Magnetised photocatalyst TiO$_2$/Fe$_3$O$_4$ nanocomposite capable to photodegrade organic dye

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Abstract. In this study, methylene blue (MB) is used as a measure of the photocatalytic capabilities of the prepared TiO$_2$/Fe$_3$O$_4$ photocatalyst nanocomposite. The nanocomposite was suspended in the dye aqueous solutions placed in a UV chamber under UV-C (254 nm) light irradiation. The TiO$_2$/Fe$_3$O$_4$ nanocomposite was characterised by XRD, FESEM, TEM and EDX analysis. The TiO$_2$/Fe$_3$O$_4$ nanocomposite crystal structure retained TiO$_2$ pure anatase of tetragonal crystal structure (SG: I4/mmd) and Fe$_3$O$_4$ cubic spinel crystal structure with average crystalline size of (62.1 ± 5.7) nm. The optimum performance of the magnetic nanocomposite was monitored through few categories, such as concentration of photocatalyst, doping amount of Fe$_3$O$_4$ nanoparticle into the nanocomposite and sintering temperature. The TiO$_2$/Fe$_3$O$_4$ nanocomposite optimum loading was detected at 3.0 wt%. The nanocomposite performed well at 1 wt% of Fe$_3$O$_4$ doping and 350 °C of sintering temperature. The reliability of the TiO$_2$/Fe$_3$O$_4$ nanocomposite was also conducted where it was successfully repeated for at least 3 times with no obvious changes observed in the degradation efficiency.

1. Introduction

Many a time there are news on the increasing problem of many countries around the world due to environmental pollution, depleted water resources and energy shortages. Wastewater from industries effluents is the main cause of environmental pollution involving water resources (Lee and Park 2013). Therefore, photocatalytic processes have been the focus of attention due to its low cost and non-toxic end product (Amornpitoksuk, Suwanboon et al. 2018). In recent years, TiO$_2$ has been a highly active photocatalyst due to its stability, nontoxicity and economically excellence (Cheng, Zhang et al. 2016).

The TiO$_2$ based semiconductors has actively gone into the area of environmental purification and CO$_2$ photoconversion into fuels. Recently, magnetic titania has received abundance reputation due to its magnetic recovery and excellent photocatalytic properties. Among the famous magnetic iron oxide nanomaterials being incorporated with TiO$_2$ are Fe$_3$O$_4$ and $\gamma$-Fe$_3$O$_2$ due to their superparamagnetic properties (Tedsree, Temnuch et al. 2017).

Abundance of trials have come up through various processing methods in producing an effective and reliable magnetic titania, such as solvothermal, co-precipitation, sol-gel and chemical deposition methods (Hong, Mao et al. 2017, Tedsree, Temnuch et al. 2017). The studies have found similar
stability and photocatalytic enhancement on MB and RhB dyes, as well as excellent magnetic recoverability which overcoming the limitations of separation. On the other hand, Dagher et al. (2018) was using a non-thermal synthesis methods to synthesise the magnetic nanoparticles, which improved the MB degradation rate and photoinduced charge generation and separation, besides magnetically separable (Dagher, Soliman et al. 2018).

A hybrid photocatalysts study conducted by An et al. (2018) on Fe3O4 magnetic particles showed promising effect on the photocatalytic activity for the MB dye under visible light irradiation. The photocatalyst was analysed and repeated for at least four successive runs by applying an external magnetic field (An, Liu et al. 2018). With a barrage of investigation on the magnetic photocatalysts, this study is trying to match TiO2 nanoparticle with Fe3O4 nanoparticle in the hope of maintaining the former photocatalytic properties and utilising the later magnetic properties. Therefore, this study was aims to scrutinising the weight fractions of Fe3O4 nanoparticle as well as the loading and sintering temperature of the magnetic nanocomposite. The TiO2/Fe3O4 magnetic nanocomposite was an effective photocatalyst and managed to degrade 87.9% of MB (12 mg·L⁻¹) in the third run.

