The effect of Fe$_3$O$_4$ concentration to photocatalytic activity of Fe$_3$O$_4$@TiO$_2$-PVP core-shell nanocomposite

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Abstract. A study on the preparation of Congo red textile dyes using nanocatalysts, Fe$_3$O$_4$@TiO$_2$ material, and Polyvinyl Pyrrolidone (PVP) has been successfully carried out. The preparation of these dyes is intended as a controller of the shape and size of particles and as a superior adhesive in solution. Fe$_3$O$_4$@TiO$_2$ core-shell (FTP) nanocomposite was carried out by coprecipitation method. The Fe$_3$O$_4$ nanoparticles were designed as cores that were synthesized from Cilacap iron sand, while TiO$_2$ nanoparticles were selected as a shell through the synthesis of Titanium (III) chloride. Fe$_3$O$_4$@TiO$_2$ core-shell nanocomposite is characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), and UV-Visible Spectroscopic (UV-Vis). Through XRD data analysis, the crystalline nano-phase composite of Fe$_3$O$_4$@TiO$_2$ core-shell did not experience significant changes with the addition of Fe$_3$O$_4$ concentration. The contribution of the addition of Fe$_3$O$_4$ concentration can be observed in changes in sample grain size. The higher the concentration of Fe$_3$O$_4$ is, the smaller the grain size of the samples produced, ranging between 6-9 nm and can increase the percentage of degradation of Congo red dyes. In addition, optimum degradation in UV-Vis characterization occurred in FTP 0.5 samples that reached 78.20% at minute 100. The photodegradation effect that occurs in Congo red dyes is caused by photocatalytic mechanisms.

1. Introduction
In recent years, the ability of communities to access clean water has become increasingly difficult. This is caused by contamination of pollutants from industrial activities, animal husbandry, agriculture and household activities, which significantly reduces water quality in water bodies such as lakes, rivers, and reservoirs [1]. One of the industrial activities that significantly affect water pollution and deterioration is the textile industry because the dyes used in the textile coloring process are forming waste. Congo red dye is one of the textile dyes, which has toxic content and is high enough to cause an ecosystem balance in unstable waters [2]. Traditional water and sewage treatment are ineffective at removing these contaminants [3]. Therefore, effective technology is needed to prevent or reduce the harmful effects of pollutants with nanomaterial engineering technology approaches.

Magnetite (Fe$_3$O$_4$) is one of the Magnetic Nanoparticles (MNP) produced from nanomaterial engineering technology [4]. Magnetic (Fe$_3$O$_4$) properties have many benefits in various applications, one of which is as a metal separator in wastewater treatment [5]. However, the weakness of Fe$_3$O$_4$ is that it is easy to experience agglomeration. In reducing the effects of agglomeration on Fe$_3$O$_4$ nanoparticles,
it is necessary to perform the functionalization on the nanomaterial by coating or Core-Shell through Titanium Oxide (TiO$_2$) catalyst material. TiO$_2$ is a transition metal that has several advantages, including having excellent optical characteristics, high photocatalytic activity, non-toxic, stable chemical properties, and relatively inexpensive [6]. Moreover, TiO$_2$ is a material that can be applied as a photocatalyst, utilization of solar cells, a health product, a biological and chemical sensor, and paint pigmentation [7].

