Adsorption performance of Ag/Fe$_2$O$_3$/ZrO$_2$ composite decorated with graphene toward methylene blue dye

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Abstract. Use of carbon-based materials, such as graphene, has drawn attention in the wastewater treatment field because of their high specific surface area. This property of graphene suggested that it had superior adsorption characteristics for removing contaminant dyes from aqueous solutions. Based on this precept, we wanted to enhance the adsorption ability of the Ag/Fe$_2$O$_3$/ZrO$_2$ photocatalyst by adding graphene, using the co-precipitation method for synthesis. The crystal structure of as-prepared specimen was characterized using X-ray diffraction, which confirmed the existence of tetragonal phase ZrO$_2$, cubic spinel phase Fe$_2$O$_3$, and cubic phase Ag. Unfortunately, the graphene characteristic peak could not be detected by X-ray diffraction (XRD). Thermal gravimetric analysis showed that mass degradation below 150 °C could be attributed to the loss of bound water from the surface of the ZrO$_2$. Mass degradation at 340 °C could be attributed to the combustion process of graphene, which indicated the presence of graphene in the prepared samples. The synthesized samples were utilized for the uptake of methylene blue (MB) as a model of an organic pollutant. The results that were obtained showed that the inclusion of graphene increased the ability of Fe$_2$O$_3$/ZrO$_2$ adsorption. Increases in the weight percentage of graphene increased the adsorption ability of the samples. The best adsorption occurred in alkaline pH conditions. The experimental data could be fitted better using the Langmuir model than it could using the Freundlich model. Finally, as-prepared samples showed good stability, even after four cycles of reuse.

1. Introduction

In a previous study, we reported on the photocatalytic activity of the Ag/Fe$_2$O$_3$/ZrO$_2$ (Ag/FZ) composite [1]. Those results showed that the Ag/FZ photocatalyst performed well in removing MB dye from an aqueous solution under UV light irradiation. However, the adsorption ability of this composite, one of the important parameters in the dye removal process, had not yet been studied. When photocatalytic activity was taking place, dyes were simultaneously removed by adsorption onto the surface of the photocatalyst [2]. It was therefore necessary to study the adsorption ability of the synthesized Ag/FZ composite.

Adsorption has been considered an efficient method to remove contaminant dyes from aqueous solutions because of low cost and simple operation [3]. A number of adsorbents have been studied for the removal of dye from the water system [4,5], but the use of these adsorbents has been hindered by their having low capacity.

The structural configuration of graphene shows that it is a 2-D material with a mono-layer framework of six-membered carbon rings. It has a high specific surface area [6], which makes it a good adsorbent because it provides more active sites for adsorption. It was therefore expected that combining graphene with Ag/FZ photocatalyst could enhance the composite’s adsorption ability.
The aim of this study was to examine the adsorption ability of the synthesized Ag/FZ photocatalyst and the effect of the graphene addition. Several parameters, such as solution pH and initial concentration of the dye, were also studied. Finally, the reusability of the adsorbent composite was tested by reusing it four times.

2. Experimental procedure

2.1. Materials and reagents
The starting materials such as iron (II) sulfate heptahydrate (FeSO₄·7H₂O, purity 99 %), zirconium(IV) chloride (ZrCl₄), silver nitrate (AgNO₃), sodium dodecyl sulfate (SDS), sodium carbonate (Na₂CO₃), ethylene glycol (EG) and sodium hydroxide (NaOH) were procured from Merck. Graphene (S.A. 400 m²/g) was procured from Angstron Materials. Analytical grade reagents which did not required any purification process were used in this study.