2. Materials and Methods

All the materials used in this study were of reagent grades. Titanium dioxide (TiO2, R & M Chemicals), iron oxide (Fe2O3, Systerm, ChemPur) and methylene blue (MB, R & M Chemicals) were used without any modification. Experimental solutions were prepared using deionised water from Favorit Water Distiller.

The TiO2/Fe3O4 magnetic nanocomposites photocatalyst materials were prepared by weighing TiO2 nanopowders and added with a series of 1, 5, 10, 12, 15 and 20 weight percentage (wt%) of iron oxide (Fe2O3) nanopowders. All nanopowders were dry mixed for duration of 20 minutes. Each series of premixed nanocomposites was calcined in the Carbolite muffle furnace from 200 to 450 °C for 5 hours. The nanocomposite was heated at 20 °C per minute. All powders were grinded by a spatula after calcination. This process is technically implemented in mixing oxides (Song and Zhang 2010).

For the characterisation, X-ray diffraction (XRD, Bruker), field emission scanning electron microscopy (FESEM, FEI) which is coupled with energy dispersive X-ray analyser (EDX), transmission electron microscope (TEM, LEO) and BET from Micromeritics were used.

The nanocomposites solutions were prepared using distilled water for concentration between 1.0 wt% to 6.0 wt%. MB dye was also premixed with distilled water for concentration between 2.00 ppm to 12.0 ppm. To initiate the experiment, 0.20 mL of premixed photocatalysts were immersed into 3.00 ml of the dye solutions. All the samples were transferred into the UV chamber (Uvitec Cambridge ultraviolet crosslinker) (Figure 1, Tan, Khiew et al. 2019). Finally, a 0.6 T magnetic field was applied on the samples to collect the nanocomposites and 2 mL solutions were tested using a UV-Visible Spectrophotometer (Varian, Cary 50).

The percentage degradation was calculated based on the Beer-Lambert law (Mantele and Denize 2017), i.e. Degradation (%) = [(C₀ – C)/C₀] × 100 = [(A₀ – A)/A₀] × 100, where C₀ and A₀ are the dye concentration and the absorbance of the dye before irradiation, whereas C and A are the dye concentration and the absorbance of the dye after the irradiation of time t.

3. Results and Discussion

3.1. Samples Morphologies for Different Sintering Temperature
The sample used is the TiO2/Fe3O4 nanocomposites with 20 wt% doped Fe3O4.
3.1.1. **FESEM Analysis.** Figure 1(a) shows relatively small size and homogeneous spherical morphology. Aggregation phenomenon was not detected across all micrographs of highly porous structures. The average particle size calcined at 350 °C is (112 ± 12) nm. The FESEM results show no significant effects on the morphological properties for the current sintering conditions.

3.1.2. **XRD Analysis.** Figure 1(b) provides XRD results for TiO$_2$/Fe$_3$O$_4$ nanocomposites sintered at 350 °C. All detected peaks represented by the TiO$_2$ and Fe$_3$O$_4$ phases. The TiO$_2$ main peaks at 25.3° for (101), 36.9° for (103), 37.7° for (004) and 38.6° for (112) diffraction planes of pure anatase phase of tetragonal structure (JCPDS 21-1272) (Dagher, soliman et al. 2018), and the Fe$_3$O$_4$ main peaks at 30.2° for (220), 35.6° for (311), 43.2° for (400) and 57.1° for (511) diffraction planes of cubic spinel structure (JCPDS 19-0629) (Wu, Wu et al. 2015). The XRD results for TiO$_2$/Fe$_3$O$_4$ nanocomposites clarify that no impurities was present throughout the preparation of the samples. In addition, an average crystallite size of (105 ± 13) nm was obtained by using the Scherer equation.

