Development of Fe$_3$O$_4$/ZrO$_2$ Composite Powered by Nanographene Platelets (NGP) for Degradation of Water Pollutants via Photo- and Sonocatalysis

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Abstract. In this study, a series of Fe$_3$O$_4$/ZrO$_2$/nanographene platelets (NGP) composite, with various weight percent (wt%) of NGP (5%, 10% and 15%), were prepared successfully using ultrasonic-assisted followed by simple hydrothermal method. Their physicochemical properties were fairly characterized by X-ray diffraction, fourier transform infrared and thermal gravimetric analysis. Furthermore, their catalytic activities were investigated toward anionic congo red (CR) and cationic methylene blue (MB) as models of organic pollutant under ultraviolet (UV) and ultrasonic (US) irradiation, respectively. The experimental results showed that the incorporation of NGP in Fe$_3$O$_4$/ZrO$_2$ composite improved its efficiency in degrading CR and MB and became maximum at 10wt% of NGP. In addition, the role of active radicals involved in catalytic activities were discussed.

1. Introduction
Recently, semiconductor-based materials have been attracted great attention due to its application in various fields, such as hydrogen production, water purification and reduction of heavy metals [1-3]. Various types of semiconductor metal oxides such as TiO$_2$, ZnO, SnO$_2$ and ZrO$_2$ have been studied for their catalytic activity [4-7]. Among various metal oxides, zirconium dioxide (ZrO$_2$) play an important role due to several unique properties, such as excellent physical and chemical properties, low cost, high stability, chemical inertness, lack of toxicity and high specific surface area [8-10] that make it versatile for several applications, especially in water purification. Peng et al. [7] and Poungchan et al. [8] reported the photocatalytic degradation of organic pollutants in wastewater by ZrO$_2$. The reports demonstrated that ZrO$_2$ could degrade organic pollutants. Unfortunately, applications of ZrO$_2$ in water purification is hindered because of high recombination of photoinduced electron-hole pairs [11], which causes low catalytic performance, and difficult to recover from wastewater solution for recycle process, which causes low efficiency when applied in large-scale.

To solve mentioned problems many researchers used magnetite and carbon-based material graphene as support materials to make composites [8,12]. Magnetite material, such as Fe$_3$O$_4$, introduced into the composite in order to provide magnetic properties so it would make the composite become more easily recovered from the solution by external magnetic field [13]. Furthermore, the Fe$_3$O$_4$ is conductive which could improve separation of electron-hole pairs [14]. The carbon-based
material graphene has superior properties that make it greatly note, such as large specific surface area and good mobility of charge carriers, as well as good electrical and thermal conductivity [15-17]. Based on these properties, the role of carbon-based material graphene in the composite is an electron transport channel, which could inhibit electron-hole recombination, enhance separation of photogenerated electron-hole pairs and increase the number of active sites.

Over the last decade, photo- and sonocatalytic using semiconductor metal oxide as photocatalyst has caused attention in the treatment of organic pollutant. Because of many advantages, such as eco-friendly, did not cause any secondary pollutant, high efficiency and simple operation, they are considered as an efficient technique for degrading organic pollutants [18,19].

Based on these issues, in this paper, we attempt to synthesize Fe$_3$O$_4$/ZrO$_2$ composite through ultrasonic-assisted method, and then combined with NGP by simple hydrothermal methods as a superior photocatalyst for degradation of water pollutants. The ability of Fe$_3$O$_4$/ZrO$_2$/NGP with various wt% of NGP photocatalyst in degrading water pollutants was tested via photo- and sonocatalytic degradation of MB and CR under UV light and ultrasonic irradiation. In addition, influence of contact time, pH of solution, catalyst stability and effect of reactive species on the catalytic activities were also investigated and the results were discussed.

2. Experimental

Materials: All the chemical reagents were of an analytical grade and were used without further purification. Iron(II) sulfate heptahydrate (FeSO$_4$.7H$_2$O, 99%), zirconium(IV) chloride (ZrCl$_4$) and sodium hydroxide (NaOH) were purchased from Merck. NGP was purchased from Angstron Materials.