2.2. Preparation of samples
The ZrO₂ and FeO nanoparticles were prepared according to previously reported methods [7,8]. Ag nanoparticles were synthesized by dissolving AgNO₃ and SDS in separate EG solutions. Na₂CO₃ was dissolved in distilled water. The Na₂CO₃ solution was mixed with the SDS solution and AgNO₃ solution was added. The mixture was then subjected to vigorous stirring on a magnetic stirrer for 10 min. The solution was then heated in a microwave oven at 800 W for one minute, and this was followed by a further 30 min of magnetic stirring. The mixed solution was centrifuged and cleaned several times with distilled water and ethyl alcohol to separate impurities. The clean precipitate was then heated to 120 °C and the temperature were maintained for 5 hours to obtain Ag nanoparticles. An ultrasonic-assisted method was used to synthesize the FeO/ZrO₂. Specifically, the prepared ZrO₂ was mixed with the FeO nanoparticles in the mixture of distilled water and ethanol under ultrasonic exposure for two hours. Centrifugation of the mixed solution was conducted to collect the precipitate. The precipitate was finally vacuum dried in an oven at 80 °C for 12 h to obtain FeO/ZrO₂ composites, which were labelled as FZ. The molar ratio of FeO to ZrO₂ was about 0.5:1. The Ag/FZ composites were prepared in a similar way as elaborated above. The amount of Ag used for this process was 15 wt.% of Ag to the FZ composites. The Ag/FeO/ZrO₂/graphene composites were then synthesized utilizing a co-precipitation method similar to experimental process detailed in our previous report [9]. The amounts of graphene were varied as follows: 1 wt.% , 3 wt.% and 5 wt.% of graphene to the Ag/FZ composites.

2.3. Characterization
X-ray diffraction (Rigaku Miniflex 600 diffractometer) using Cu K-α radiation (λ = 1.5406 Å) was performed to observe the crystalline phase of the synthesized specimen. An Oxford Type 1.2 T vibrating sample magnetometer (VSM) was used to investigate the magnetic behavior of the synthesized samples. Thermal gravimetric analysis (TGA) was used to analyze the thermal stability of the synthesized samples in an oxygen atmosphere. The morphology of all prepared samples was investigated and elemental analysis was done using a high-resolution transmission electron microscope (HRTEM) and an energy dispersive x-ray measurement (EDX).

2.4. Adsorption experiments
The effect of graphene weight percentage, initial concentration of dye and pH on the adsorption of MB was investigated by varying the parameter under study and keeping the other parameters constant. In a typical procedure, 30 mg of synthesized samples were introduced into a 100 mL MB solution. The solution containing the suspensions was stirred under dark conditions. The MB concentration was then determined at a characteristic peak of 663 nm using a UV-Vis spectrophotometer. The amounts of MB adsorbed per unit mass of adsorbent and removal percentage were calculated using the equations below:

\[
q_t = (C_0 - C_t) \times \frac{V}{m} \\
\text{removal percentage} (%) = \frac{(C_0 - C_t)}{C_0} \times 100 \%
\]
Figure 1. (a) XRD and (b) TGA spectra of the as-prepared samples.

where \( q_t \) (mg/g) is adsorption capacity at any time, \( t \), is time (min), \( C_0 \) and \( C_t \) (mg/L) are initial and time \( (t) \) spent immersed in the MB solution, \( V \) (L) is the volume of MB solution used, and \( m \) (g) is the weight of the adsorbent.

Adsorption kinetics tests were conducted to study the controlling mechanism of MB adsorbed onto the synthesized samples [10]. Adsorption isotherm models were used to predict the interaction between adsorbate and adsorbent when the adsorption balanced was reached. Langmuir and Freundlich models were used to explain these interactions. One of the key assumption of the Langmuir isotherm is that a monolayer adsorption process takes place on homogenous adsorption sites. The equation of the Langmuir isotherm is as follows [11]:

\[
\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}
\]

where \( C_e \) (mg/L) is the equilibrium concentration of MB, \( k_L \) (L/mg) is the Langmuir equilibrium constant and \( q_m \) (mg/g) is the maximum adsorption capacity. However, the Freundlich isotherm assumes that a multilayer adsorption process occurs on a heterogenous surface, which is given as follows [11]:

\[
\log q_e = \log k_F + n \log C_e
\]

where \( k_F \) is the Freundlich adsorption constant and \( n \) represents intensity of adsorption.

