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PHOTOCATALITIC ACTIVITY OF $Fe_3O_4/SiO_2/TiO_2$ COMPOSITE BY MECHANOCHEMICAL PREPARATION

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ABSTRACT

PHOTOCATALITIC ACTIVITY OF $Fe_3O_4/SiO_2/TiO_2$ COMPOSITE BY MECHANOCHEMICAL PREPARATION. A simple mechanochemical activation was used to prepare $Fe_3O_4/SiO_2/TiO_2$ composite. Fe_3O_4, and SiO_2 nanoparticles powder were prepared by co-precipitation method respectively, while TiO_2 was synthesized by sol-gel method. All of the samples were mixed into vial and milled by wet milling process. The all prepared sampel were characterized by various equipments i.e. X-ray diffractometry (XRD), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM), Fourier transform infrared (FTIR) and UV-Vis Spectrometer. The result shows that $Fe_3O_4/SiO_2/TiO_2$ composite consisted of anatase TiO_2 and Fe_3O_4 phases. The superparamagnetic behavior of Fe_3O_4 nanoparticle, Fe_3O_4/SiO_2, and $Fe_3O_4/SiO_2/TiO_2$ composites exhibit the saturation magnetic (M_s) of 89.43. and 13emu/g, respectively. The particle size of $Fe_3O_4/SiO_2/TiO_2$ composite was distributed in spherical shape and about 100 nm in diameter. Photocatalytic test showed that $Fe_3O_4/SiO_2/TiO_2$ composite can elimininate the methylene blue (MB) dye solution higher than that pure TiO_2 commercial product (TiO_{2M}) catalyst. The $Fe_3O_4/SiO_2/TiO_2$ composites can be easily taken back from treated water by using magnetic bar.

Keywords: Mechanochemical, $Fe_3O_4/SiO_2/TiO_2$ composite, methylene blue dye, photocatalytic

ABSTRAK

AKTIFITAS FOTOKATALITIK KOMPOSIT $Fe_3O_4/SiO_2/TiO_2$ DENGAN PREPARASI *MECHANOCHEMICAL*. Aktivasi *mechanochemical* sederhana digunakan untuk preparasi komposit $Fe_3O_4/SiO_2/TiO_2$. Serbuk nanopartikel Fe_3O_4 dan SiO_2 masing-masing dibuat dengan metode kopresipitasi, sementara TiO_2 dibuat dengan metode sol-gel. Semua sampel dicampur bersamaan di dalam vial baja tahan karat dan dihaluskan dengan proses wet milling. Sampel yang telah dibuat dikarakterisasi dengan berbagai peralatan yaitu difraksi sinar-X (XRD), mikroskop elektron transmisi (TEM), *Vibrating Sample Magnetometer* (VSM), *Fourier Transform Infrared* (FTIR) dan UV-Vis Spektrofotometer. Hasil penelitian menunjukkan bahwa $Fe_3O_4/SiO_2/TiO_2$ komposit terdiri dari fasa TiO_2 anatase dan fasa Fe_3O_4. Perilaku *superparamagnetic* dari nanopartikel Fe_3O_4, komposit $Fe_3O_4/SiO_2/TiO_2$, dan $Fe_3O_4/SiO_2/TiO_2$ menghasilkan saturasi magnet (Ms) berturut-turut adalah 89, 43 dan 13 emu/g. Ukuran partikel $Fe_3O_4/SiO_2/TiO_2$ komposit terdistribusi berbentuk speris dan berukuran diameter sekitar 100 nm. Uji fotokatalitik menunjukkan bahwa komposit $Fe_3O_4/SiO_2/TiO_2$ dapat menghancurkan larutan pewarna metilen biru (MB) lebih tinggi dari pada dengan katalis TiO_2 murni (TiO_2M) dari produk komersial dan komposit $Fe_3O_4/SiO_2/TiO_2$ dapat dengan mudah diambil kembali dari air yang diolah menggunakan magnet eksternal.

