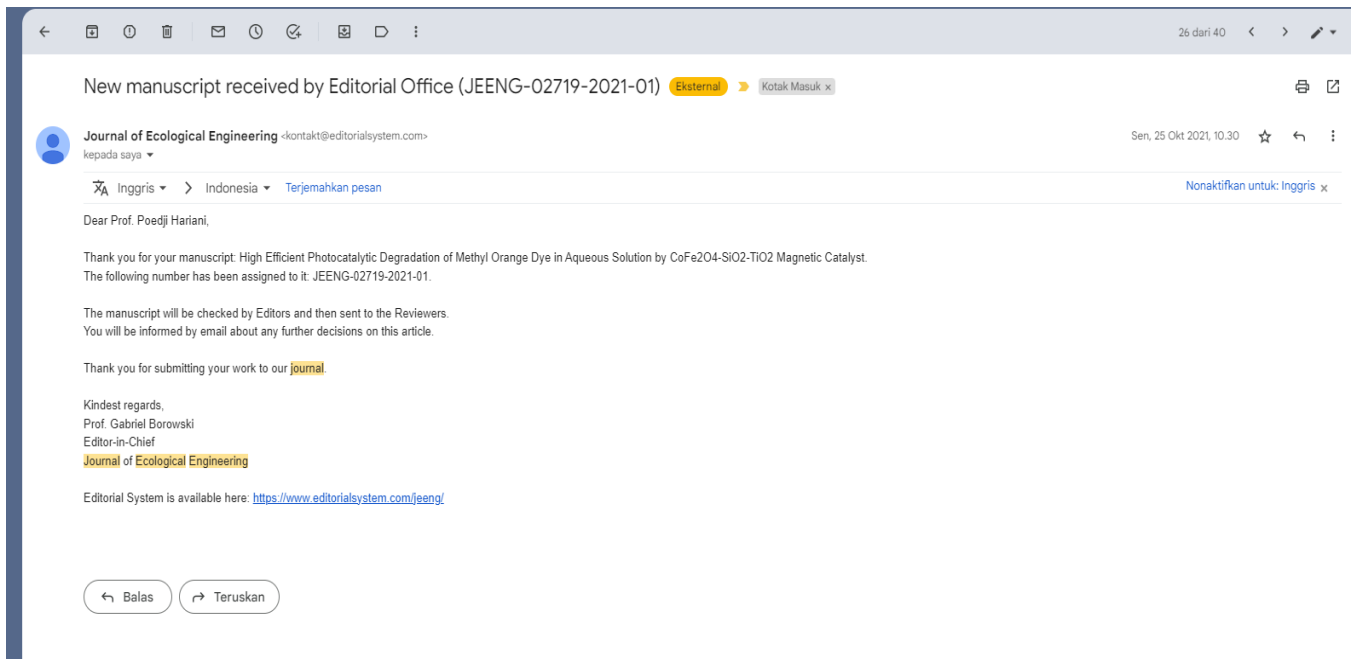


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Judul: High Efficient Photocatalytic Degradation of Methyl Orange Dye in Aqueous Solution by CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> Magnetic Catalyst

Author: Poedji Loekitowati Hariani, Muhammad Said, Salni Salni, Nabila Aprianti Yohanna Asina Lasma Rohana Naibaho



