Enhancement of Photo- and Sonodegradation of Methylene Blue using Fe$_3$O$_4$/ZrO$_2$ by Adding Two Different Graphene Material

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Abstract. In this study, magnetite Fe$_3$O$_4$/ZrO$_2$/nanographene platelets (NGP) and Fe$_3$O$_4$/ZrO/graphene composites were prepared successfully by depositing the Fe$_3$O$_4$/ZrO$_2$ composites onto the surface of NGP and graphene using co-precipitation method as an effort to improve photo- and sonocatalytic performance. The structure and magnetic properties of the as-prepared samples were characterized by XRD and TGA. The catalytic activity of Fe$_3$O$_4$/ZrO$_2$/NGP and Fe$_3$O$_4$/ZrO$_2$/graphene composite towards methylene blue (MB) from the aqueous solution were investigated under UV light and ultrasound irradiation, separately. It was found that the incorporation of NGP and graphene in Fe$_3$O$_4$/ZrO$_2$ could greatly improve photo- and sonocatalytic performance. The incorporation of graphene with the higher surface area than NGP exhibits the best catalytic performance. In addition, scavengers of reactive species on the degradation activity were investigated.

1. Introduction
Due to widely used in industries, dye, such as methylene blue (MB), has become one of the most dangerous organic pollutant, because they are hardly degraded and has been suspected as mutagen and carcinogen [1,2]. Therefore, scientists proposed some techniques to degrade dyes from aqueous solutions, such as coagulation, electrochemical treatment and chemical oxidation. Compared to the other techniques, advanced oxidation processes (AOPs), such as photo- and sonocatalysis, using metal oxide semiconductor (MOS) have shown excellent removal of various contaminant dye [3].

Among the various of MOS, zirconium dioxide (ZrO$_2$) has been widely studied as a catalyst to support wastewater treatment due to their several reasons, such as high stability, non-toxicity, low cost, and environmentally-friendly [4,5]. Unfortunately, single metal oxide ZrO$_2$ has limitations such as high recombination rate, indicating low catalytic performance.

Recently, graphene as a two-dimensional material provides several unique properties such as high specific surface area, good electron acceptor and excellent charge carrier mobility [6-8]. Based on these features, depositing MOS into the graphene materials can effectively enhance separation of photogenerated electron-hole pairs, prevent their recombination rate, and increase the number of active sites, which is mean could improve catalytic performance. Another way to improve catalytic
performance by depositing MOS with magnetite material \((Fe_3O_4)\) because it could facilitate separation of the electron-hole pairs effectively [9]

In these regards, we tried to depositing \(Fe_3O_4/ZrO_2\) composites onto the surface of NGP and graphene via co-precipitation method. The photo- and sono-catalytic of both prepared samples were tested for the degradation of MB as an organic pollutant model. The aim of this work is to evaluate the influence of adding as-prepared composites on the graphene materials for degrade MB.

2. Experimental

Materials: All the chemical reagents were of an analytical grade and were used without further purification. Iron(II) sulfate heptahydrate \((FeSO_4\cdot7H_2O, 99\%)\), zirconium(IV) chloride \((ZrCl_4)\) and sodium hydroxide \((NaOH)\) were purchased from Merck. NGP \((S.A. 30 \text{ m}^2/g)\) and graphene \((S.A. 400 \text{ m}^2/g)\) were purchased from Angstrom Materials.

Preparation of samples: Step 1. The \(Fe_3O_4\), \(ZrO_2\) nanoparticles were synthesized using the same method as described previously [10,11]. Step 2. The \(Fe_3O_4/ZrO_2\) composites were synthesized using ultrasonic-assisted method. Briefly, \(ZrO_2\) nanoparticles were mixed with \(Fe_3O_4\) in aqueous and ethanol mixture. Then, the mixed solution was given ultrasonic for 2 h, followed by centrifugation to obtain the product on its precipitated. The obtained product was dried in vacuum at 80°C for 12 h to obtain \(Fe_3O_4/ZrO_2\) composites. Step 3. To coupled NGP and graphene with \(Fe_3O_4/ZrO_2\) composites same method as described in our previous publication was used [12].

Characterization: X-ray Diffraction (XRD) performed on a Rigaku Miniflex 600 diffractometer with Cu K-\(\alpha\) radiation \((\lambda =1.5406 \text{ Å})\) was used to obtain the crystal structure of samples and the thermal stability of samples was investigated using Thermal gravimetric analysis (TGA).