Studies investigating the fabrication and characterization of Fe$_3$O$_4$ and TiO$_2$ nanoparticles have been widely reported by researchers. Khashan et al. [8], for instance, successfully fabricated Fe$_3$O$_4$@TiO$_2$ core-shell nanocomposites through a novel method. They reported that the average size of Fe$_3$O$_4$@TiO$_2$ core-shell nanocomposites is around 50 -100 nm, where these results differ significantly compared to the size of Fe$_3$O$_4$ which has an average size of 2-10 nm and TiO$_2$ material as the shell has a thickness of about 5 nm [8]. Obtaining this size indicates that Fe$_3$O$_4$ tends to be agglomerated inside the TiO$_2$ shell [8]. Xue et al. [9] also successfully synthesized Fe$_3$O$_4$@TiO$_2$ core-shell nanoparticles and reported that the obtained TiO$_2$ core-shell did not function optimally because of the photodisolution effect on Fe$_3$O$_4$@TiO$_2$ core-shell nanocomposites. The photodissolution effect occurs because of electronic interactions between Fe$_3$O$_4$ and TiO$_2$, causing the activity of TiO$_2$ to weaken. To reduce this effect, we need a barrier material between Fe$_3$O$_4$ and TiO$_2$. The barrier material will work if it has special characteristics, which are materials that can maintain the effectiveness of the physical properties of the TiO$_2$ catalyst and the stability of the Fe$_3$O$_4$ nanoparticles. An effective material to maintain the physical properties of nanomaterials and prevent the effects of photodilution in this study is Polyvinylpyrrolidone (PVP). PVP is a polymer that can control the shape and size of particles [10]. PVP can also be used as a good adhesive in a solution of water or alcohol [11]. Therefore, it is important to study the optimization of Fe$_3$O$_4$@TiO$_2$ core-shell nanoparticles on their photocatalytic activity. Fe$_3$O$_4$@TiO$_2$-PVP core-shell nano materials in this study were synthesized using the coprecipitation method with a mass variation of Fe$_3$O$_4$. Fe$_3$O$_4$@TiO$_2$-PVP core-shell nano materials composite was characterized using X-Ray Diffractometry (XRD), Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM) respectively to determine the structural properties, functional groups and morphology of the samples. To examine the degradation of the Congo Red dye, UV-Vis characterization was used.

2. Methods

2.1. Synthesis of Fe$_3$O$_4$-PVP Nanoparticles

Fabrication of Fe$_3$O$_4$ nanoparticles was carried out through a simple coprecipitation method using natural iron sand. The process began by drying the iron sand and separating it using a permanent magnet. Separated iron sand was then dissolved into hydrochloric acid (HCl) and distilled on a hot plate at a certain temperature. The solution was mixed with 5 mL of PVP solution and distilled water in a ratio of 1:10. Furthermore, mixed solution was titrated with Ammonium Hydroxide (NH$_4$OH) to form a black precipitate. The precipitate formed was then washed repeatedly with distilled water until the pH of the solution reaches 7. The final step in this process was drying the precipitate (Fe$_3$O$_4$-PVP nanoparticle powder) using an oven at 100 C.

2.2. Synthesis of Fe$_3$O$_4$@TiO$_2$-PVP Core-Shell

The initial step of forming Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites were to mix 5 mL of Titanium Trichloride (TiCl$_3$) solution with HCl and stirred on a hot plate. The process was continued by adding 0.5 g of Fe$_3$O$_4$-PVP nanoparticle powder to the solution until it was evenly mixed. The mixture that had been formed was then titrated with NH$_4$OH to form a precipitate. The resulting precipitate was then washed to normal pH using ethanol. The process was continued at the stage of drying the precipitate using an oven set at a temperature of 100 °C. The final stage of synthesis was to perform calcination processes on the sediment using a furnace at 500 °C for 2 hours to produce Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanoparticle powder. This process was repeated for variations in the mass of Fe$_3$O$_4$-PVP nanoparticles as much as 0.7 and 0.9 g. The results of Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanoparticles with
a mass variation of Fe₃O₄@TiO₂–PVP of 0.5, 0.7, and 0.9 g referred to as FTP 0.5, FTP 0.7, and FTP 0.9.

2.3. Characterization Fe₃O₄@TiO₂–PVP Core-Shell Nanocomposites

The Fe₃O₄@TiO₂–PVP core-shell nanocomposites that had been successfully synthesized were then characterized using XRD, FTIR, SEM, and UV-Vis. XRD characterization was used to decide the phase composition, crystal size, and lattice parameters of the sample. FTIR characterization was performed to determine the functional group of the sample. Absorption at certain wavenumbers is a characteristic of the bond between elements in the Fe₃O₄@TiO₂–PVP core-shell nanocomposites that need to be confirmed. SEM characterization was used to analyze the morphology and size of Fe₃O₄@TiO₂–PVP core-shell nanocomposites. To analyze the ability of absorption of light in the visible area of the sample Fe₃O₄@TiO₂–PVP core-shell, the characterization used in this study was UV-Visible spectrophotometer.

