(a) 

(b) 

(c)
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