# SYNTHESIS OF THE MAGNETIC ADSORBENT BASED OF GRAPHENE OXIDE AND ZNO NANOPARTICLES FOR ENVIRONMENTAL APPLICATIONS

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***Abstract:*** In this study $Fe_3O_4$-ZnO and GO-$Fe_3O_4$-ZnO are synthesized as photocatalysis for decomposition of of methyl orange (MO) as organic dye pollutant model. The XRD results show that the prepared nanocomposites contain the modified GO with cubic structure of $Fe_3O_4$ and hexagonal wurtzite structure of ZnO nanoparticles. The photocatalytic results show that the degradation of MO using both of the synthesized photocatalysts enhances with respect to the time and weight fraction. The removal efficiency of MO using GO-$Fe_3O_4$-ZnO at each concentration and irradiation time is more than that of $Fe_3O_4$-ZnO.

***Keywords:*** GRAPHENE OXIDE; FE3O4; ZNO; REMOVAL EFFICIENCY

## *1. Introduction*

The application of different semiconductors as photocatalyst has been widely investigated for elimination of organic pollutants from the wastewater. The importance of the semiconductor photocatalysts such as $TiO_2$, $SnO_2$ and ZnO in the environmental purification may be due to the application of them in the ambient conditions [1]. The decomposition of the organic pollutants such as methylene blue (MB) and methyl orange (MO) using semiconductor photocatalysts can be initiated in the presence of a light supply and oxidant acting such as $O_2$ [2]. Among different kinds of the semiconductor photocatalysts, ZnO nanoparticles are known as more applicable photocatalyst. It can be due to its environmental friendly, wide band gap, inexpensive and chemical stability[3]. The illumination of the photocatalysts leads to the production of the electron and hole in the valence band and conduction band, respectively [4, 5].

The produced electron hole pairs ($h^+$ - $e^-$) in the dye organic solution can spread on the surface of the semiconductors and contribute into the reaction between organic pollutants and donor and acceptor of electron [6]. Because of this reaction, the different kinds of the oxidant species such as hydroxyl radicals are produce. Therefore, the surface enhancement of the photocatalysts can be effective in the separation of the generated electron hole pairs and degradation of the dye pollutants. Graphene is one of the carbon materials that have been great deal of interests due to the excellent properties such as electronic properties and high specific surface area. Thus, the presence of the graphene oxide (GO, containing functional groups such as hydroxyl and carboxyl) in the magnetic photocatalysts matrix can enhance the active surface area of the photocatalysts.

## *2. Experimental*

### *2.1. Materials*

For the synthesis of GO-$Fe_3O_4$ , 45 mg of GO is dispersed into 45 ml of Ethylene glycol and agitated for about 30 min. Then, 0.225 g of $Fe(acac)_3$ is disperesed to the suspension and mixed for about 30 min using an ultrasound bath at room temperature. Subsequently, 1.5 g $NH_4Ac$ is dissolved in the solution, followed by stirring for 30 min. Then, the obtained mixture is transferred into a 100 ml Teflon lined autoclave. The autoclave is sealed and kept at 200°C for 24 h. Afterward the autoclave is cooled to ambient temperature. The synthesized products are separated from the suspension using an external magnetic field. Finally, the separated powders are washed several times with distilled water and dried at 60°C for 12 h. For the synthesis of ZnO nanoparticles, 0.5 g of $ZnCl_2$ is dispersed in a suspesion containing 0.1g of GO-$Fe_3O_4$. After increasing the temperature to 90°C, 5.3 ml of aqueous solution of NaOH (5 M) is added drop wise under vigorous agitation. Subsequently, the precipitated powder is separated from suspension, washed several times with distilled water and dried at 80°C for 12 h. Finally, the dried powder is calcined at 300°C for about 3 h.