3. Results and Discussion

3.1. X-ray Diffraction Patterns and Crystal Structures

The results of XRD characterization and refinement of Fe₃O₄ and TiO₂ nanoparticles are indicated in Figure 1. Figure 1 shows that the diffraction patterns generated from Fe₃O₄ and TiO₂ nanoparticles correspond to magnetite and titanium dioxide phases according to the AMICSD database 0002400 and COD 2310710. Profile of the diffraction peaks of Fe₃O₄ samples was detected in crystal orientation with index positions (220), (311), (400), (422), (511), (440) and (533), respectively, as shown in Figure 1a. In contrast, the profile of the diffraction peaks of TiO₂ sample was recorded in crystal orientation with index positions (110), (400), (020), (510), (121), (420), (611), (022) and (521), respectively, as shown in Figure 1c. Crystal orientation in the TiO₂ sample correlates with the results of the study reported by Yokosuka et al. [12]. They revealed that the crystallinity of TiO₂ is anatase in the form of marked diffraction peaks at an angle of 2θ 25.1° with a crystal orientation (110) [12]. The results of this characterization were then refined using the Rietica application and portrayed nanoparticle sizes of Fe₃O₄ (9.98 nm) and TiO₂ (20.67 nm), respectively. The Fe₃O₄ nanoparticles and TiO₂ are close to the results reported by previous studies, each at 11.56 [13] and 24.07 nm [12]. The refinement results also revealed that the confirmed sample of Fe₃O₄ nanoparticles was cubic, whereas the TiO₂ nanoparticles had a tetragonal (anatase) crystal structure.

Other fitting methods are also performed as a comparison or confirmation of results to determine the particle size of Fe₃O₄ and TiO₂ samples, which are calculated using the Debye Scherrer equation [14]. FWHM values were taken from the highest diffraction peaks of Fe₃O₄ and TiO₂ nanoparticles as shown by Figures 2a and 2b and portrayed particle sizes of 10.12 and 14.45 nm, respectively. The results of calculations on Fe₃O₄ nanoparticles indicate similar findings from that of Rietica refinement, but different from TiO₂ nanoparticles. This difference is partly due to the suboptimal results of the fittings when using the Debye Scherrer equation model for TiO₂ nanoparticles. The considerable deviation between the experimental data and the model data causes the FWHM value obtained to be larger than it actually is, causing the TiO₂ nanoparticle size to be slightly smaller than the refinement calculation.
Figure 1. XRD characterization of Fe$_3$O$_4$ (a) and TiO$_2$ (c) and refinement Fe$_3$O$_4$ (b) and TiO$_2$ (d) samples

Figure 2. Results of the fittings from the highest peaks of Fe$_3$O$_4$ (a) and TiO$_2$ (b) using the Lorentz equation
Figure 3 shows the results of XRD characterization of TiO$_2$, Fe$_3$O$_4$, and Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanoparticles with mass variations of Fe$_3$O$_4$–PVP. The entire diffraction pattern of Fe$_3$O$_4$@TiO$_2$–PVP core-shell is dominated by the diffraction peak of Fe$_3$O$_4$ nanoparticles and corresponds to the ICSD database (30680), which is in the form of a cubic structure. Based on XRD data analysis using Rietica software, the greater the concentration of Fe$_3$O$_4$–PVP in the Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites, the lower the peak intensity of the Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites. This can be observed from the change in diffraction intensity at the crystal orientation position (311) at an angle of 2$\theta$ = 35.61°. As the diffraction intensity decreases, the FWHM value of the core particles Fe$_3$O$_4$@TiO$_2$–PVP core-shell increases with the enhanced concentration of Fe$_3$O$_4$–PVP. This results in a reduction in the size of the Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites to around 6–9 nm. The acquisition of particle size is corroborated by the results of research by Dagher S et al. [15], which explained that the nanoparticle size of Fe$_3$O$_4$@TiO$_2$–PVP core-shell has dimensions of 5–10 nm. Furthermore, the results of XRD data analysis revealed that the peak intensity of TiO$_2$ diffraction was very low, even undetectable. This is caused by the dominance of Fe$_3$O$_4$ nanoparticles and the effect of PVP polymers during the synthesis process. PVP polymers effectively reduce the agglomeration of Fe$_3$O$_4$ nanoparticles with the smallest size in the FTP composition of 0.9. However, the presence of PVP polymers results in reduced crystallinity of the sample, which causes the composition of TiO$_2$ nanoparticles not to be detected perfectly. Thus, the composition of TiO$_2$ nanoparticles is not optimal enough for the synthesis of Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites.