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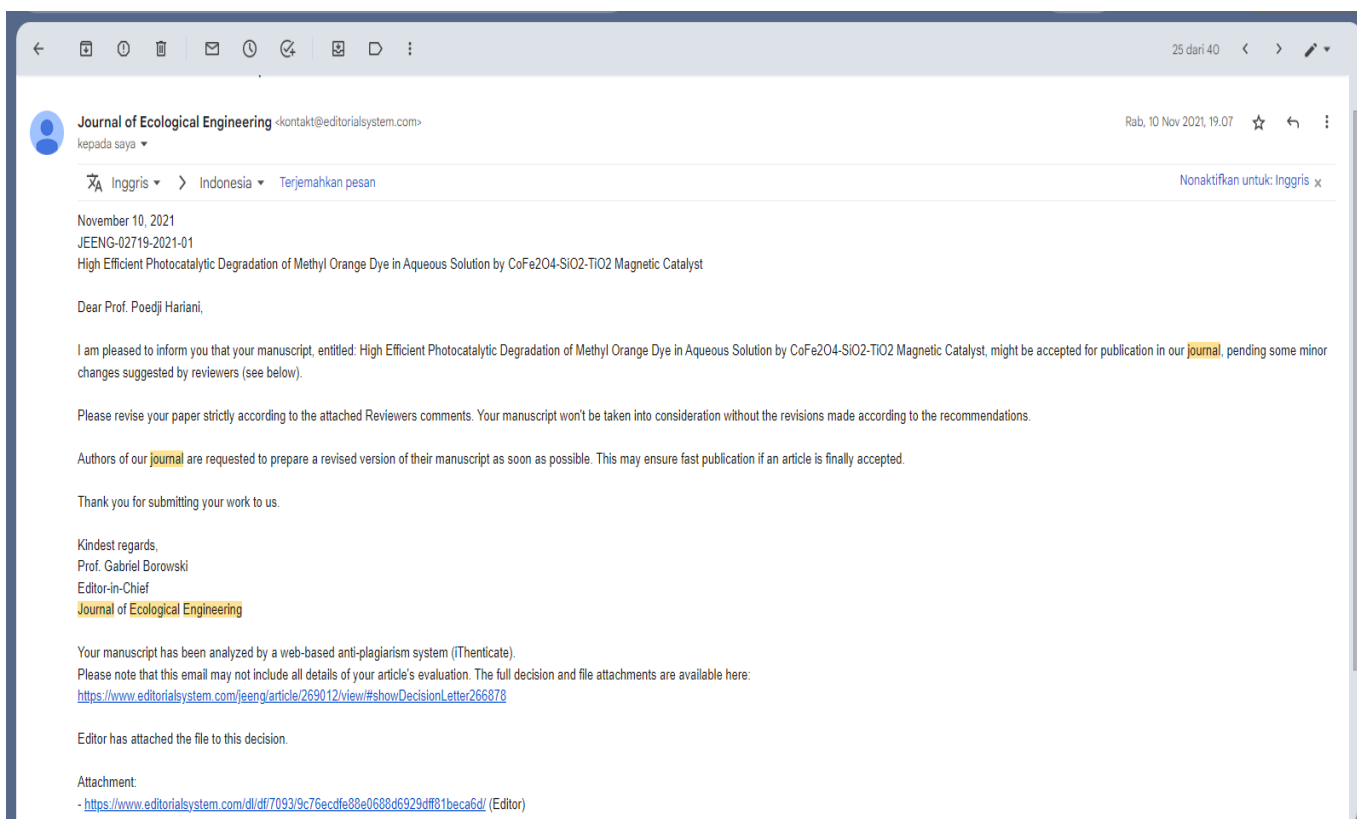
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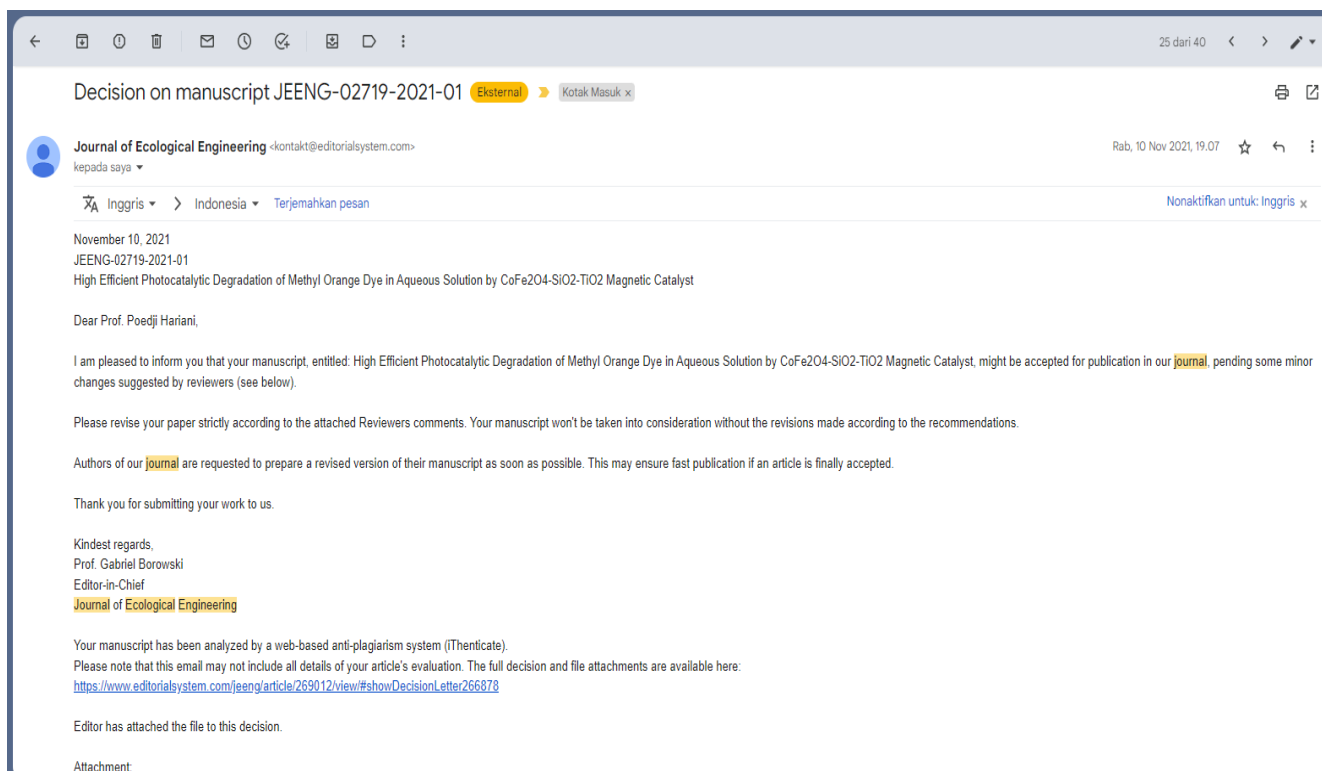
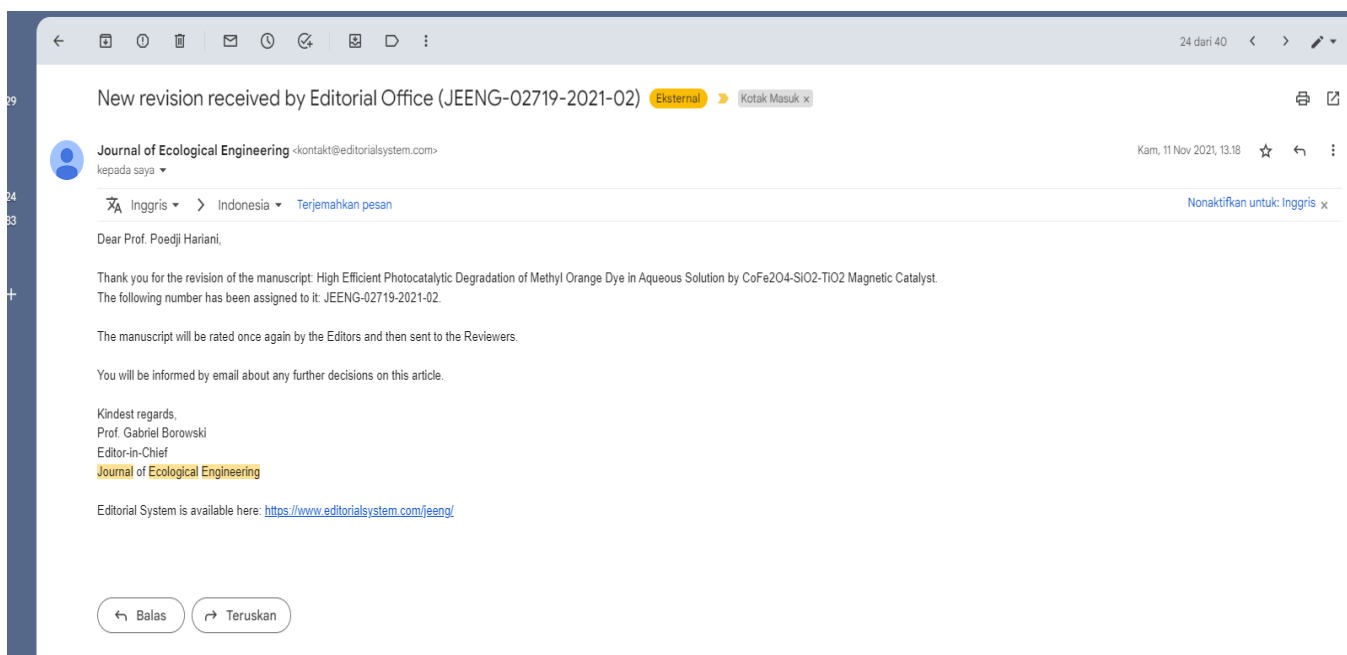
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# High Efficient Photocatalytic Degradation of Methyl Orange Dye in an Aqueous Solution by $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$ Magnetic Catalyst