Keywords: *Mechanochemical*, Komposit $Fe_3O_4/SiO_2/TiO_2$, Zat warna metilen biru, Fotokatalitik

INTRODUCTION

Titania can catalyze the decomposition of a wide range of chemicals such as pharmaceutical, methyl orange (MO), and methylene blue (MB) dyes [1-3]. The properties of titania are well known for the high productivity of hydroxyl free radicals, and good stability [4,5]. However, the use of catalysts with the addition of chemicals substances to form coagulation is less effective, and it requires a mechanical filtration process. One approach is to introduce the superparamagnetic properties and recover the catalyst using a magnetic field.

Many efforts have been made in the development of the design and preparation of magnetic core-shell microspheres. Alvarez et. al. [3] reported the fabrication of $Fe_3O_4/SiO_2/TiO_2$ by ultrasonic-assisted sol–gel method, and Z. Wang et. al. [6] prepared Fe_3O_4-SiO_2-TiO_2 composite trough chemical method heir resultant samples exhibit good photodegradation ability and can be easily recycled by applying an external magnetic field.

In this work the preparation procedure of $Fe_3O_4/SiO_2/TiO_2$ composite was carried out using mechanochemical activation by wet milling method. Mechanochemical treatment is a simple method and can affect significantly to the photo-activity of titanium dioxide [7]. $Fe_3O_4/SiO_2/TiO_2$ composites were characterized by some equipment: X-ray diffractometer (XRD), transmission electron microscope (TEM), vibrating sample magnetometer (VSM), fourier transform infra-red (FTIR) and UV-Vis spectrometer. Finally, the effectiveness of the photo-catalysts assisted by $Fe_3O_4/SiO_2/TiO_2$ composite and pure TiO_{2M} nanoparticles to eliminate the organic compounds of MB dye is reported.

EXPERIMENTAL METHOD

All the chemical reagents were analytical grade from Merck Company, and used without further purification.

Synthesis of Fe_3O_4 Nanoparticles

Fe_3O_4 nanoparticles were prepared by the co-precipitation method according to previous research [8] with minor modification. Briefly, a solution of $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ with 1: 2 molar ratio dissolved in 10 ml of HCl and then in 150ml of water. The precipitate agent of NaOH and TMOH (with 5: 2 molar ratio) solution dissolved in 350ml of water. The resulting of the precipitate agent was added drop wise into the iron solution at 70ºC under vigorous magnetic stirring until pH 12. The black precipitates were collected by magnetic bar and washed with water and absolute ethanol until pH 7. The precursor was dried at 70ºC for 16 h.

Synthesis of SiO_2 Nanoparticles

The silicon oxide (SiO_2) was prepared by precipitation method from sodium silicate (Na_2SO_3) follows Musić et. al. [9].

Synthesis of TiO_2 Nanoparticles

The preparation of TiO_2 nanoparticles was carried out according to a previous report [10] with modification. For TiO_2 preparation, $TiCl_4$ was added drop wise to de-ioniosed water under vigorous stirring in an ice water bath. The mixture was refluxed under vigorous stirring at 70°C for 7h as titania sol was prepared. The sol–gel derived precipitates are amorphous, and it requires a heat treatment to induce crystallization.

Synthesis of $Fe_3O_4/SiO_2/TiO_2$ Composite

The preparation of $Fe_3O_4/SiO_2/TiO_2$ composite was conducted through mechanochemical by wet milling method (CertiPrep 8000M). Firstly, Fe_3O_4 and SiO_2 powder were mixed with a weight ratio of 1: 1. Then, the dry Fe_3O_4/SiO_2 was mixed with un-calcined TiO_2 powder of a weight ratio = 1: 1, and then dried, followed by calcinations at 500ºC for 2 h. Each process of the wet milling was carried out in a Tungsten Carbide vial (Spex. 804) in ethanol medium, for 9 h respectively. The weight ratio of precursor and agate balls were arranged with a weight ratio of 1: 5.