Photo- and sono-catalytic activity: MB was used as a model organic pollutant. The photo- and sono-catalytic activity of samples was investigated via degradation of an MB aqueous solution with a concentration of 20 mg/L at room temperature with UV light irradiation and ultrasound (US) irradiation, respectively. The catalyst was dissolved into MB solution. The solution was continuously stirred in the dark for 30 min to ensure that an equilibrium of adsorption/desorption. Subsequently, the solution was exposed to UV light and US irradiation, respectively. A small amount of the water sample was collected through centrifugation every 15 min to measure the MB concentration with UV-vis spectrophotometer. Two lamp of 40 W UV-C was used as UV light source and commercially ultrasonic bath which operated at a fixed frequency and power of 40 kHz and 150 W was used as an ultrasound source.

Scavenger experiment: In order to determine the species involved in photo- and sono-catalytic activities, different radical scavengers were added to the solutions of MB. Di-ammonium oxalate, sodium sulfate, and tertbutyl alcohol (TBA) were used as scavengers 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 patterns of all prepared samples. As seen, XRD patterns of NGP and graphene are quite different. NGP has a sharp peak at 26.49° indicating graphitic-like structure while graphene has a broad peak around 23° indicating amorphous structures [13]. The observed diffraction peaks at \(20 = 30.18^\circ, 35.03^\circ, 50.36^\circ, \text{and } 59.94^\circ\) correspond to the \([111], \[200], \[220], \text{and } \[311]\) plane, respectively, which can be readily assigned to the tetragonal phase of \(ZrO_2\). Meanwhile, peak at \(20 = 30.14^\circ, 35.49^\circ, 43.28^\circ, 53.76^\circ, 57.20^\circ \text{and } 62.83^\circ\) which shows each plane \([220], \[311], \[400], \[422], \[511] \text{and } \[440]\) of cubic spinel phase. The XRD patterns of FZ/NGP and FZ/graphene composites show the presence of cubic spinel phase of Fe_3O_4 and tetragonal phase of ZrO_2, followed by the addition of graphitic-like structure from NGP for FZ/NGP. However, no typical diffraction peaks of graphene are observed within the FZ/graphene composites, probably due to the low content (10wt\%) and relatively weak diffraction intensity of graphene. Furthermore, there were no characteristic peaks from other crystalline impurities that were detected by XRD, suggesting that the as-prepared samples have good purity.
Figure 1 (b) shows the typical TGA plot of FZ, FZ/graphene and FZ/NGP composite. As shown in fig. 1 (b), TGA plot of FZ exhibit one decomposition region while FZ/graphene and FZ/NGP exhibits two decomposition region to significantly weight loss upon the increase in temperature. The first one occurring in the temperature around 100°C, which can be attributed to the loss of absorbed water on the surface of FZ, FZ/graphene and FZ/NGP samples. The next one in the temperature around 430°C and 670°C for FZ/graphene and FZ/NGP, respectively. It indicated the combustion process of graphene and NGP in the FZ/graphene and FZ/NGP composites, respectively, which proves the presence of graphene and NGP.

The photo- and sono- catalytic activity of the prepared samples is shown in fig. 2 (a). The obtained results revealed that the presence of graphene materials in FZ composites could improve greatly catalytic performance. The incorporation of graphene with higher specific surface area (S.A.) than NGP area exhibit the best catalytic performance in both photo- and sono- catalytic. The reason is that

Figure 2. (a) Degradation of methylene blue on photocatalytic activities (left) and sonocatalytic activities (right). (b) The effect of main active species on FZ/graphene: photo- (left) and sonocatalytic (right).
increasing surface area of samples may also relate to increasing the opportunity for contact between the catalyst and light, thereby increase the rate of oxidation process [14]. Moreover, supportive properties of NGP and graphene could trap electron to hinder recombination of electron-hole pairs, which also increase degradation rate [15]. In the sonocatalytic activity, ultrasound irradiation could disaggregate catalyst particles, thus increasing surface area [16]. That’s one reason why sonocatalytic could bring better degradation efficiency than photocatalytic.

The effect of scavengers was performed to study the main active species in the photo- and sono-catalytic process. The control experiment was carried out by adding several trapping agents, Di-ammonium oxalate, sodium sulfate, and TBA as holes, electrons and hydroxyl radicals scavenger, respectively. From fig. 2 (b) we can see that, in photocatalytic the main active species follows: hole > electron > hydroxyl radicals, while in sonocatalytic the main active species follows: hole > hydroxyl radicals > electron. The different trend of the main active species between photo- and sono- catalytic might be because the different mechanism on them. In sonocatalytic, there is a process called hot spot which can pyrolysis water molecules into hydroxyl radicals, thus increasing the population of hydroxyl radicals as strong oxidation agent [17].

4. Conclusions
In this study, FZ/NGP and FZ/graphene composites were successfully synthesized by depositing the FZ onto the surface of NGP and graphene which confirmed by XRD and TGA measurements. The results revealed that incorporation of NGP and graphene could enhance the photo- and sono- catalytic performance. The sample with an incorporation of graphene exhibits better catalytic performance compared to NGP in both photo- and sono-catalytic activity.

5. References
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