Figure 3. Profile of XRD nanoparticles TiO$_2$, Fe$_3$O$_4$, and Fe$_3$O$_4$@TiO$_2$–PVP core-shell

### 3.2. FTIR Characterization

The results of FTIR characterization of Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites with Fe$_3$O$_4$–PVP nanoparticle mass composition can be shown in Figure 4. Based on the FTIR data analysis, bonding of Ti-O-Fe functional groups were detected at the absorption of wavenumbers 416.62–785.03 cm$^{-1}$. These results are similar to research conducted by Nadimi et al. [16], which states that the presence of Ti-O-Fe bonds occurs at wavenumbers 500–800 cm$^{-1}$. The findings were reported by Li et al. [17], contending that the bonding of the functional group Ti-O-Fe occurs at the absorption of wavenumber of 449 cm$^{-1}$. This finding was also corroborated by Zheng et al. [18], which shows that the bonding group of stretching vibrating functions of Ti-O and Fe-O at wavenumbers 700-1000 cm$^{-1}$. Determination of the functional group bonds of Fe-O, Ti-O, and Ti-O-Fe shows that the synthesis of Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites were successful.
In addition, the results of data analysis also observed the stretching of O-H functional groups detected at wavenumber 1629.85 cm\(^{-1}\). This finding is in accordance with studies that have been reported by several researchers who yielded that stretching functional groups of O-H are at wavenumber \(~1600\) cm\(^{-1}\) [16,19,20]. Stretching of O-H functional group bonds that experience vibrating also occurs at wavenumber 3298.28-3400.50 cm\(^{-1}\). The functional group stretching is in accordance with previous studies by Chen et al., Ghafuri et al., and Li et al., which found that stretching O-H functional groups are at wavenumber \(~3400\) cm\(^{-1}\) [17,20,21]. This result was also corroborated by research carried out Zheng et al., which shows that O-H stretching occurs at wavenumbers 2800-3600 cm\(^{-1}\) [18]. Detection of the O-H stretching functional group is as a result of the presence of H\(_2\)O residues excluded in the Fe\(_3\)O\(_4\)@TiO\(_2\)–PVP core-shell nanocomposites and the formation of O atomic bonds with PVP polymers and H atomic bonds with secondary functional groups.

![Figure 4. FTIR characterization from Fe\(_3\)O\(_4\)@TiO\(_2\)–PVP core-shell nanoparticles](image)