Poedji Loekitowati Hariani<sup>1\*</sup>, Muhammad Said<sup>1</sup>, Salni<sup>2</sup>, Nabila Aprianti<sup>3</sup> Yohanna Asina Lasma Rohana Naibaho<sup>1</sup>

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## ABSTRACT

This study successfully synthesized a core-shell-shell in the form of  $\text{CoFe}_2\text{O}_4/\text{SiO}_2/\text{TiO}_2$  catalyst magnetic and recyclable. The catalyst was employed for the photocatalytic degradation of methyl orange (MO) dye. Subsequently, the catalyst was subjected to XRD, FTIR, SEM-EDS, VSM, as well as UV-DRS characterizations. The photocatalytic degradation was studied as a function of the solution pH, MO concentration, and irradiation time, while the kinetics of photocatalytic degradation and the catalyst's reusability were also evaluated. ~~Based-On the basis of on~~ the XRD, FTIR, and SEM-EDS characterizations, the  $\text{CoFe}_2\text{O}_4$  coating was successfully carried out using  $\text{SiO}_2$  and  $\text{TiO}_2$ .  $\text{CoFe}_2\text{O}_4/\text{SiO}_2/\text{TiO}_2$  was discovered to possess magnetic properties with a saturation magnetization of 17.59 emu/g and a bandgap value of 2.4 eV. The photocatalytic degradation of MO followed the Langmuir-Hishelwood model. The optimum degradation was obtained at the MO concentration of 25 mg/L, solution pH of 4, catalyst dose of 0.05 g/L, irradiation time of 160 minutes, MO removal efficiency achieved 93.46%. The regeneration study showed  $\text{CoFe}_2\text{O}_4/\text{SiO}_2/\text{TiO}_2$  after 5 cycles were able to catalyze the photocatalytic degradation with an MO removal efficiency of 89.96%.

