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Synthesis and Characterization of Magnetized Photocatalyst $Fe_3O_4/SiO_2/TiO_2$ by Heteroagglomeration Method

Sari Hasnah Dewi[1,2], Sutanto[1], A Fisli[2], and S Wardiyati[2]
[1]Chemistry Dept, Pakuan University. Bogor City.
[2]Center for Science and Technology of Advanced Materials – National Nuclear Energy Agency. Kawasan Puspiptek Serpong. 15314. Indonesia.

Corresponding author : hasyarri@batan.go.id

Abstract. Magnetic photocatalysts $Fe_3O_4/SiO_2/TiO_2$ have been prepared using heteroagglomeration method. Synthesis of magnetic photocatalyst $Fe_3O_4/SiO_2/TiO_2$ was carried out through four stages : (1) synthesis of photocatalyst TiO_2 nanoparticles by $TiCl_4$ co-precipitation in ammonia solution, (2) synthesis of Fe_3O_4 nanoparticles through precipitation method using a mixture of Fe (III) / Fe (II) (2: 1 mole ratio) in ammonia solution, (3) coating with SiO_2 through hydrolysis of silicate ion, (4) in the final stage, Fe_3O_4/SiO_2 was mixed with TiO_2 in hetero-agglomeration manner. Structure and morphology of resultan composites have been investigated by X-ray diffraction (XRD), Vibrating sample magnetometer (VSM), Fourier transform infrared (FTIR) and Transmission electron microscopy (TEM) were confirmed that composite $Fe_3O_4/SiO_2/TiO_2$ succefully synthesized. The functionality photocatalyst of the particles was tested by eliminating of methylene blue (MB) under UV light. The result showed the magnetite photocatalyst $Fe_3O_4/SiO_2/TiO_2$ has phototacalytic and absorbtion properties so that it has good performance at dyes removal in water higher than pure TiO_2, and capable to perform repeatition process at least 4 times.

1. Introduction

In the area of advanced oxidation technology, titanium dioxide (TiO_2) photocatalyst has been used for a long time as a solution to overcome the environmental problems such as water purification, disinfectant materials and waste processing. The properties of TiO_2 is well known as a semiconductor that has the best catalytic characteristic, chemically stable, has good oxidizing strength, non-toxic and low usage cost [1,2,3].

Photocatalyst nanoparticles faces obstacles in application, for example release and fate nanoparticles in the environtment. Many effort have been made in photocatalyst design to recover the challenge. Magnetite technology introduced to coupled with photocatalyst. Magnetite photocatalyst is excelent because can be recolected by external magnetic field in suspension system [4].

Another technical challenge occur if magnetite iron oxide (Fe_3O_4) directly interacting with titanium oxide (TiO_2), the photodissolution phenomenon will occur due to bandgap interaction. This phenomenon can reduce the overall photocatalytic activity. Coating with SiO_2 between magnetic and photocatalyst phase can serve as a barrier between both of phase and inhibit the photodissolution [5].

Many effort have been made in development of composite synthesis method, such as core sell [4,6], and sol gel method [7], but still face the shortcoming because those are using organic complex materials. Hetero-agglomeration synthesis method introduced as excellent method because it easy processes and environment friendly [2,6,8]. The process in hetero-agglomeration occurs through aggregation where the coating particles stick on the surface of the particles that will be coated. This process is an interaction between two different phases. The particles in the liquid agglomerated