3.1.3. **BET and EDX Analysis.** The BET for TiO$_2$/Fe$_3$O$_4$ nanocomposites shows no significant difference with the values around 7.8 m$^2$/g. Similar with the pore size and pore volume which are around 0.05 nm and 27 cm$^3$/g, respectively. The EDX spectrums show the acquired elemental map, i.e. O, Ti and Fe, which clarified Fe$_3$O$_4$ were deposited onto the TiO$_2$/Fe$_3$O$_4$ nanocomposites surface. This result, combined with the XRD analysis validates the purity TiO$_2$/Fe$_3$O$_4$ nanocomposites.

3.2. **Samples Morphologies when Doped with Different wt% of Fe$_3$O$_4$.** The FESEM results show the acquired elemental map, i.e. O, Ti and Fe, which clarified Fe$_3$O$_4$ were deposited onto the TiO$_2$/Fe$_3$O$_4$ nanocomposites surface. The average particle size was (92.6 ± 7.2) nm with observable porosity.

3.2.2. **XRD Analysis.** The XRD results in Figure 1(d) show highly crystalline nanocomposites without any impurities. The main peaks at 25.3° for (101), 36.9° for (103), 37.7° for (004) and 38.6° for (112) diffraction planes are of pure anatase phase of TiO$_2$ tetragonal structure (JCPDS 21-1272), as well as the main peaks at 30.2° for (220), 35.6° for (311), 43.2° for (400) and 57.1° for (511) diffraction planes are the Fe$_3$O$_4$ crystal of cubic spinel structure (JCPDS 19-0629). This confirmed that both TiO$_2$ and Fe$_3$O$_4$ nanocomposites bind well through the applied mixing. Calculation from the Scherer equation yield the average value of (120 ± 17) nm. This experimental study shows the amount of Fe$_3$O$_4$ nanoparticles used does not affecting the crystallite structure of the nanocomposites.

3.2.3. **BET and EDX Analysis.** The amount of Fe$_3$O$_4$ incorporated shows insignificant effect on the BET and pore size of all the samples. The EDX spectrum acquired the main elements, i.e. O, Ti and Fe, which conformed Fe$_3$O$_4$ mixed well with TiO$_2$ in producing the TiO$_2$/Fe$_3$O$_4$ nanocomposites. These double confirmations of EDX and XRD analysis ascertained the purity of the crystalline structure.

3.3. **Transmission Electron Microscopy (TEM) analysis**
The TEM film in Figure 2(a) is the 1 wt% Fe$_3$O$_4$ incorporation calcined at 350 °C sample. It shows the mixture of small size and variation of globular structures. The average particle size is (86.2 ± 9.0) nm.

3.4. **The study of photocatalytic effects**
Photocatalyst loading has been the focused on the effects of photodegradation of organic dyes in wastewaters (Anwer, Mahmood et al. 2019). This study has used 12.0 ppm MB for experimenting the metal oxides photocatalysts loading range between 1.0 to 6.0 wt% with the increment of 1.0 wt%.

3.4.1. **TiO$_2$/Fe$_3$O$_4$ Loading.** Loading amount was significantly affecting the kinetic constant of the photocatalytic processes, as depicted by the 1 wt% to 3 wt% samples, which was gradually
accelerating from 0.0296 to 0.0406 min\(^{-1}\), respectively, as shown in Figure 2(b). The pronounced increase in the degradation rate was contributed by the increase of the surface area, which is the sites for the photocatalytic interactions (Salama, Mohamed et al. 2018). However, if the loading keep on increases, the degradation rate will decline as the 3 wt% showed and dropped to 0.0362 min\(^{-1}\) for the 6 wt% loading. This is due to the reducing yield of the photogenerated electrons and holes, as a consequence of reduced exposure of the photocatalyst to light (Chung, Nguyen et al. 2018).

3.4.2. Different sintering temperature. Generally, kinetic rate in Figure 2(c) shows equal rate of degradation. The rate constant for the nanocomposite samples attributed to the LH model and correspond with the pseudo-first-order kinetics. This experiment infers that sample with 350 °C sintering temperature having the highest degradation rate 0.0377 min\(^{-1}\).