**Keywords:**  $\text{CoFe}_2\text{O}_4/\text{SiO}_2/\text{TiO}_2$ , magnetic, degradation, photocatalytic, and methyl orange.

## INTRODUCTION

The continuous discharge of industrial liquid waste containing toxic compounds into water bodies tends to cause environmental pollution and presents several health risks [Ojemaye et al., 2015]. The Previous studies by Chan et al. [2008] and Trabelsi et al. [2016] described dyes as toxic compounds produced by several industries, including the textile, pharmaceutical, chemical, paper, foodstuff, soap, cosmetic, and leather industries, where over 50% of the dyes used are azo-based. According to Koohestani et al., [2016], azo dyes are the compounds with an azo bond in the form of  $-\text{N}=\text{N}-$ , ~~and o~~Over 15% of the dyes are discharged as liquid waste during the dyeing and coloring process [Nair et al., 2014; Ahmad et al., 2014]. Azo dyes and their intermediates, for instance, aromatic amines, are highly stable, toxic, carcinogenic, mutagenic, and not easily degraded [Konstantinou and Albanis, 2004; Alghamdi et al., 2019]. A report by Huang et al. [2008] showed that dyes block the penetration of light into the water, consequently lowering the photosynthetic efficiency and impeding the growth of aquatic organisms. These dyes also cause aesthetic changes which are harmful to the environment. Methyl orange (MO) is an azo dye with the molecular formula  $\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{Na}$  and is classified as an anionic dye with a sulfonic group. In addition to being used as an industrial coloring agent, MO is also used as a pH indicator in the laboratory, with a pH indicator range of 3.1 to 4.4 [Alghamdi et al., 2019].

Recently, advanced oxidative processes (AOPs) were discovered to be the most effective method for degrading organic matter from water and wastewater [Suzuki et al., 2015; Mrotek et al., 2020]. These processes are based on the formation of highly reactive radicals, including hydroxyl groups, which oxidize and convert organic compounds into harmless products, for instance,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [Ge et al. 2019; Takdastan et al., 2018]. Heterogeneous photocatalysis using semi-conductors is an effective technique for the degradation of toxic organic compounds. In wastewater treatment,  $\text{TiO}_2$  in various forms is a widely used photocatalyst due to the compound's its ease and low cost of production, high photoactivity, non-toxicity, as well as good electrical and thermal conductivity [Shojaie et al., 2018; Stefan et al., 2016, Subramonian et al., 2017].

However, TiO<sub>2</sub> is suspended in a solution, which makes it difficult to separate and energy-consuming processes [Lee et al., 2001; Jorfi et al., 2017], electron-hole recombination of the photo-generated charge carriers [Pastravanu et al., 2014], as well as a wide bandgap (about 3.2 eV) [Djellabi et al., 2019]. Therefore, TiO<sub>2</sub> is only suitable for use under UV light to generate electron-hole pairs. Alternatively, magnetic photocatalysts in which semiconductor nanoparticles are deposited on the ferrite surface (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>), ~~have has~~ been used to facilitate the ~~photocatalyst's~~ separation ~~of the photocatalyst~~ from the solution, using an external magnet [Jurek et al., 2017, Mishra et al., 2019]. The coating of Fe<sub>3</sub>O<sub>4</sub> as the core, with TiO<sub>2</sub>, reduces the bandgap of TiO<sub>2</sub>, making the compound suitable for the photocatalytic visible region while increasing the speed and efficiency of the separation process [Mercyrani et al., 2017]. However, direct contact between ferrite compounds and TiO<sub>2</sub> causes TiO<sub>2</sub> to enter the core oxidizing iron, and consequently, the ferrous ions dissolve into solution (photo-dissolution) [Gebrezgiabher et al., 2019; Wysocka et al., 2018]. According to Rashid et al. [2015] and Jurek et al. [2017], the formation of a layer on the magnetic core helps to prevent degradation, photo-dissolution, and adverse effects of the magnetic core on TiO<sub>2</sub>. Silica protects the magnetic core, prevents the transmission of electron holes from the photocatalyst layer to the magnetic part, and is, therefore, often used as an intermediary [Awazu et al., 2008; Cheng et al., 2012].