Characterization

The synthesized samples were characterized by equipment of X-rays diffractometer (Pan-Analytical, Empyrean), TEM – JEOL, JEM 1400, VSM - Oxford 1.2T, FTIR – Tensor 27 Brucker, and UV-Vis spectrometer – Perkin Elmer, λ-25. An amount of $Fe_3O_4/SiO_2/TiO_2$ composite was dispersed into the MB dye solution of 30 ppm, then stirred at room temperature under irradiation and non-irradiation of UV. To fit the experiment data, the photocatalytic is shown in the apparent pseudo first-order kinetic equation as follows:

$$-\ln\left[{}^{C_t}/_{C_0}\right] = K_{app} \times t \quad \text{....................} \quad (1)$$

Where:

K_{app} = Apparent rate constant,
t = Exposure time,
C_o = Represent initial concentration
C_t = Concentration at particular time

RESULT AND DISCUSSION

The XRD patterns of Fe_3O_4, Fe_3O_4/SiO_2, and $Fe_3O_4/SiO_2/TiO_2$ composites are shown in Figure 1. The result show that the prepared Fe_3O_4 is similar to the magnetite phase in the JCPDS card no. 19–0629 as shown in Figure 1a. Figure 1b shows XRD pattern of Fe_3O_4/SiO_2 composite. The XRD pattern of synthesized titanium dioxide (TiO_2) after calcinations at 500ºC for 2h is shown in Figure 1c. It indicates that titanium dioxide has an anatase structure, where the peaks at 25.3, 37.8, 48.0,

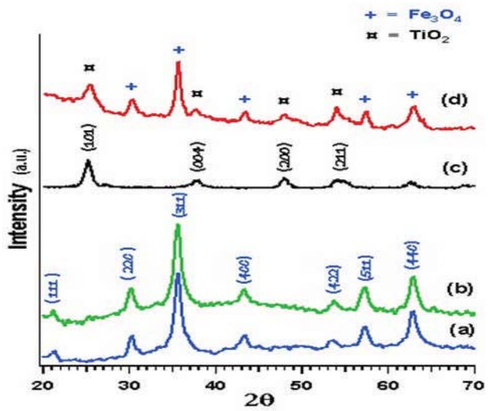

Figure 1. XRD pattern of (a). Fe_3O_4, (b) Fe_3O_4/SiO_2, (c). synthesized TiO_2 after calcinations at 500°C, and (d). $Fe_3O_4/SiO_2/TiO_2$ composite through mechano chemical.

and 53.9° with *Miller* index : (101), (004), (200) and (211) respectively, are anatase structure of TiO_2 phase (JCPDS: No. 21-1272). The diffraction peak of $Fe_3O_4/SiO_2/TiO_2$ composite is shown in Figure 1d. The Diffraction peak in this pattern can be classified into two groups. The peaks that marked with "+" can be indexed as the Fe_3O_4 phase, while the other peaks that marked with "¤" can be indexed as TiO_2 phase.

The morphology and size of the synthesized products were characterized by TEM. Figure 2a displays a TEM image of the Fe_3O_4 nanoparticles. It is shown that