**3.3. SEM Characterization**

The image of TiO\(_2\) nanoparticles was successfully characterized using SEM instruments, and the results are shown in Figure 5. Based on data analysis, TiO\(_2\) nanoparticles undergo agglomeration with an average particle size distribution of 34.64 nm. This value is quite large when compared with the results obtained by previous studies, which reported that the average size of TiO\(_2\) nanoparticles is around 25-30 nm [22]. The average particle size of TiO\(_2\) through SEM characterization is also greater than the results of the XRD refinement that is equal to 20.67 nm. Two factors cause differences in the results of the TiO\(_2\) particle sizes between SEM and XRD characterization. First, TiO\(_2\) nanoparticles undergo agglomeration so that the detected particle size becomes larger than the main particle. Second, there are differences in detection instruments between SEM and XRD characterization. SEM characterization uses electron clouds to scan the surface of TiO\(_2\) nanoparticles. The scanning result of the electron cloud is a representation of the surface of TiO\(_2\) nanoparticles characterized. Meanwhile, XRD characterization is an instrument that uses an X-ray to observe diffraction scattering, which is reflected by nano TiO\(_2\) particles. XRD characterization can observe the crystal fields of TiO\(_2\) nanoparticles. A collection of crystal fields observed at a certain diffraction limit is a representation of the size of the TiO\(_2\) nanoparticles from the XRD test results. Thus, the TiO\(_2\) nanoparticle size resulting from XRD characterization will be of smaller value compared to using SEM characterization.
Figure 5. Morphology and graph distribution of TiO$_2$ nanoparticles

SEM characterization was also performed on Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites for 0.5 FTP samples. The morphology and distribution of Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanocomposites is shown in Figure 6. The results of direct observations documented that Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanoparticles also experience agglomeration as in TiO$_2$ nanoparticles. Based on data analysis, the average particle size distribution of Fe$_3$O$_4$@TiO$_2$–PVP core-shell is 24.77 nm. These results are significantly different from the results obtained from the XRD refinement of around 9 nm. This difference is caused by two factors, as explained in the previous paragraph. However, the average particle size of Fe$_3$O$_4$@TiO$_2$–PVP core-shell produced in this study is relatively smaller than the study reported by Li et al. [23]. They contend that the grain size of Fe$_3$O$_4$-TiO$_2$ ranges from 20-50 nm. By looking at the average grain size produced by Fe$_3$O$_4$@TiO$_2$ in the presence of PVP and the absence of PVP, the finding shows different results. In the absence of PVP the grain size produced by Fe$_3$O$_4$@TiO$_2$ tends to be greater than the addition of PVP polymers. Thus, it can be concluded that the addition of PVP composites can control the grain size of Fe$_3$O$_4$@TiO$_2$ to avoid agglomeration.

Figure 6. Morphology and graph distribution of Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanoparticles for FTP 0.5

3.4. **UV-VIS Characterization**

UV-Vis characterization was successfully carried out to observe photocatalyst activity in Fe$_3$O$_4$@TiO$_2$–PVP core-shell nanoparticles. The maximum wavelength used in this study is 497.5 nm. Figure 7 shows the comparison of the Congo Red concentration with the exposure time given during the experiment. The final concentration value of Congo Red coloring after exposure to UV lamps has decreased with the duration of the irradiation process from the duration of 20 minutes to 100 minutes. It can be concluded that Congo Red coloring can be degraded in the presence of sunlight. This phenomenon can occur because not all Fe$_3$O$_4$ nanoparticles are covered by TiO$_2$ nanoparticles. Therefore, Fe$_3$O$_4$ nanoparticles can behave as adsorbents from Rongo Red dyes.
Figure 7. Curve plot between exposure time and Congo Red dye concentration

Percentage degradation of Congo Red coloring can be calculated using equation 1. Calculation of degradation is calculated by recording the concentration of the sample after degradation ($A'$) and before degradation ($A_o$) obtained by entering into the linear regression Equation 1.

\[
\text{% degradation} = \frac{A_o - A'}{A_o} \times 100\%
\]  

(1)

Figure 8. Curve plot between exposure time and percentage of degradation of Congo Red coloring