In this study, a core-shell-shell in the form of CoFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> was prepared as a photocatalyst for the degradation of MO. CoFe<sub>2</sub>O<sub>4</sub> was selected as the core due to its high thermal and chemical stability, low toxicity, high coercivity, as well as moderate magnetization [Rajput and Kaur, 2014; El-Shobaky et al., 2010]. Subsequently, the photocatalytic efficiency of the degradation, including the effect of solution pH, irradiation time, as well as catalyst dose, were investigated, and the ~~catalysts'~~ reusability ~~of catalysts~~ was evaluated.

## MATERIAL AND METHODS

### Materials

~~The study involved the use of~~ Cobalt chloride hexahydrate (CoCl<sub>2</sub>.6H<sub>2</sub>O), Iron(III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O), Trisodium citrate dihydrate (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>.2H<sub>2</sub>O), ethanol (C<sub>2</sub>O<sub>5</sub>OH), Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Tetraethyl orthosilicate (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>), Ammonium hydroxide (NH<sub>4</sub>OH), Methyl orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>SO<sub>3</sub>Na), Titanium (IV) butoxide (Ti(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>), Ethylene glycol (CH<sub>2</sub>OH)<sub>2</sub>, Sodium nitrate (NaNO<sub>3</sub>), Titanium dioxide (TiO<sub>2</sub>) from Merck, Germany.

### CoFe<sub>2</sub>O<sub>4</sub> Preparation

CoFe<sub>2</sub>O<sub>4</sub> was synthesized using the coprecipitation method. For this process, 9.517 g of CoCl<sub>2</sub>.6H<sub>2</sub>O and 21.623 g of FeCl<sub>3</sub>.6H<sub>2</sub>O were dissolved in 100 mL of distilled water. Subsequently, 2 M NaOH was added to the solution in drops, while nitrogen gas was passed across until a pH of 10 was obtained. The precipitate obtained was then collected by magnetic separation, washed ~~severally-several~~ ~~times~~ with distilled water until the pH was neutral, and oven-dried at 110°C for 1 hour. This was followed by subjecting the CoFe<sub>2</sub>O<sub>4</sub> obtained to further calcination at 800°C for 2 hours.

### CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub> Preparation

~~The S~~ynthesis of CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub> was carried out using the sol-gel method. For this process, 0.8 g of CoFe<sub>2</sub>O<sub>4</sub> and 0.8 g of Trisodium citrate dihydrate were dissolved in 20 mL of ethanol and 8 mL of distilled water. The mixture was then homogenized by sonification for 10 minutes, and 4 mL of ammonium hydroxide, as well as 3.2 mL of TEOS, were added to the solution, and sonification was continued for 3 hours at 40°C to form a silica layer around CoFe<sub>2</sub>O<sub>4</sub>. Subsequently, the precipitate obtained was separated by centrifugation, washed severally with ethanol, and dried using rotary evaporation.

### CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> Preparation

~~The~~ CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> composites were prepared using the method reported by Habila et al. [2015], with some modifications. For this process, 2 g of CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub> was suspended in a mixture of 24 mL ethanol, 30 mL distilled water, and 800 L ammonium hydroxide (28%), using sonification, for 30 minutes. Subsequently, 20 mL of ethylene glycol and 2 mL of TBT solution were slowly added and the mixture was homogenized using a magnetic stirrer at 45°C, for 24 hours. The CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>

obtained was washed with distilled water, as well as ethanol, then oven-dried at 110°C for 1 hour and calcined at 450°C for 3 hours.

### Characterization

The crystal structure and phase of catalyst were analyzed using X-Ray Diffraction (XRD PANalytical), while the functional groups were identified using Fourier Transform Infra-Red (FTIR Prestige 21 Shimadzu). In addition, the morphology and elemental composition were analyzed using a Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS JOEL JSM 6510 LA). The magnetic moment was determined using a Vibrating Sample Magnetometer (VSM Oxford Type 1.2 T). At the same time, the wavelength and band gap were analyzed using Diffuse Reflectance Ultra Violet-Visible Spectroscopy (UV-Vis DRS Pharmaspec UV-1700). The radiation source for photocatalytic degradation was UV light (12 W Phillips) and the MO absorbance was measured using a UV-Vis Spectrophotometer (Type Orion Aquamate 8000). Mineralization degree was measurement by Total Organic Carbon (TOC Teledyne Tekmar). Determination of pH<sub>pzc</sub> was carried out following a modification of the technique reported by Bezahdi et al. [2020] using NaNO<sub>3</sub> solution as an electrolyte.

