

# Synthesis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO magnetic composite: Evaluation of its catalytic activity for methylene blue degradation

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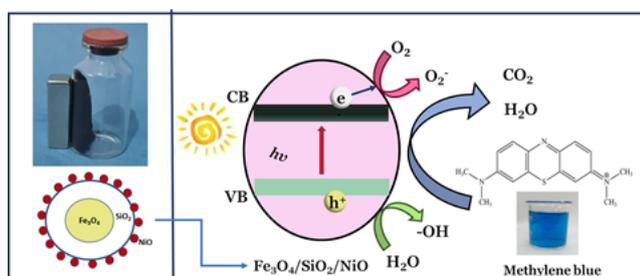
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## Graphical abstract



## Abstract

Photocatalytic degradation for wastewater treatment is a method that has recently attracted attention. In this research, a synthesized composite of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO with magnetic properties was used for the photocatalytic degradation of methylene blue dye under UV light. Furthermore, the composites were characterized using XRD, FTIR, BET surface area, SEM-EDS, VSM, and UV-DRS. The results showed that the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composite is magnetic with a saturation magnetization of 53.84 emu/g. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composite has a surface area of 128.8 m<sup>2</sup>/g, large than Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O/SiO<sub>2</sub>. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composite has a band gap of 2.83 eV. The photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composite against the methylene blue dye exhibited high degradation efficiency reaching 98.51%. The pseudo-first-order is appropriate to describe the kinetics model of photocatalytic degradation on methylene blue dye. The decrease in the degradation efficiency of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composite after 5 times for the photocatalytic degradation of methylene blue dye from 98.02% to 94.97% indicates that the catalyst has high stability. Considering these results, the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composites could be used as a potential catalyst in industrial wastewater.

**Keywords:** Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO, magnetic composite, photocatalytic, degradation, methylene blue dye

## 1. Introduction

Wastewater discharged from industry often contains pathogenic organisms in organic and inorganic

contaminants that harm the environment (Pham *et al.*, 2018). It contains dyes with several characteristics, including a large volume of waste, high chromaticity, high organic matter concentration, poor biodegradability, disturbing aesthetics, and blocking the transmission of sunlight, thereby reducing the photosynthetic activity in the waters. Additionally, a low concentration of dye (< 1 mg/L) can disturb the waters (Vandevivere *et al.*, 1998). Methylene blue (C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S) is a cationic dye widely used in the coloring industry and as a chemical indicator (Khodai *et al.*, 2013; Kuang *et al.*, 2020). It has an aromatic group and a complex structure that is hydrophilic and stable to light, temperature, and chemicals (Hou *et al.*, 2018).

Various technologies, such as biological, physical, and chemical treatment have been used to reduce the concentration of dyes. The methods used to removal dye include adsorption (Ziaadini *et al.*, 2019), precipitation (Ali *et al.*, 2006), coagulation-flocculation (Moghaddam *et al.*, 2010), filtration (David *et al.*, 2020), ozonation (Dias *et al.*, 2019) and others. Adsorption is often applied because it effectively reduces the concentration of dyes but causes secondary pollutants (Fu *et al.*, 2019). Presently, Advanced Oxidation Processes (AOPs) have been an effective method for degrading organic pollutants (Behzadi *et al.*, 2020) due to their low cost and high efficiency (Behzadi *et al.*, 2020; Jarariya, 2022).

The AOPs method often used is heterogeneous photocatalysis based on semiconductor materials. The irradiation of the semiconductor by photons on the band gap energy produces positive and negative electrons. Furthermore, the positive hole reacts with a water molecule to produce a hydroxyl radical (•OH), while electrons react with O<sub>2</sub> molecules to form superoxide radicals (•O<sub>2</sub>). The hydroxyl and superoxide radicals degrade dye into smaller non-toxic compounds, CO<sub>2</sub> and H<sub>2</sub>O (Gao *et al.*, 2013; Salomon *et al.*, 2012). The several semiconductor materials used include TiO<sub>2</sub> (Hou *et al.*, 2018), NiFe<sub>2</sub>O<sub>4</sub> (Hariani *et al.*, 2021), NiO (Lett *et al.*, 2022), ZnO (Chen *et al.*, 2017), and CoFe<sub>2</sub>O<sub>4</sub> (Loan *et al.*, 2019).