Figure 8 shows the results of the photodegradation test affected by the length of UV light irradiation of the Congo Red dye from Fe$_3$O$_4$@TiO$_2$-PVP core-shell nanocomposites. The longer the irradiation was given, the greater the percentage of Congo Red dyes that degraded. These results are consistent with the study reported by Fowsiya et al. [26]. They report that the percentage of photodegradation from Congo Red increases with the time of UV irradiation [26]. In this study, the highest percentage of degradation of Congo Red dye that was 78.20% occurred in the Fe$_3$O$_4$@TiO$_2$-PVP core-shell nanoparticles with a mass variation of Fe$_3$O$_4$-PVP nanoparticles of 0.5 g and irradiation time of 120 minutes. When the Fe$_3$O$_4$@TiO$_2$-PVP core-shell nanoparticles are irradiated using UV, a catalytic process will occur where photons produced by UV light will be absorbed by Congo Red coloring. If the photon has an energy level that matches the surface of the sample, it will produce an electron-hole pair.
in the conduction and the valence band. Holes are representations of positive electrons that can oxidize contaminants that are absorbed directly and can produce hydroxyl radicals (OH-) that are very reactive. Meanwhile, the electrons in the conduction band can reduce the oxygen absorbed in the photocatalyst process, so that it will degrade contaminants that are absorbed [27]. Materials that are often used in this photocatalytic process are ZnO and TiO₂ because their superiority, which is sensitive to light, has excellent chemical stability and is inexpensive [28].

In this study, the Fe₃O₄@TiO₂-PVP core-shell nanoparticles were conditioned at normal pH. This condition was created to reduce the occurrence of agglomeration events, which tend to increase when in an acidic state so that it will cause a reduction in the surface area of the nanoparticles formed. For normal pH conditions, the photocatalyst surface tends to be negative and will reject anionic dye (Congo Red), as has been reported in previous studies by Ullah et al. [29]. They used tungsten doped TiO₂ to reduce Congo Red coloring with a maximum treatment time of 40 minutes [29]. The time difference obtained in the study of Ullah et al. [29] with this research it is assumed because of the role of PVP as a polymer that wraps Fe₃O₄@TiO₂-PVP core-shell nanoparticles thereby reducing the ability of TiO₂ to degrade faster. Interestingly, the research report reported by Thomas et al. [30] express different findings. They tested the catalytic process that occurred on Ba/Alg/CMC/TiO₂ nanocomposites with Congo Red coloring and obtained 30 minutes of degradation time with the amount of Congo Red lost by 41% and not even observed changes in the Congo Red dye effect when characterization was continued up to 240 minutes [30]. Thus, the Fe₃O₄@TiO₂-PVP core-shell nanocomposites produced in this study are more effective for use in the catalytic process in the Congo Red dye degradation process that occurs in river waste. Thus, the Fe₃O₄@TiO₂-PVP core-shell nanocomposites have the potential to be applied in tackling textile dye waste produced by industry.

4. Conclusion

Fe₃O₄@TiO₂-PVP core-shell nanocomposites have been successfully synthesized with a variation of Fe₃O₄-PVP mass of 0.5, 0.7, and 0.9 g. Crystal structure formed from Fe₃O₄ and TiO₂ nanoparticles is in the form of cubic and anatase structures with an average particle size of 9.98 and 20.67 nm. Meanwhile, Fe₃O₄@TiO₂-PVP core-shell throughout the diffraction peaks is dominated by diffraction peaks of Fe₃O₄ nanoparticles in the form of cubic structures. The greater the concentration of Fe₃O₄-PVP in the core particles of Fe₃O₄@TiO₂-PVP core-shell, the smaller the size of the Fe₃O₄@TiO₂-PVP core-shell nanoparticle is, which is around 6-9 nm. The surface morphology of TiO₂ nanoparticles and Fe₃O₄@TiO₂-PVP core-shell was successfully characterized using SEM instruments, and it produced particle sizes of 34.64 and 24.77 nm, respectively. The investigation of the effect of photodegradation of Fe₃O₄@TiO₂-PVP core-shell nanoparticles was also successfully carried out using a UV-Vis instrument. Photodegradation of the sample is affected by the length of UV irradiation of Congo Red dyes from the Fe₃O₄@TiO₂-PVP core-shell nanoparticles. The longer the irradiation is given, the greater the percentage of Congo Red dye that is degraded. FTP 0.5 samples were nanoparticles with the highest percentage of degradation of Congo Red dye, which was 78.20% with extended irradiation of 120 minutes. Photodegradation of Congo red dyes is caused by the content of Fe₃O₄@TiO₂-PVP core-shell nanoparticles through the process of absorption and photocatalytic mechanism.

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