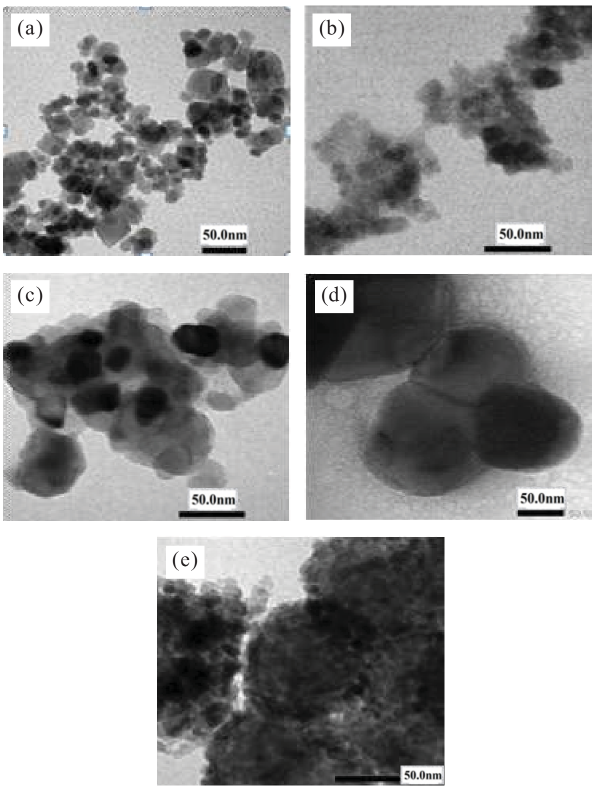

Figure 2. TEM images of (a) Fe_3O_4, (b) Fe_3O_4/SiO_2, (c). as-prepared TiO_2 after calcinations at 500°C, (d). pure TiO_2M, and (e), $Fe_3O_4/SiO_2/TiO_2$ composites.

the use of TMOH organic base produce spherical particle about 10 nm in diameter with a low level agglomeration. Figure 2b shows a TEM image of the Fe_3O_4/SiO_2 composite. It is an evidence that Fe_3O_4 nanoparticles has been coated by SiO_2 layer. Figure 2c show TEM image of synthesized TiO_2 produced by sol-gel method after calcination at 500°C for 2 h, and Figure 2d is pure TiO_{2M}. The particle size of the synthesized TiO_2 nanoparticles is less than 20nm, while pure TiO_{2M} was observed about 100nm in diameter. Figure 2e is a TEM image of $Fe_3O_4/SiO_2/TiO_2$ composite prepared by mechanochemical. It is seen that $Fe_3O_4/SiO_2/TiO_2$ composite has the diameters greater than 200nm.

The magnetization behavior of Fe_3O_4, Fe_3O_4/SiO_2, and $Fe_3O_4/SiO_2/TiO_2$ composite is shown in Figure 3. Figure 3a shows the magnetic saturation of Fe_3O_4 nanoparticles. The observed value of magnetic saturation (M_s) of Fe_3O_4 nanoparticles was found to be 89emu/g, which is greater than in the previous experiment [8]. It is suggested that TMOH organic base contribute to the improvement of magnetic properties. The M_s value than derease to 43emu/gr, and finally to 20emu/g, after being coated with SiO_2 and TiO_2 layers, respectively. The decrease of M_s value after coating processes is due to the presence of non-magnetic coating layers of SiO_2 and TiO_2. However, the magnetism of $Fe_3O_4/SiO_2/TiO_2$ composite is still high enough to be magnetically separated by applying amagnetic field, which can facilitate the separation of photocatalysts from treated solutions. The functional group in $Fe_3O_4/SiO_2/TiO_2$ composite formed during milling process is shown in Figure 4.

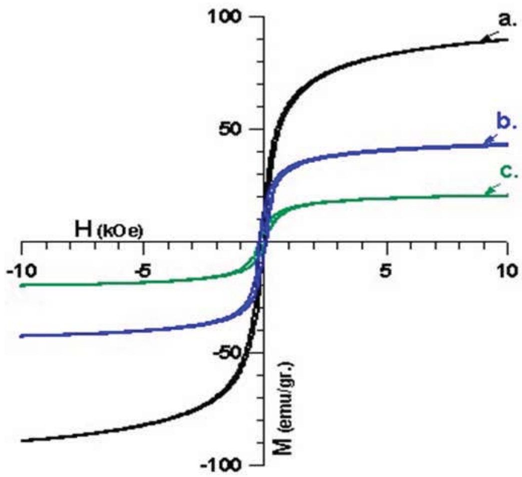

Figure 3. Magnetization behavior of a). Fe_3O_4, b). Fe_3O_4/SiO_2, and c). $Fe_3O_4/SiO_2/TiO_2$ composite.