The photocatalytic measurements are carried out for degradation of MO (10 ppm MO aqueous solution) using a Hg vapor lamp (150 W) at different concentration of synthesized photocatalysts (0.1, 0.2 and 0.3 %wt). The concentration of MO at any intervals can be calculated according to the Equation 1[7].

$$Photocatalytic\ \text{performance}\ (\%) = \frac{A_0 - A_t}{A_0} \times 100 = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

The A and C refer to the absorbance and concentration of MO. The subscript of 0 and t refer to the initial and remainder parameter.

## *3. Results and discussion*

In the XRD pattern of the synthesized GO-$Fe_3O_4$-ZnO (Fig. 1), the presence peaks at $2\theta$=30.21°, 35.27°, 56.81° and 62.45° are assigned to the (220), (311), (511) and (440) reflections, respectively. The mentioned peaks are in agreement with the XRD pattern of $Fe_3O_4$ nanoparticles with a cubic structure. Meanwhile, the characteristic peak of GO can be observed at $2\theta$ value of 10.75°. In addition to the mentioned peaks, several peaks are centered at $2\theta$ values of 31.65°, 34.3°, 36.2°, 47.4°, 56.5° and 62.7° are assigned to the ZnO nanoparticles with the hexagonal wurtzite structure.

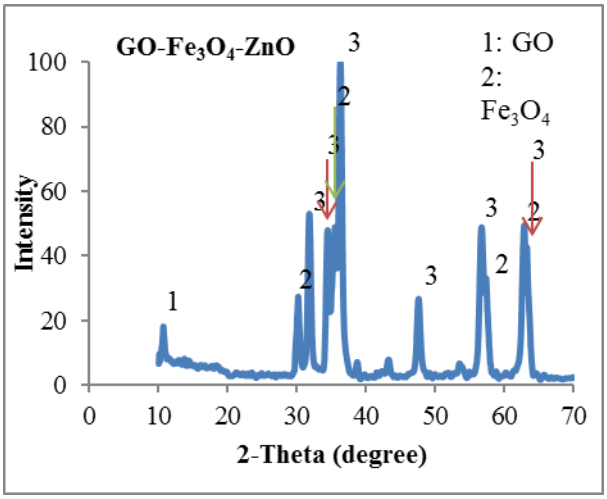


***Fig. 1****. XRD pattern of the synthesized GO-$Fe_3O_4$-ZnO.*

Fig. 2 and Fig. 3 show the variation of the removal efficiency of MO using $Fe_3O_4$-ZnO and GO-$Fe_3O_4$-ZnO, respectively. As can be seen, the removal efficiency of MO using both of the synthesized photocatalysts enhance with respect to the irradiation time and weight fraction of the applied photocatalyst. The enhancement of the removal efficiency of MO with respect to the irradiation time can be attributed to the production the large amount of excited electrons[8]. The variation of the removal efficiency of MO with

weight fraction of $Fe_3O_4$-ZnO and GO-$Fe_3O_4$-ZnO in the range of 0.1 %wt to 0.3 %wt reveals that the removal percentage of MO enhances by increasing the concentration of $Fe_3O_4$-ZnO and GO-$Fe_3O_4$-ZnO. It may be due to the enhancement of active sites of photocatalysts that are exposed to MO [9].