3.4.3. Different wt% of Fe\(_3\)O\(_4\). The kinetic constant was the highest when the amount of Fe\(_3\)O\(_4\) incorporated was the lowest with the value of the kinetic constant of 0.0729 min\(^{-1}\), as shown in Figure 2(d). However, as the incorporation values increased to 20 wt%, the value of \(k\) dropped more than half to 0.0330 min\(^{-1}\). This experimental values show the incorporation of Fe\(_3\)O\(_4\) into the nanocomposite significantly block its active sites. Similar finding was obtained by Shojaei et al. (2017) with their TiO\(_2@\)Fe3O4 microsphere which show significant increase in the photocatalytic performance (Shojaei, Shams-Nateri et al. 2017). The optimum amount of Fe\(_3\)O\(_4\) doped is therefore 1.0 wt%.

3.5. The magnetic and reliability analysis

The 3.0 wt% loading of TiO\(_2@\)Fe\(_3\)O\(_4\) nanocomposites was used with MB dye.

3.5.1. Vibrating sample magnetometry analysis (VSM). The magnetization curves versus the magnetic field for TiO\(_2\) nanoparticle and TiO\(_2@\)Fe\(_3\)O\(_4\) nanocomposite were depicted in Figure 3. The TiO\(_2\) clearly exhibits no magnetic properties, which characterized as diamagnetic material. On the other hand, TiO\(_2@\)Fe\(_3\)O\(_4\) nanocomposite clearly displays magnetic hysteresis loops with ferromagnetic feature, which is the soft ferromagnetic material. Similar hysteresis loops were obtained by Lendzion-Bielun at al. (2020) where they deduced the significant dropped of the magnetization in Fe\(_3\)O\(_4@\)TiO\(_2\) is attributed to the contribution of TiO\(_2\) mass and a lower volume fraction of Fe\(_3\)O\(_4\) (Lendzion-Bielun, Wojciechowska et al. 2020). Due to the minimal coercivity exhibited by the nanocomposite, the presence of low magnetic field could easily induced the saturation magnetisation. This is clearly indicated by the curve where 92.7% magnetization was achieved with just 1584 Oe of magnetic field. TiO\(_2@\)Fe\(_3\)O\(_4\) nanocomposites exhibits high susceptibility because with only 4033 Oe of applied magnetic field, it able to attain magnetisation value of 5.543 emu/g.
3.5.2. Magnetic separation analysis. Figure 4 shows the induced separation experiment for 3.0 wt% loading of TiO$_2$/Fe$_3$O$_4$ nanocomposites with magnetic field strength of 0.6 T. The suspension of the TiO$_2$/Fe$_3$O$_4$ nanocomposites was clearly induced by moving toward the wall of the vial closer to the magnet and the colloidal suspension slowly becoming clear. The colloidal TiO$_2$/Fe$_3$O$_4$ nanocomposite remains dispersible manifestation of permanent agglomeration.

3.5.3. Repeatability analysis. Similar experimental conditions was applied in performing the repeatability analysis for TiO$_2$/Fe$_3$O$_4$ nanocomposite. After each photodecomposition process was completed, the nanocomposite was retrieved and reused. The percentage degradation for all the three runs were 84.19, 87.32 and 87.92%, respectively. This experiment provides attractive results for the TiO$_2$/Fe$_3$O$_4$ nanocomposite which shows high photocatalytic stability, retrievable and recyclable.

4. Conclusion
A successful preparation of magnetically separable TiO$_2$/Fe$_3$O$_4$ nanocomposite was achieved in this study. The optimum loading for TiO$_2$/Fe$_3$O$_4$ nanocomposites is found to be 3.0 wt%. TiO$_2$/Fe$_3$O$_4$ nanocomposites for the optimisation of doped Fe$_3$O$_4$ is 1.0 wt% and sintering temperature is achieved at 350 °C. The nanocomposite was successfully recycled for up to three successive photodegradation and exhibited similar photocatalytic performance.

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