FTIR spectrum of Fe_3O_4, and $Fe_3O_4/SiO_2/TiO_2$ are shown in Figure 4. The peak at 1,620 and 3,420 cm^{-1} can be assigned to the H-O-H stretching modes and bending vibration of adsorbed water, respectively. The peak at 570 cm^{-1} is related to the Fe-O-Fe bending vibration [11], while the peak around 964 cm^{-1} is assigned to Si-O-Si symmetric stretching mode. In spectrum of $Fe_3O_4/SiO_2/$

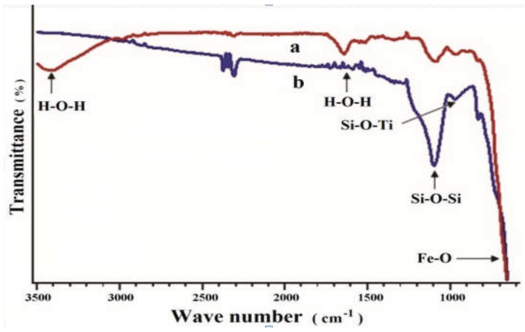

Figure 4. FTIR Spectrum of (a). Fe_3O_4 nanoparticle, and (b). $Fe_3O_4/SiO_2/TiO_2$ composite.

TiO_2 as seen in curve b, the broad high intensity band at 1,100 cm^{-1} is associated with the motion of oxygen in Si-O-Si anti-symmetric stretch, due to the asymmetric stretching bonds of Si-O-Si in SiO_2 [9], while the absorption peak around 940 cm^{-1} is related to the vibration of Si-O-Ti [1]. The peak at 940 cm^{-1} proves that the bonds of ≡Si-O-Ti≡ has been formed as a result of the incorporation between Fe_3O_4@SiO_2 with TiO_2 through wet milling method.

Figure 5 shows the photo-catalytic activity of various samples in 30 ppm of MB dye solution for contact time 3 hours. As shown in curve (Figure 5a), the de-colorization ratio of MB dye in non-catalyst (blank) under UV irradiation was less than 3% after 3 hours irradiation due to the photodecomposition through photolysis process.

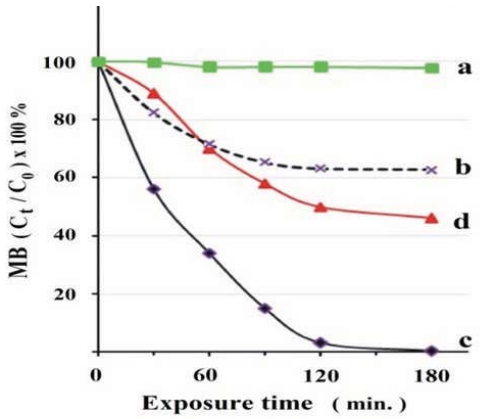

Figure 5. The elimination of MB dye solution of 30 ppm in concentration at pH 7 (a). In absence (blank), and the presence of (b). $Fe_3O_4/SiO_2/TiO_2$ composite (dark), (c). $Fe_3O_4/SiO_2/TiO_2$ composite (UV), and (d). pure TiO_2M (UV).

In the mean time, $Fe_3O_4/SiO_2/TiO_2$ composites can remain MB dye of 37% without UV irradiation (dark), as shown in Figure 5b. This result indicates that $Fe_3O_4/SiO_2/TiO_2$ composites can eliminate the MB dye through adsorption process. The adsorption properties of $Fe_3O_4/SiO_2/TiO_2$ composite comes from silanol group (-OH) of SiO_2 layer [12].