through electrostatic interaction between opposite surface charge of particles, and Van der Waals force. Produce new bond of agglomerated particles which are permanent and irreversible [5]. But there is barrier from hydrogen bonding of water that impede the agglomeration process. Ultrasonic technique allows the agglomeration of particles because of the collisions between particles. Ultrasonic wave disturbing the water layer by cavitations process, creating a dipole moment, increasing the interaction between molecules, causing particles interest and coagulation [9,10].
This study developed a method to regain the nanoparticles photocatalyst that were dispersed in the water easily. Place the nanoparticles photocatalyst in a magnetic material allows it to be collected magnetically. Previously study, Fisli et. al, 2015[11] have successfully prepared $Fe_3O_4/SiO_2/TiO_2$. This composite was made used TiO_2 nanoparticles commercial and prapared Fe_3O_4/SiO_2 nanoparticles on hetero-agglomeration process. In this study, photocatalyst magnetic composites ($Fe_3O_4/SiO_2/TiO_2$) was prepared used synthesized TiO_2 nanoparticles by sol-gel method and prepared Fe_3O_4/SiO_2 in hetero-agglomeration process.

2. Materials and Method

2.1. Materials

Titanium Chloride ($TiCl_4$), ammonium hydroxide (25% wt% NH_4OH), ferric chloride hexahydrate ($FeCl_3$. $6H_2O$) ferro chloride tetrahydrate ($FeCl_2$. $4H_2O$), sodium hydroxide (NaOH), ammonium sulphate (NH_4 (SO_4)), sodium silicate ($NaSiO_3$), methylene blue (MB), ethanol and demineralized water.

2.2. Preparations of photocatalyst particles

TiO_2 nanoparticles were prepared using sol-gel method, with a modified procedure refers to the articles of Zang et al, 1999 [12]. A solution of titanium chloride and ammonium hydroxide was used as precursor. All chemicals were obtained from Merck were used as received. $TiCl_4$ was added into beaker glass at temperature of 5 °C, then diluted until a concentration of 3 M. The NH_4OH 2.5 M solution was added dropwise to $TiCl_4$ solution on heating conditions 70 °C until reaching a pH of 7. The stirring was continued for 1 hour. Separating and washing of the sediment from the solvent was conducted by centrifugation to remove free chloride ions. Then the sediment was dispersed in the absolute ethanol to remove adsorbed water and to eliminate agglomeration during the drying process.The sample finally has dried in the oven at 60 °C for 48 hours.
Preparation of magnetic particles coated by silica (Fe_3O_4 /SiO_2), the magnetic particles were prepared by precursor salt of ferrous and ferric chloride ($FeCl_3$ and $FeCl_2$) that were dissolved in 1 N HCl and stirred with a magnetic stirrer. The molar ratio of $FeCl_3$ and $FeCl_2$ was 1: 2, then the solution of iron salt was precipitated using 1.5 M NH_4OH. Stirring was continued up to 1 hour to ensure a perfect mixing of precursors. Then, the addition of sodium silicate was added dropwise into the magnetic sediment that have been made previously, while stirred rapidly. After that, the pH was adjusted to 10 with the addition of HCl 1 N. Stirring of the mixture was conducted for 4 hours, then soaked overnight. Formed Fe_3O_4/SiO_2 particles were washed up to neutral pH using demineralised water. The mixture from washing process was stored in the demineralised water for further process.
Preparation of Fe_3O_4 /SiO_2/TiO_2 , the used materials were came from material that has been prepared above that are TiO_2 and Fe_3O_4/SiO_2. A total of 3.52 grams of TiO_2 was added into $(NH_4)SO_4$ 0.02 M and ultrasonicated for 5 minutes to make a good mixture. TiO_2 suspension was mixed into the mixture of magnetic Fe_3O_4 /SiO_2 that have been made before and the solution pH was adjusted to 5. Then this mixture was ultrasonicated for 30 minutes at room temperature. Then the sediment was separated by centrifugation at a speed of 400 rpm for 10 minutes. The solid from that process was dried by heating in the oven at 60 ˚C overnight, then heated at 100 ˚C for 2 hours. The dried solids were crushed using a mortar to produce fine powder.
Characterization of the photocatalyst samples was carried out by X-ray diffraction (XRD), Vibrating sample magnetometer (VSM), Fourier transform infrared (FTIR) and Transmission electron microscopy (TEM) and analysis of isoelectric point by Zeta potential.