### Photocatalytic degradation

In this experiment, 50 mL of MO was mixed with CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> at a dose of 0.05 g/L in separate quartz pipes, with the MO concentrations of 25, 50, 75, and 100 mg/L. Using UV light ~~was~~ as the irradiation source, the mixture was placed in a photoreactor with a vessel distance of 30 cm from the light source. Furthermore, the effects of the pH and irradiation time were ~~further~~ studied by varying the pH in the range of 2 to 7, as well as the irradiation time between 0 to 200 minutes. Subsequently, the MO removal (%) was calculated using the following formula (Eq. 1).

$$\text{MO Removal (\%)} = \frac{C_o - C_t}{C_o} \quad (1)$$

Where  $C_o$  and  $C_t$  are the initial and final concentrations of MO (mg/L).

The ~~catalyst's~~ reusability of the catalyst was also investigated using the same method, under the optimum conditions for photocatalytic degradation. For this evaluation, the CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> was separated using a permanent magnet after the photocatalytic degradation, then washed with ethanol and distilled water, dried in an oven for 60 minutes at 80°C, and reused for photocatalytic degradation [Ajabshir and Niasari, 2019]. This experiment was repeated 5 times, and the ~~catalyst's~~ efficiency was measured after each cycle.

## RESULT AND DISCUSSION

### Properties of the materials

Figure 1 shows the XRD spectra of the synthesized CoFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>, and CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>. Based-On the basis of ~~on~~ the diagram, the 2θ angle of CoFe<sub>2</sub>O<sub>4</sub> was observed at 30.31° (220), 35.57° (311), 43.21° (400), 53.61° (422), 57.23° (511), and 62.81° (440). This peak is a characteristic of the cubic spinel structure phase following the standard CoFe<sub>2</sub>O<sub>4</sub> spectra (JCPDS card No. 78-1744). Meanwhile, CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub> was discovered to possess the same diffraction angle as CoFe<sub>2</sub>O<sub>4</sub>, but with lower peak intensity. Furthermore, the crystalline properties of CoFe<sub>2</sub>O<sub>4</sub> were maintained after coating with SiO<sub>2</sub>. The peak for SiO<sub>2</sub> at 2θ = 15-25 was not observed in the XRD spectra of CoFe<sub>2</sub>O<sub>4</sub>.SiO<sub>2</sub> and CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>, due to the amorphous nature of SiO<sub>2</sub>. Habila et al. [2020] reported a similar pattern in the synthesis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>, where a reduction occurred in the Fe<sub>3</sub>O<sub>4</sub> diffraction peak after coating with SiO<sub>2</sub> and TiO<sub>2</sub>, due to the shielding effect of the two compounds.

Figure 1. XRD spectra of (a)CoFe<sub>2</sub>O<sub>4</sub> (b) CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub> and (c) CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>

The XRD spectra of CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> shows the presence of a 2θ angle, which is characteristic of TiO<sub>2</sub> at 25.63 (101), 37.25 (004), 48.87 (200), and 62.91 (204), based on the anatase phase ~~'s~~ structure (JCPDS card No. 21-1272). Table 1 shows the average crystallite size of CoFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>, and CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> calculated by the Scherrer formula. The crystallite size of CoFe<sub>2</sub>O<sub>4</sub> before and after coating remained at a constant value of ± 33 nm. Meanwhile, the average crystal size of TiO<sub>2</sub> calculated at the peak of the anatase diffraction was 18.3 nm.



Table 1. The average ~~eyrstallite~~-crystallite size of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  dan  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$

Figure 2 shows the FTIR spectra of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ , and  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$ . The wavenumbers observed at about  $3400\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$  in all spectra are stretching vibrations of the hydroxyl functional group (O-H) originating from free water molecules on the catalyst surface [Ojemaye et al., 2017]. Meanwhile, the  $\text{CoFe}_2\text{O}_4$  spectra in the form of sharp peaks at  $576\text{ cm}^{-1}$  are the vibrations of Fe-O. The strong peak at  $1093\text{ cm}^{-1}$  observed in  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ , and  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$ , is an asymmetric vibration of Si-O-Si [Fu et al., 2019], while the wavenumber around  $950\text{ cm}^{-1}$  is the vibration of the Si-O-H band [Mortazavi et al., 2017]. According to Fu et al., [2019], the presence of  $\text{TiO}_2$  in the  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  spectra visible at  $450$  to  $700\text{ cm}^{-1}$ , is the vibration of Ti-O-Ti and Ti-O-Si.

Figure 2. FTIR spectra (a) $\text{CoFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  and (c)  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$

The SEM and EDS ~~analysis~~-analyses are used to investigate the morphology and composition of the catalyst elements. Figure 3 shows the morphology of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ , and  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  with the same magnification. The morphology of  $\text{CoFe}_2\text{O}_4$  appears spherical because due to the small size which tends to agglomerate and the morphology of  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  is similar to  $\text{CoFe}_2\text{O}_4$  but more homogeneous. This is consistent with the XRD results which show the  $\text{SiO}_2$  coating is not observed in the spectra due to the ~~compound's~~-amorphous nature of the compound. Meanwhile, a heterogeneous and rough surface is visible in the morphology of  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  where the  $\text{TiO}_2$  aggregates appear to be round and coat the  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ . Table 2 shows the elemental composition of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ , and  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  from the EDS analysis, where the presence of Si and Ti elements in  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  indicates a successful synthesis. Furthermore, no other elements were detected as impurities.