3. Results and discussion

Figure 1a reveals the XRD patterns of the prepared samples. As indicated in figure 1a, bare ZrO found that all diffraction peaks at \( 2\theta = 30.18^\circ, 35.03^\circ, 50.36^\circ, \) and \( 59.94^\circ \) could be well indexed to a tetragonal phase of ZrO. These peaks corresponded to the [111], [200], [220], and [311] planes of tetragonal ZrO, respectively. As for FeO, six diffraction peaks were observed for the synthesized Fe3O4; that is at \( 2\theta = 30.14^\circ, 35.49^\circ, 43.28^\circ, 53.76^\circ, 57.20^\circ \) and \( 62.83^\circ \), and were identified as the [220], [311], [400], [422], [511] and [440] planes of cubic spinel FeO. The most prominent diffraction peaks of Ag were observed at \( 2\theta = 38.14^\circ \) and \( 44.26^\circ \) and were assigned to the [111] and [200] planes of cubic Ag. All the main diffraction peaks of ZrO, FeO, and Ag were observed in the Ag/FZ/graphene composite, indicating successful formation of these nanoparticles into a composite. However, the graphene characteristic peak could not be observed in the Ag/FZ/graphene for any variation of the graphene amount: 1 wt.%, 3 wt.% or 5 wt.%. This might be due to the weak diffraction intensity of graphene. Notably, no diffraction peaks arising from possible impurities were detected, implying that the products had high levels of purity.

Figure 1b shows the TGA plot of synthesized samples that obtained under an oxygen condition. It was observed that there was an initial weight loss until a temperature of 180 °C was reached, which
corresponded to the loss of adsorbed water [12]. The major thermal decomposition occurred from 340 °C to 1000 °C in which range the graphene underwent a combustion process [13], indicating the existence of graphene in the Ag/FZ/graphene composite, even though it could not be detected by XRD. The total weight loss due to the combustion process represents the total amount of graphene in the samples.

The HRTEM images of Ag/Fe$_3$O$_4$/ZrO$_2$ and Ag/Fe$_3$O$_4$/ZrO$_2$/graphene composites were plotted in figure 2a and figure 2b, respectively. As can be seen from the figure showing Ag/Fe$_3$O$_4$/ZrO$_2$, there are several lattice fringes of various lengths: 0.23 nm which corresponds to the 111 plane of Ag; 0.25 nm which belongs to the 311 plane of Fe$_3$O$_4$; and 0.28 nm which corresponds to the 111 plane of ZrO$_2$. It confirms that the Ag/Fe$_3$O$_4$/ZrO$_2$/graphene was successfully formed. To further confirm the existence of Ag/Fe$_3$O$_4$/ZrO$_2$/graphene composites, EDX measurements were performed to identify the atomic composition of the samples. The EDX measurement of the Ag/Fe$_3$O$_4$/ZrO$_2$/graphene samples were plotted in figure 3. The figure shows that the EDX spectra of the Ag/Fe$_3$O$_4$/ZrO$_2$/graphene composites consisted of Ag (silver), Fe (Iron), Zr (Zirconium), and O (Oxygen). The presence of graphene in the Ag/Fe$_3$O$_4$/ZrO$_2$/graphene composites could be confirmed by the existence of a carbon atom in the EDX measurement. This result further confirms that the samples were successfully formed.

Figure 4a shows the adsorption of MB onto Ag/FZ and Ag/FZ/graphene with various graphene weight percentages. The removal percentage of the Ag/FZ sample was lower than that of any of the
Figure 4. (a) removal percentage and (b) reusability of catalyst.

Figure 5. (a) Langmuir isotherm model of MB adsorption (b) Freundlich isotherm model of MB adsorption.

Ag/FZ/graphene composites regardless of the graphene weight percentage. The maximum removal percentage was achieved by the Ag/FZ 5 wt.% graphene sample. It is clear that the introduction of graphene into the Ag/FZ composite enhanced the adsorption ability and increasing the amount of graphene in the sample similarly enhanced the adsorption ability of the composite owing to its superior specific surface area.

The ability to reuse the adsorbent is an important factor in evaluating the efficiency and stability of an adsorbent. We therefore studied the reusability of the Ag/FZ/5 wt.% graphene composite, because it was the best adsorbent. After the first use of the composite for the adsorption of MB, the recovered Ag/FZ/5 wt.% graphene was then reused to adsorb further MB without any further treatment of the adsorbent. As is shown in figure 4b, the Ag/FZ/5 wt.% graphene composite can be reused up to four times without any significant loss of its removal percentage.