Preparation of samples: The Fe$_3$O$_4$ and ZrO$_2$ nanoparticles were synthesized using the same method as described previously [20,21]. The Fe$_3$O$_4$/ZrO$_2$ composites were synthesized using the ultrasonic-assisted method. Briefly, ZrO$_2$ nanoparticles were mixed with Fe$_3$O$_4$ in distilled water and ethanol mixture. Then, the mixed solution was given ultrasonic for 2 hours followed by centrifugation to obtain the product on its precipitation. The obtained product was dried in vacuum condition at 80°C for 12 hours to obtain Fe$_3$O$_4$/ZrO$_2$ composites, which labelled as FZ. The molar ratio of Fe$_3$O$_4$ to ZrO$_2$ is set 0.5:1. The FZ/NGP composites were synthesized using the simple hydrothermal method. Briefly, the NGP powder was dispersed in distilled water and an ethanol solution via ultrasonic treatment for 2 hours, which was followed by addition of the prepared FZ composites into NGP solution. The mixed solution was stirred for 1 hour. Then, the suspension was heated at 120°C for 3 hours to effect deposition on to the graphene sheets. The product was collected through centrifugation and was dried in a vacuum at 70°C for 12 hours in order for FZ/NGP composites to be obtained.

Characterization: X-ray Diffraction (XRD) performed on a Rigaku Miniflex 600 diffractometer with Cu Kα radiation (λ =1.5406 Å ) was used to obtain the crystal structure of samples. The infrared absorption spectra of samples were recorded using a fourier transform infrared (FT-IR). The thermal stability of samples was analyzed using a thermal gravimetric analysis (TGA).

Photo- and sonocatalytic activity: MB and CR were used as models organic pollutant. The photo- and sonocatalytic activity of samples was investigated via degradation of MB and CR in aqueous solution with the initial concentration of 20 mg/L at room temperature with UV light / ultrasonic, respectively. Firstly, the catalyst was dissolved into MB and CR solution, separately. The solution was continuously stirred in the dark for 30 minutes to ensure that an equilibrium was reached between the adsorption and desorption dyes molecules on the catalyst surface. Subsequently, the solution was exposed with UV light / ultrasonic, respectively. A small amount of the sample water was collected through centrifugation every 15 min to measure the MB concentration with UV-vis spectrophotometer. Two lamps of 40 W UV-C were used as UV light source and commercially ultrasonic bath which operated at fixed frequency and power of 40 kHz and 150 W was used as ultrasonic source.

Scavenger experiment: In order to determine the species involved in photo- and sonocatalytic activities, different radical scavengers were added to the solutions of MB and CR, separately. Di-
ammonium oxalate, sodium sulfate, and tert-butyl alcohol (TBA) were used as trapping agents for holes, electrons, and hydroxyl radical, respectively. The same measurements as described above were used.

3. Result and Discussion

Figure 1 (a) shows the XRD spectra of the FZ/NGP with various NGP wt%. For comparison, the XRD spectra of Fe$_3$O$_4$, ZrO$_2$ and NGP were also plotted. Peaks at $2\theta = 30.14^\circ$, 35.49$^\circ$, 43.28$^\circ$, 53.76$^\circ$, 57.20$^\circ$ and 62.83$^\circ$ were attributed to the cubic spinel phase of the Fe$_3$O$_4$, and peaks at $2\theta = 30.18^\circ$, 35.03$^\circ$, 50.36$^\circ$, and 59.94$^\circ$ were attributed to the tetragonal phase of the ZrO$_2$. In addition, graphitic-like structure of the NGP was detected at $2\theta = 26.49^\circ$, indicating the presence of NGP in the FZ composites. Furthermore, it can be seen also that the intensity of the NGP, increases as increasing wt% of NGP, indicating there is more NGP content in the FZ/NGP composite. No undesired peaks were detected by XRD, suggesting that the as-prepared samples have good purity.

Evaluation of the thermal stability of FZ and FZ/NGP composites with various NGP wt% were carried out by means of TGA under argon atmosphere, from ambient temperature until 1000°C, and the results are displayed in fig. 1 (b). The TGA plot showed the thermal degradation of the samples passed through one weight loss stages for FZ and two stages for FZ/NGP. The first weight loss, which took place below 150°C was attributed to the removal of adsorbed water [22]. The second weight loss in the region above 670°C corresponded to the combustion process of NGP in the FZ/NGP composite [23]. The percentage loss of the samples in region above 670°C could be identified as the total amount of NGP in the sample.