Figure 3. Morphology of (a)  $\text{CoFe}_2\text{O}_4$  (b)  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  and (c)  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$

Table 2. Elements of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  dan  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$

Figure 4 shows the magnetization curves of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ , and  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  obtained using VSM. According to the results, the saturation magnetization of  $\text{CoFe}_2\text{O}_4$  is  $57.05\text{ emu/g}$ , and this value is close to the saturation magnetization of  $\text{CoFe}_2\text{O}_4$  synthesized using the combustion, coprecipitation, and precipitation methods, which are  $56.7$ ,  $55.8$ , and  $47.2\text{ emu/g}$ , respectively [Houshiar et al., 2014]. In addition, the saturation magnetization of  $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  and  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  are  $40.01\text{ emu/g}$ , as well as  $17.59\text{ emu/g}$ , respectively, and these values are lower, compared to the  $\text{CoFe}_2\text{O}_4$  counterpart. This means that coating with non-magnetic material leads to a reduction in saturation magnetization. However,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  still has possessed good magnetic properties, considering the material is quickly and easily separated from the solution after degradation, using a permanent magnet.

Figure 4. Saturation magnetization curves of (a) $\text{CoFe}_2\text{O}_4$ , (b) $\text{CoFe}_2\text{O}_4\text{-SiO}_2$  and (c) $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$

Furthermore, Figures 5a and b show the UV-DRS spectra of  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  and pure (commercial)  $\text{TiO}_2$ , which provide the information about the wavelength at which the catalyst absorbs energy. The results showed  $\text{TiO}_2$  absorbs in the ultraviolet region with a maximum absorbance of about  $345\text{ nm}$ , and this activity is due to the fairly large bandgap. Meanwhile,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  not only absorbs in the ultra-visible region but also in the visible region, at wavelengths of  $341$  and  $425\text{ nm}$ , respectively. The bandgap value was obtained by plotting  $(\alpha h\nu)^2$  against  $h\nu$  (Figure 5b). A  $\text{TiO}_2$  bandgap of  $3.2\text{ eV}$  was obtained, and coating  $\text{CoFe}_2\text{O}_4$  with  $\text{SiO}_2$  and  $\text{TiO}_2$  reduces the bandgap. Therefore,  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  has a bandgap of  $2.4\text{ eV}$ . According to Sonu et al., (2019),  $\text{CoFe}_2\text{O}_4$  has a fairly small bandgap ( $\sim 1.76\text{ eV}$ ).

Figure 5. (a) UV-DRS spectra of  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  and pure  $\text{TiO}_2$  and (b) band gab of  $\text{CoFe}_2\text{O}_4\text{-SiO}_2\text{-TiO}_2$  and pure  $\text{TiO}_2$

## Photocatalytic properties

In photocatalytic degradation, the solution pH influences the charge of the catalyst surface. The solution pH is an important parameter. A report by Behzadi et al. [2020] showed the optimum pH depends on the type of pollutant and the pH<sub>pzc</sub>, which shows the pH on the material surface in total is zero or the catalyst surface is neutrally charged [Amulya et al., 2020]. The pH<sub>pzc</sub> value must be investigated to determine the appropriate pH for an effective photocatalytic degradation process. The pH<sub>pzc</sub> of CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> is 5.2.

Figure 6. pH<sub>pzc</sub> of CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>

Figure 7 shows the effect of solution pH on the removal of MO, which has a pH range of 3.1-4.4 with a pK<sub>a</sub> of 3.7. At a solution pH < pH<sub>pzc</sub>, CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> is positively charged, while MO is an anionic dye, and consequently, the attraction is more effective. MO removal increases at pH 2 to 4 and subsequently decreases at pH 5. Meanwhile, at a solution pH > pH<sub>pzc</sub>, there is a repulsion of electrostatic charges between the anionic dye and the negatively charged CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>. The highest MO removal was obtained at pH 4 with variations in the initial MO concentrations of 25, 50, 75, and 100 mg/L.

Figure 7. Effect of solution pH on removal MO

Figure 8 shows the effect of irradiation time on the photocatalytic degradation of MO at concentrations of 25, 50, 75, and 100 mg/L, the catalyst dose of 0.05 g/L, as well as pH of 4, under UV light. The results showed MO removal increases along with increasing irradiation time; however, at 160 minutes of irradiation, there was no increase in the amount of degraded MO. Furthermore, the highest MO removal was obtained at a concentration of 25 mg/L (93.46%). This is because higher concentrations tend to block light from reaching the catalyst, consequently, reducing the rate of removal.