The photocatalytic activity of photocatalyst $Fe_3O_4/SiO_2/TiO_2$, Fe_3O_4/SiO_2 and TiO_2 were tested by photodegradation of MB aqueous solution at ambient temperature. The photodegradation was carried out at close box, of which UV radiation source is Pen Ray 100 Watt, its wave length is 365 nm (Model UVP Pen Ray 90-006-01). The initial MB was (C_0) 20 mg/L, the photocatalyst concentration was 1 g/L. The concentration of MB (C_t) was analyzed through Perkin Elmer Lambda 25 Spectrophotometer at λ_{max} = 663 nm. The decolouration rate (D) or efficiency can be obtained by the following formula :

$$D = \frac{C_0 - C_t}{C_0} x100\%$$

3. Result and Discussion

3.1. Characterization of photocatalyst

3.1.1. X-Ray Diffraction(XRD)

Figure 1 shows XRD diffraction pattern of Fe_3O_4 after coated by SiO_2 has similarities with the diffraction pattern of pure Fe_3O_4 (JCPDS-ICDD 030 863) which has not been coated with SiO_2. SiO_2 phase as amorphous does not show diffraction pattern. After forming composite with TiO_2 anatase phase, it shows the peaks from combination of Fe_3O_4 and TiO_2 anatase phases. This phenomenon shows that the magnetite phase and crystal phase of anatase TiO_2 retained in $Fe_3O_4/SiO_2/TiO_2$ composite photocatalyst.