Furthermore, the elimination of MB dye by $Fe_3O_4/SiO_2/TiO_2$ under UV irradiation increased dramatically. The MB dye can be eliminated close to 100% for 3 hours contact time (Figure 5c). It means that in $Fe_3O_4/SiO_2/TiO_2$ composite exhibited the photo-catalytic activity is 63% under UV-light, and 37% due to adsorption process. Photocatalytic activity of $Fe_3O_4/SiO_2/TiO_2$ composites in this experiments is better when compared to the photocatalytic activity of Fe_3O_4-SiO_2-TiO_2 composites synthesized with co-precipitation method which have been reported earlier [13]. Otherwise, pure TiO_{2M} only able to remain MB dye of 56 % (Figure 5d). Thus, the photo-catalytic activity of $Fe_3O_4/SiO_2/TiO_2$ composites is higher of 9% than that of pure TiO_{2M}. In fact, the amount of active fraction of pure TiO_2 in $Fe_3O_4/SiO_2/TiO_2$ and TiO_{2M} is the same.

Photocatalytic properties come from the anatase TiO_2 located on the out surface of $Fe_3O_4/SiO_2/TiO_2$ composite, and it can utilize the light effectively. This is suggested that the role of SiO_2 middle layer and the particle size of the TiO_2 catalyst in $Fe_3O_4/SiO_2/TiO_2$ composite play an important rule to eliminate the organic pollutant, so that eliminated MB dye in solution increased.

Figure 6 shows the apparent pseudo first-order kinetic of eliminated MB dye by $Fe_3O_4/SiO_2/TiO_2$, and TiO_2 which calculated from equation (1). From the linier plot in the Figure 6, the slopes yield the apparent rate constant (K_{app}), and correlation coefficient (R^2) values for TiO_2 nanopaticles and $Fe_3O_4/SiO_2/TiO_2$ composite as mentioned in Table 1. Based on the Table 1, it is clear that K_{app} and R^2 of $Fe_3O_4/SiO_2/TiO_2$ composite are greater

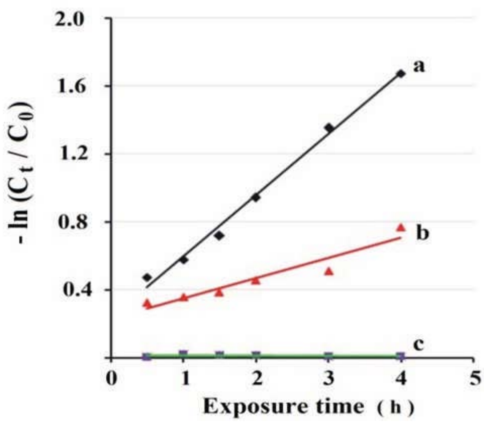

Figure 6. The Kinetic curves of MB dye disappearance for (a). $Fe_3O_4/SiO_2/TiO_2$ composite, (b). pure TiO_2M and (c). blank (non-catalysts), under illumination of UV.

Table 1. The Parameters of apparent pseudo first-order kinetic of photo-degraded MB dye by (blank), pure TiO_2M, and $Fe_3O_4/SiO_2/TiO_2$ composite

Catalyst	Apparent rate Constant, k_{app} (hour^{-1})	Correlation coefficient (R^2)
Blank (Non-catalyst)	0.012	0.122
Pure TiO_{2M}	0.464	0.866
$Fe_3O_4/SiO_2/TiO_2$ composite	0.956	0.992

than those of pure TiO_{2M}. This indicates that the reaction rate and the degree of linearity of $Fe_3O_4/SiO_2/TiO_2$ composite (plot a) for the linear plots of $-\ln (C_t/C_o)$ against irradiation time were observed higher than those of pure TiO_{2M} (plot b).

CONCLUSION

$Fe_3O_4/SiO_2/TiO_2$ composite has been synthesized through a mechanochemical method using wet milling process. The $Fe_3O_4/SiO_2/TiO_2$ composite possesses both of ferromagnetic and photocatalytic properties. TEM observation revealed that the particle size of as-prepared TiO_2 is 20nm which is smaller than that pure TiO_{2M} commercial product (100nm). Thus, the photocatalytic property of $Fe_3O_4/SiO_2/TiO_2$ is higher than that pure TiO_{2M} commercial product for elimination of methyl blue in water. In addition, $Fe_3O_4/SiO_2/TiO_2$ composite is more simple because of easily recovered from water using external magnetic.

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