Figure 2 (a) represents FT-IR spectra of NGP, FZ and FZ/10% NGP. The broad band around 3400 cm$^{-1}$ and small band around 1400 cm$^{-1}$ correspond to the physical adsorbed water on the sample [24]. The characteristic features in the FT-IR spectra of NGP are the absorption bands corresponding to C=C and carboxyl groups vibration in range 1500 - 1630 cm$^{-1}$ [25]. The strong bands at 587 cm$^{-1}$ were assigned to Fe–O in the Fe$_3$O$_4$ phase [26]. The absorption band below 500 cm$^{-1}$ was attributed to the symmetric stretching vibrations of Zr–O–Zr [27].

The photo- and sonocatalytic of MB and CR were conducted to evaluate the ability of FZ and FZ/NGP with various NGP wt%. As we can see in fig. 2 (b) and fig. 3 (a), the incorporation of NGP could improve catalytic performance of FZ composite for degrading MB and CR, respectively. It is due to the superior properties of carbon-based material, such as large specific surface area and could inhibit recombination rate of electron-hole pairs, leading to increased catalytic performance [15-17].

![Figure 1](attachment:figure1.png)  
Figure 1. (a) XRD patterns of all prepared samples. (b) TGA plot of FZ and FZ/NGP with various wt% of NGP.
The catalytic performance of the sample increases as increasing NGP wt% until 10%, but at 15% it decreases. It might be due to excessive NGP content can causes agglomeration of NGP, causes a stacking and decrease of interlayer distance, leading to low electron conductivity and the light-harvesting competition between catalyst and NGP was intensified, leading to decrease in catalytic performance [28]. From the figure, it can be seen also that sonocatalytic could presents better catalytic performance than photocatalytic.

As an important variable in catalytic reactions, the effect of solution pH on the degradation reaction

Figure 2. (a) FT-IR spectra of NGP, FZ and FZ/10% NGP. (b) Catalytic activities of FZ and FZ/NGP various NGP wt% in degrading MB.

Figure 3. (a) Catalytic activities of FZ and FZ/NGP with various NGP wt% in degrading CR. (b) Effect of pH solution of FZ/10% NGP in degrading MB.
was investigated by maintaining pH of solution at 3, 5, 7, 9, 11 and 13. The results of pH effect on degradation reaction are plotted in fig. 3 (b) and fig. 4 (a). At higher pH, electrostatic attractions between the negative catalyst surface and MB cations lead to strong adsorption and enhancing degradation rate. Meanwhile, in anionic CR, there would be electrostatic repulsions between catalyst and CR, resulting in negligible adsorption and lower degradation rate. In the case of lower pH, the catalyst surface will be positively charged and hence the MB experience electrostatic repulsions, while the CR electrostatic attractions [29].

In order to investigate the role of the reactive radicals that involve in photo- and sonocatalytic activity, three typical chemicals, Di-ammonium oxalate (a quencher of hole), sodium sulfate (a quencher of electron), and TBA (a quencher of hydroxyl radical) were adopted as the scavengers at the optimum condition of both dyes, respectively. The result was shown in fig. 4 (b) and fig. 5 (a). The catalytic performance of MB and CR were obviously suppressed in the presence of Di-ammonium oxalate. In addition, sodium sulfate and TBA slight impeded the degradation of both dyes. It can be concluded that holes are the main active species for the degradation of MB and CR.
Easily recoverable and good reusability are superior advantages for their practical application in large scale. Therefore, it is quite necessary to investigate the reusability of the catalyst. Four cycles of MB and CR catalytic activities were performed with the same FZ/10% NGP to investigate its reusability, also at optimum condition. At the end of each run, the catalysts were separated by external magnetic field and reused in the next run for fresh MB and CR, respectively. Results are shown in the fig. 5 (b) and fig. 6. It is clear that the catalyst has good reusability and retains its activity the successive degradation reaction.

4. Conclusions
In summary, we reported a series of Fe$_3$O$_4$/ZrO$_2$/NGP composites with NGP wt% as photocatalyst for for degradation of water pollutants via photo- and sonocatalytic that characterized by XRD, TGA and FT-IR. Catalytic activities of prepared samples were investigated by degradation of MB and CR in aqueous solution. Compared to photocatalytic, sonocatalytic could presents better catalytic performance. The catalytic performance greatly increases with weight percent of NGP up to 15% and became maximum at 10%. Based on the effects of solution pH, cationic MB could be effectively degraded at alkaline condition, while anionic CR at acid condition. In addition, from scavenger experiment, it was concluded that holes have vital role in photo- and sonocatalytic degradation of both dyes. In the last, the composites have good reusability for successive four runs.

5. References
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