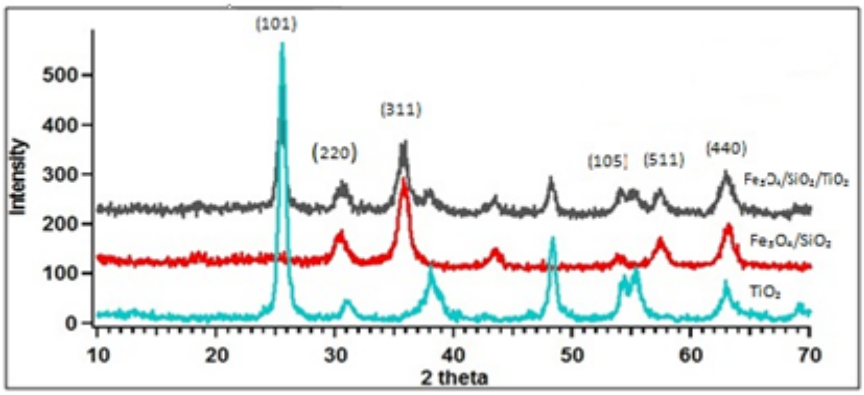

Figure 1. XRD pattern of TiO_2, Fe_3O_4/SiO_2 and $Fe_3O_4/SiO_2/TiO_2$

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

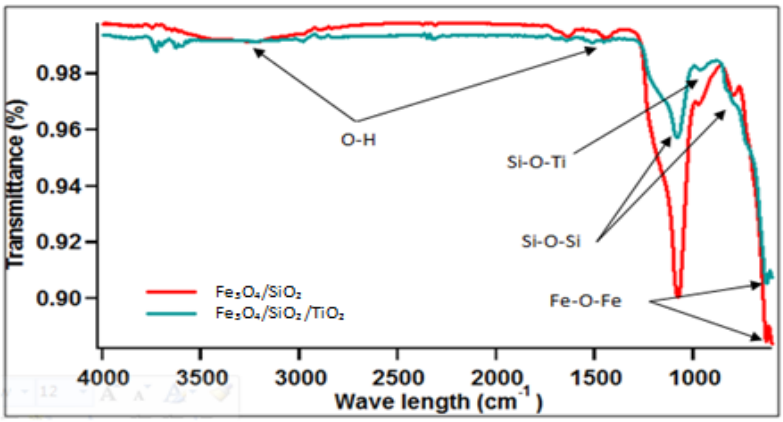

Figure 2. FTIR spectra of Fe_3O_4 /SiO_2 and $Fe_3O_4/SiO_2/TiO_2$

Identification of functional groups and oxide metal bonding on Fe_3O_4 /SiO_2 and Fe_3O_4/SiO_2/ TiO_2 was conducted through measurement using Fourier Transformation Infra Red Spectroscopy (FTIR). Referring to the report of Wang et al, 2011 [7], that the spectrum of the signal at wavelength 800 cm^{-1} is the symmetric vibration of Si-O-Si ,whereas the signal at 1080 cm^{-1} is the asymmetric stretching vibration of Si-O-Si. The spectrum of Si-O-Ti vibration will be visible at wavelength 940-960 cm^{-1}. The presence of water appears to be visible in the spectrum at wavelength 1600 cm^{-1} for the bending vibration and 3300 cm^{-1} for stretching vibration. The presence of iron oxide will be visible in the vibration spectrum at wavelength 628 cm^{-1}. In the spectrum of Fe_3O_4/SiO_2/TiO_2 shows a new absorption at 940 cm^{-1} compare to Fe_3O_4/SiO_2 spectrum. This is a vibration of Si-O-Ti. The appearance of absorption peaks in Fe_3O_4/SiO_2/TiO_2 sample shows the presence of a new bond between Si and Ti that is connected by oxide after TiO_2 composited with $Fe3O_4$/SiO_2 [13].

3.1.3. Vibrating Sample Magnetometer (VSM)

The result of VSM measurements displayed on the hysteresis curve of Fe_3O_4, Fe_3O_4/SiO_2 and Fe_3O_4/ SiO_2/TiO_2. The shape of that hysteresis curve resembles a superparamagnetic behavior. Magnetic saturation values produced by Fe_3O_4 magnetite is 93 emu/g, almost approach the magnetic saturation value of Fe_3O_4 magnetite phase 92 emu/g (Cullity, 1972) [14]. Furthermore, the magnetic saturation value generated by Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2/TiO_2 respectively 60 emu/g and 40 emu/g. This phenomenon shows that a growing number of non-magnetic phase (SiO_2 and TiO_2) contained in the sample produced lower magnetic saturation value.