The interactions between adsorbate and adsorbent are evaluated by studying the adsorption isotherm at room temperature. Langmuir and Freundlich adsorption isotherm models for Ag/FZ, Ag/FZ 1 wt.% graphene, Ag/FZ 3 wt.% graphene and Ag/FZ 5 wt.% graphene are displayed in figure 5a and figure 5b. Table 1 summarizes the corresponding data. When the correlation coefficients (R) is
Table 1. The computed parameters for the Langmuir and Freundlich models

| Samples            | Langmuir model | Freundlich model |
|--------------------|----------------|------------------|
|                    | \( \frac{q_m}{(mg/g)} \) | \( K_l \times 10^{-2} \) (L/mg) | \( R^2 \) | \( K_F \) (mg/g(mg/L)^{-n}) | \( n \) | \( R^2 \) |
| Ag/FZ              | 84.034         | 3.806            | 0.99   | 2.874                   | 0.385 | 0.96  |
| Ag/FZ/1 wt% graphene | 103.09        | 3.900            | 0.99   | 3.011                   | 0.40  | 0.95  |
| Ag/FZ/3 wt% graphene | 133.69        | 4.038            | 0.99   | 3.257                   | 0.43  | 0.95  |
| Ag/FZ/5 wt% graphene | 159.74        | 6.089            | 0.99   | 4.058                   | 0.384 | 0.95  |

compared, the Langmuir isotherm proves to be more suitable in describing the experimental data than the Freundlich isotherm. This result suggested that the adsorption sites in the prepared samples are finite and the adsorption process takes place as monolayer adsorption.

4. Conclusions
The present work showed that Ag/FZ composite could be used as an adsorbent for the removal of MB dye from an aqueous solution. The introduction of graphene into the Ag/FZ composite enhanced its adsorption ability greatly, and increased weight percentages of graphene further increased adsorption performance. The best performance of MB adsorption was achieved at pH = 13. Increases in initial dye concentration increased the amount of dye adsorbed onto the adsorbent. The adsorption kinetics can be well predicted by a pseudo-second-order model. The Langmuir adsorption isotherms were found to be a better fit to the experimental data than the Freundlich isotherms. The results of the present study indicate that the Ag/FZ 5 wt.% composite was the best adsorbent and when reused four times it showed good reusability.

References
[1] Guan Y, Wang S, Wang X, Sun C, Huang Y, Lie C and Zhao H 2017 Appl. Catal. B Environ. 209 329–38
[2] Lei C, Pi M, Jiang C, Cheng B and Yu J 2017 J. Colloid Interface Sci. 490 242–51
[3] Malwal D and Gopinath P 2017 J. Hazard. Mater. 321 611–21
[4] Kumar K Y, Raj T N V, Archana S, Prasad S B B, Olivera S and Muralidhara H B 2016 J. Water Process Eng. 13 44–52
[5] Liu S H, Wie Y S and Lu J S 2016 Chemosphere 154 118–23
[6] Kristianto Y, Taufik A and Saleh R 2016 J. Phys. Conf. Ser. 776 012040
[7] Taufik A, Susanto I K and Saleh R 2015 Mater. Sci. Forum 827 37–42
[8] Kristianto Y, Taufik A and Saleh R 2017 AIP Conf. Proc. 1788 030126
[9] Song N, Wu X L, Zhong S, Lin H and Chen J R 2015 J. Mol. Liq. 212 63–9
[10] Wang H, Gao H, Chen M, Xu X, Wang X, Pan C and Gao J 2016 Appl. Surf. Sci. 360 840–8
[11] Li W, Jiang X, Yang H and Liu Q 2015 Appl. Surf. Sci. 356 812–6
[12] Qin J, Zhang X, Yang C, Cao M, Ma M and Liu R 2017 Appl. Surf. Sci. 392 196–203
[13] Sharma P, Kaur R, Baskar C and Chung W J 2010 Desalination 259 249–57