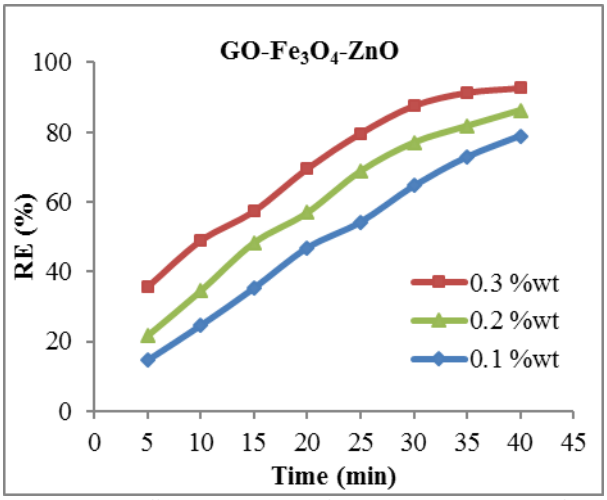


***Fig. 2.*** *Removal efficiency variation of MO using $Fe_3O_4$-ZnO, influence of weight fraction.*

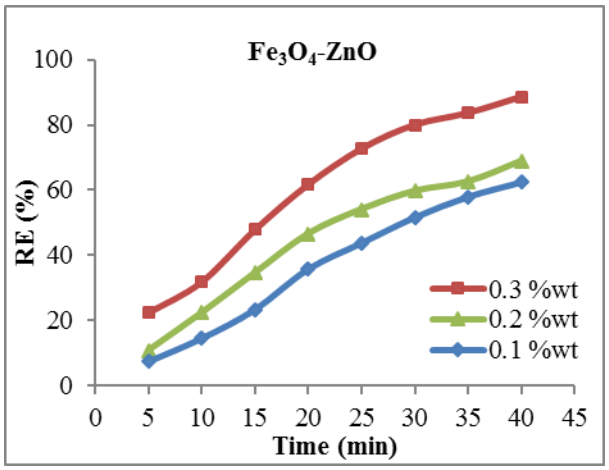


***Fig. 3.*** *Removal efficiency variation of MO using GO-$Fe_3O_4$-ZnO, influence of weight fraction.*

The comparison between removal efficiency of MO using $Fe_3O_4$-ZnO and GO-$Fe_3O_4$-ZnO is presented in Fig. 4. Based on this Figure, it can be seen that at concentration equal to 0.2 %wt and each interval of irradiation time, the removal efficiency of MO using GO-$Fe_3O_4$-ZnO is higher than that of $Fe_3O_4$-ZnO (the same results are obtained at the other concentrations). The higher photocatalytic activity of the synthesized GO-$Fe_3O_4$-ZnO is related to the presence of GO in the matrix of the photocatalyst. The produce electron-hole pairs in $Fe_3O_4$-ZnO are not stable and can be recombined and produce heat. It can decrease the photocatalytic performance of $Fe_3O_4$-ZnO. However, the presence of GO in the matrix of GO-$Fe_3O_4$-ZnO reduces the rate of electron-hole pairs recombination.

## *4. Conclusions*

Here, we applied magnetics adsorbents for degradation of MO. The synthesized adsorbents are characterized using XRD and the results confirm that ZnO nanoparticles and $Fe_3O_4$ nanoparticles are synthesized successfully on the GO sheets. The photocatalytic results reveals that irradiation time and weight fraction have a significant effect on the decomposition of MO. Meanwhile, the presence of GO in the structure of $Fe_3O_4$-ZnO leads to the enhancemet of removal efficiency of Mo.

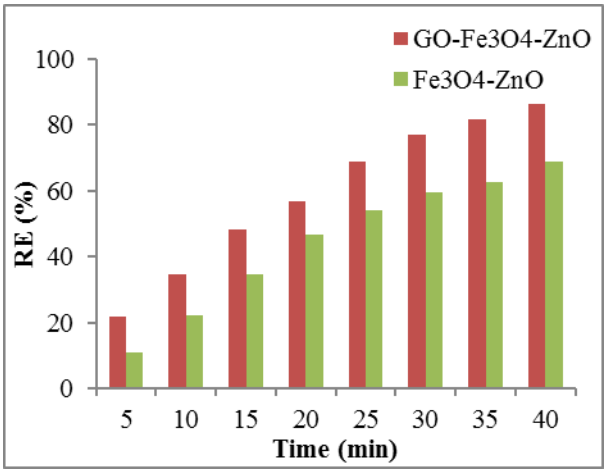


***Fig. 4.*** *Comparison between removal efficiency of MO using $Fe_3O_4$-ZnO and GO-$Fe_3O_4$-ZnO at 0.2 %wt.*

## *Acknowledgements*

We sincerely thank the Esfarayen University of Technology for its contribution to this study.

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