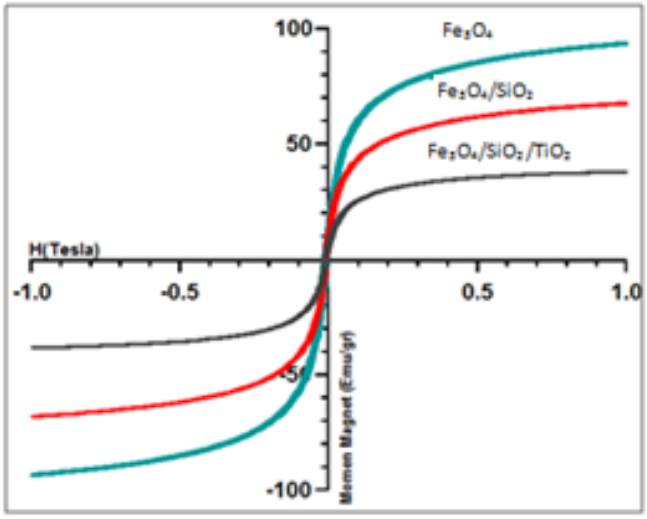

Figure 3. The hysteresis curve of Fe_3O_4 /SiO_2 and Fe_3O_4/SiO_2/ TiO_2

3.1.4. Transmission Electron Microscopy (TEM)

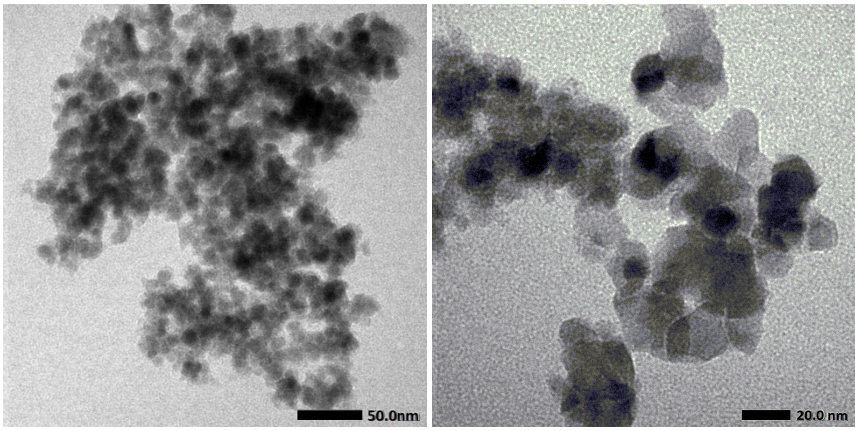

Figure 4. Photo Tem of $Fe_3O_4/SiO_2/TiO_2$

The morphology samples was investigated by transmission electron microscopy (TEM) (Figure 4). Based on images can be concluded that the hypothesis of agglomeration pattern of magnetic particles Fe_3O_4/SiO_2 with TiO_2 photocatalyst was achieved. It can be estimated that the average agglomeration size is 20 nm.

3.1.5. Determination of the isoelectric point

The isoelectric point (particle surface charge in the water) was measured by a Zeta potential. In this study, the used materials have different isoelectric point. Theoritically, Fe_3O_4 isoelectric point is at pH 7.9 (Fisli, 2014). In this study, the measured isoelectric point of Fe_3O_4/SiO_2 material occurs at pH 3, the results of these measurements approach the isoelectric point of SiO_2 at pH 3.2. This phenomenon indicates that the Fe_3O_4 magnetite has been coated by a layer of SiO_2. Measurement of isoelectric point was also conducted to TiO_2 and obtained at pH 6.2. Based on the isoelectric point, we can adjust the pH of the solution suitable for the heteragglomeration process. In this research the agglomeration procces formed at pH 5. A condition in which two composite particles have the opposite surface charge in the water, so that the mixing of two particles with opposite charge will produce electrostatic interactions between the particles and facilitate the attachment of composite materials.