Figure 8. Effect of irradiation time on removal MO

The Langmuir Hinshelwood equation model is generally used to describe the kinetics of heterogeneous photocatalytic degradation. This equation is further simplified to pseudo-first-order kinetics to obtain the following equation (Eq. 2) [Amulya et al., 2020]:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (2)$$

Where  $C_0$  and  $C$  are the initial concentration and the concentration after the photocatalytic degradation process, respectively, at a time ( $t$ ). Figure 8 shows the photocatalytic degradation kinetics of MO at concentrations of 25, 50, 75, and 100 mg/L, catalyst dose of 0.05 g/L, as well as pH of 4, under UV light. The concentrations produced  $R^2$  values indicating the photocatalytic degradation has adequate linearity and follows the Langmuir-Hinshelwood model expressed in pseudo-first-order. Similar results were reported for the photocatalytic degradation of the Methylene blue dye using TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>-bentonite [Chen et al., 2015], as well as the photocatalytic degradation of Cr(VI) using NiFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> [Ojemaye et al., 2017]. Table 3 shows the kinetics parameters of MO photocatalytic degradation where the  $t_{1/2}$  value is calculated using  $0.693/k$ .

Figure 9. Kinetic photocatalytic degradation of MO by CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>

Table 3. Kinetic parameter of photocatalytic degradation MO

## Reusability of the photocatalyst

The regenerability and reusability of catalysts are highly significant in industrial contexts, because these properties are related to cost, pilot-scale remediation systems, and environmental safety [Moosavi et al., 2020T; Ajabshir and Niasari, 2020]. Reusing catalysts reduces the discharge of secondary pollutants into the environment. Photocatalytic degradation is carried out using a MO concentration of 25 mg/L, a pH of 4, a catalyst dose of 0.05 g/L, as well as an irradiation time of 160 minutes. According to Figure 10, the catalyst's effectiveness reduced by 3.74%, from 93.46% to 89.96%, after 5 cycles. Moosavi et al. [2020] reported similar results in the effectiveness of Fe<sub>3</sub>O<sub>4</sub>/AC/TiO<sub>2</sub> in photocatalytic degradation which reduced from approximately 98% to about 93% after 7 cycles. This study obtained better results, compared to MO degradation using Ti<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>-bentonite, where the catalyst's effectiveness decreased by approximately 20% after 6 cycles.



Furthermore, the reduction in the catalyst's effectiveness is possibly due to the loss of material during the photocatalytic degradation process (separation, washing, and drying), as well as the occurrence of catalyst aggregation.

Figure 10. Reusability of ~~photocatalyst the~~ CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> ~~photocatalyst~~

A total organic carbon (TOC) analysis was also performed to determine the amount of organic matter or the level of mineralization. According to Pourzad et al., [2020], the level of mineralization is usually not fully achieved. The TOC efficiency on photocatalytic degradation of methylene blue dye using Ag<sub>2</sub>O-NiO/CuFe<sub>2</sub>O<sub>4</sub> catalyst is 78.64% [Liu et al., 2020], while the TOC efficiency of paraquat using N-doped TiO<sub>2</sub>@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> is 84.71% [Pourzad et al., 2020]. In this study, the efficiency of TOC removal for photocatalytic degradation of MO under optimal conditions with a concentration of 25 mg/L, catalyst dose of 0.05 g/L, solution pH of 4, and irradiation time of 160 minutes is 82.68%. This result indicates a successful dye decomposition process.

## CONCLUSIONS

A ~~C~~core-shell-shell composite in the form of CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> was successfully synthesized and effectively used for photocatalytic degradation of methyl orange dye under UV light irradiation. ~~Based On the basis of en~~the XRD analysis, CoFe<sub>2</sub>O<sub>4</sub> was discovered to possess a cubic spinel structure and TiO<sub>2</sub> was in the anatase phase. In addition, the FTIR and SEM-EDS analyses confirmed the presence of SiO<sub>2</sub> and TiO<sub>2</sub> shells. The CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> composite possessed magnetic properties with a saturation magnetization of 47 emu/g, as well as a bandgap of 2.4 eV. Furthermore, the removal efficiency of MO using CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> was discovered to be 93.46% with a MO concentration of 25 mg/L, solution pH of 4, catalyst dose of 0.05 g/L, and irradiation time of 160 minutes under UV light irradiation. ~~Also~~In addition, the photocatalytic degradation followed the Langmuir-Hinshelwood model expressed in pseudo-first-order. These results show ~~that~~ CoFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> has the potential for use in wastewater treatment, especially for organic pollutant removal. The catalyst's effectiveness decreased by only 3.74% after 5 cycles ~~used for of~~ photocatalytic degradation.

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