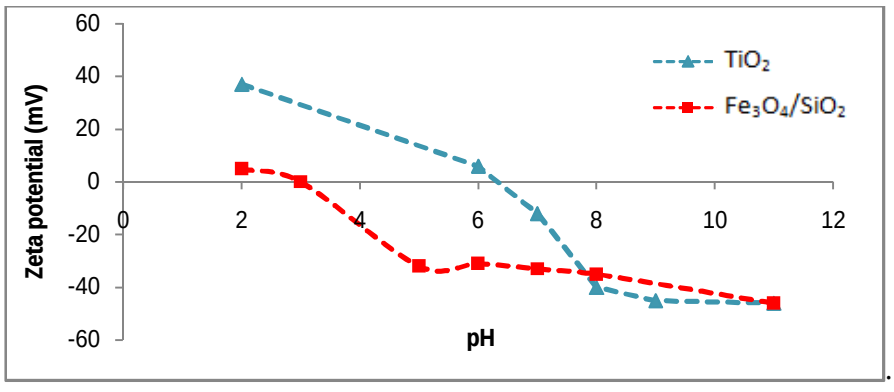

Figure 5. The isoelectric point of Fe_3O_4/SiO_2 and TiO_2

3.2. Photocatalytic Activity Test Result $Fe_3O_4/SiO_2/TiO_2$

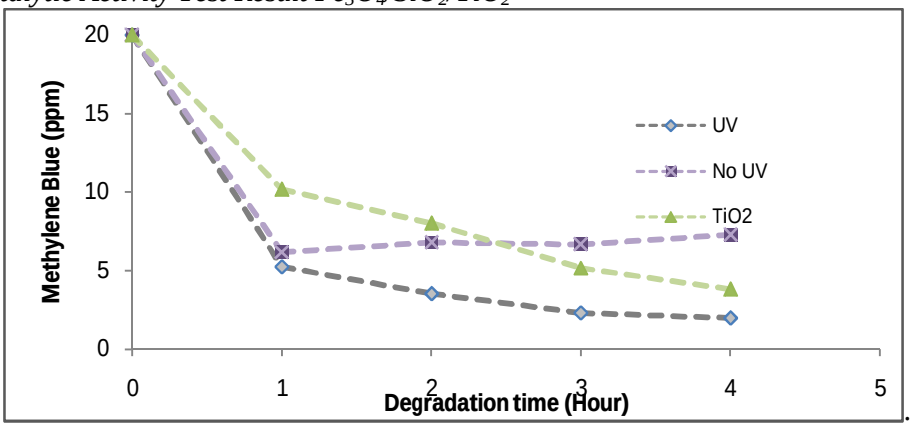

Figure 6. Degradation of Methylene Blue by photocatalyst $Fe_3O_4/SiO_2/TiO_2$ irradiated and non-irradiated with UV light and TiO_2.

Figure 6 is the elimination rate of methylene blue by the photocatalyst $Fe_3O_4/SiO_2/TiO_2$ with irradiation and without UV irradiation. The curve above shows that without irradiation of UV light (dark), concentration of methylene blue decreased significantly by 65% in the first 1 hour and constant until the next 4 hours. This phenomenon proves the adsorption processes that occur in these materials. Adsorption properties is expected come from SiO_2 (Fisli, et al, 2014). In the experiments with UV light irradiation, $Fe_3O_4/SiO_2/TiO_2$ in the first 1 hour also capable to decrease the concentration of methylene blue by 15 ppm. The process of methylene blue elimination still continues until the concentration close to 1 ppm after 4 hours, which only photocatalytic process that is occured. This result is better compared to pure TiO_2 that is only able to eliminate the methylene blue as much as 10 mg/L at 4 hours process. As Zhou et al reported that a mixture of metal oxides (TiO_2-SiO_2) causes an increase in photocatalytic performance because of the increase of surface adsorption and the increase of hydroxyl radicals present on the surface.

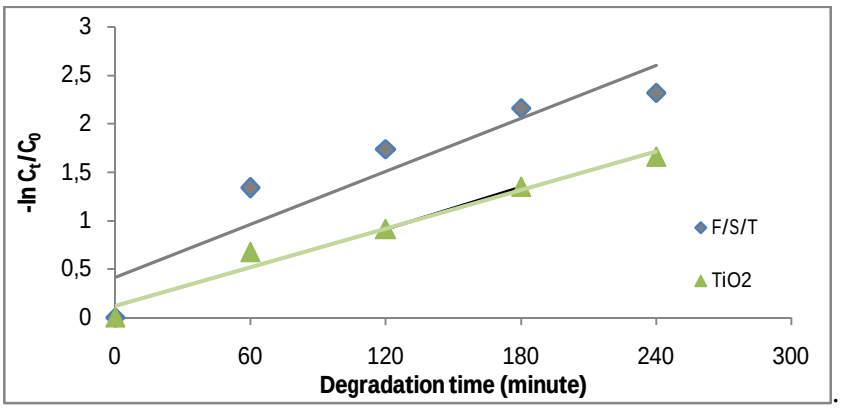

Figure 7. Curve of the pseudo-order linear elimination of methylene blue

Figure 7 shows the first order pseudo linear curve of methylene blue elimination. This curve shows the relationship between -ln (Ct/C0) versus decomposition time of methylene blue by two photocatalysts, namely $Fe_3O_4/SiO_2/TiO_2$ and TiO_2. In Table 1, it can be seen that the value of apparent rate constant for photocatalyst $Fe_3O_4/SiO_2/TiO_2$ and TiO_2 are respectively 0.5464/hour and 0.3992/hour. By using the formula $t_{½} = \frac{\ln 2}{k_{app}}$, the half-life of decomposition that was achieved by the two of photocatalysts can be calculated. Based on this formula, the half time of decomposition by catalyst $Fe_3O_4/SiO_2/TiO_2$ was 1.2 hours, that is shorter compared to the half-time of decomposition by TiO_2 1.7 hours. From

these data, it can be concluded that the performance of synthesized photocatalyst $Fe_3O_4/SiO_2/TiO_2$ is better compared to pure TiO_2.

Table. 1. Parameters of the pseudo-order kinetics of elimination of methylene blue

Catalyst	Apparent rate constant k($hour^{-1}$)	Correlation coefficient (R^2)	Half life $t_{1/2}$ (hour)
$Fe_3O_4/SiO_2/TiO_2$	0.5464	0.8665	1.2683
TiO_2	0.3992	0.9734	1.7359

3.3. Repeatability test result of catalyst $Fe_3O_4/SiO_2/TiO_2$

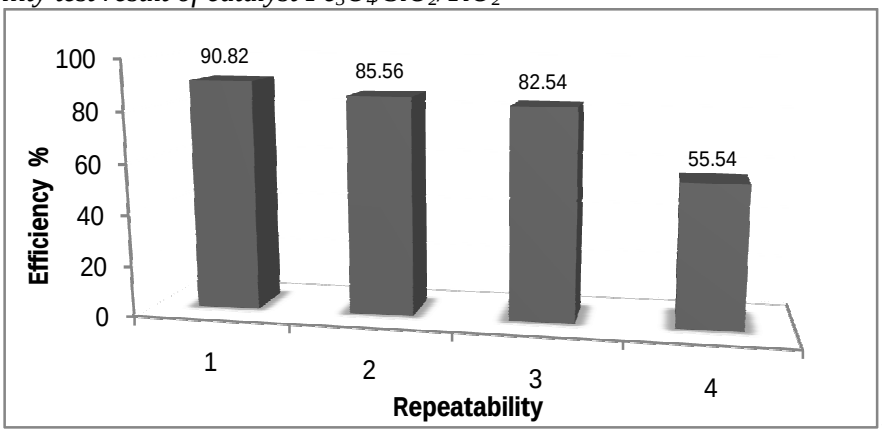

Figure 8. Repeatability process using a magnetic photocatalyst $Fe_3O_4/SiO_2/TiO_2$ in the degradation of methylene blue.

Figure 8 shows that fresh $Fe_3O_4/SiO_2/TiO_2$ can degrade 10 mg/L methylene blue as much as 91% for 1 hour. $Fe_3O_4/SiO_2/TiO_2$ that has been used previously can be reused but decreased by 85% at photodegradation capability on the second repetition, 82.5% at third repetition and 55, 5% in fourth repetition. From these data, it appears that the synthesized $Fe_3O_4/SiO_2/TiO_2$ photocatalyst has a good photocatalytic properties stability, at least for 4 times repeated use. This is in good agreement with Fanun's reports [15], stating that the maximum effectiveness of the use of photocatalyst is in 4 repetitions.

4. Conclusion

Synthesis of a magnetic photocatalyst $Fe_3O_4/SiO_2/TiO_2$ has been successfully carried out by the heteroagglomeration method. The structure of phase was analyzed by XRD which shows the present of TiO_2 anatase phase that are combined with Fe_3O_4/SiO_2 phase. Magnetic properties of the material shows that the substance has superparmagnetic behaviour. Functional groups that show the formation of a new bond of Si-O-Ti. The agglomeration patterns of TiO_2 and Fe_3O_4/SiO_2 with size of 20 nm. Elimination test of the dye shows that synthesized photocatalyst magnetite $Fe_3O_4/SiO_2/TiO_2$ have photocatalytic and also adsorption properties so that it has a good performance in methylene blue removal in water. This photocatalyst is also capable to perform the repeatition process at least for 4 times.

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