Nickel oxide (NiO) is a p-type transition metal oxide semiconductor with a band gap of about 3.5 eV, antiferromagnetic, high conductivity, stable, and catalytic properties (Hosny, 2011; D'Amario *et al.*, 2018; Barakat *et al.*, 2013). It performs effectively in the photodegradation of orange II dye (Khan *et al.*, 2022), methylene blue (Let *et al.*, 2022; Wan *et al.*, 2013), and methyl orange dye (Barzinjy *et al.*, 2020). The combination of magnetic ferrite with NiO is a strategy to increase the efficiency of the catalytic process and the separation of the catalyst from the solution. The magnetic ferrite serves as a core. SiO<sub>2</sub> is a layer to avoid the interaction between NiO and magnetic ferrite. The core-shell-shell structure increases the surface area, reduces the cost of catalyst usage, and increases lifespan (Channei *et al.*, 2014; Girginova *et al.*, 2010). For example, Fe<sub>3</sub>O<sub>4</sub> coated with activated carbon and TiO<sub>2</sub> showed better catalytic ability than used with only TiO<sub>2</sub> (Gebrezgiabher *et al.*, 2019).

This research synthesized a magnetic composite of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO, with Fe<sub>3</sub>O<sub>4</sub> as the core, SiO<sub>2</sub> as the inner shell, and NiO as the outer shell. Fe<sub>3</sub>O<sub>4</sub> is the most widely used magnetic iron oxide compared to other ferrite compounds with an inverse spinel structure and superparamagnetic. The advantage of using Fe<sub>3</sub>O<sub>4</sub> as a core in composites, after being used for photocatalytic degradation process, the composite can easily be separated from the solution using an external magnet, without filtering. Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO were applied for photocatalytic degradation of methylene blue dye under UV light irradiation. Finally, the kinetic photocatalytic degradation and reusability of these composites were investigated.

## 2. Materials and methods

### 2.1. Materials

The materials used are of analytical grade without purification, including FeCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, NaOH, HCl, C<sub>2</sub>H<sub>5</sub>OH, NH<sub>4</sub>OH, NH<sub>4</sub>HCO<sub>3</sub>, Tetraethyl orthosilicate (TEOS), Diethylene Glycol (DEG), methylene blue dye purchased from Merck (Germany), distilled water, and N<sub>2</sub> gas.

### 2.2. Synthesis of Fe<sub>3</sub>O<sub>4</sub>

Fe<sub>3</sub>O<sub>4</sub> was synthesized using the coprecipitation method. First, a total of 1.988 g FeCl<sub>2</sub>·4H<sub>2</sub>O and 5.406 g FeCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in 20 mL of distilled water. Afterward, 1 M NaOH was added to the solution dropwise while slowly stirring with a magnetic stirrer at a speed of 100 rpm, and N<sub>2</sub> gas was emitted until the pH reached ± 10. The precipitate was separated from the solution using a magnet and washed several times with distilled water and ethanol until the pH was neutral. Finally, it was dried in an oven at 70°C for 3 hours.

### 2.3. Synthesis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>

The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> was synthesized using the Stober method. First, 0.5 g Fe<sub>3</sub>O<sub>4</sub> was dispersed in 20 mL of ethanol using an ultrasonic bath for 30 minutes at room temperature. The obtained product was added 5 mL of ammonia solution (28%), followed by the gradual addition of 2 mL

TEOS solution (1 mL TEOS in 20 mL ethanol) using a magnetic stirrer for 3 for 5 hours. The precipitate was washed several times with distilled water and ethanol until the pH was neutral. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> were dried in an oven at a temperature of 70°C for 3 hours.

### 2.4. Synthesis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

An amount of 0.5 g of NiCl<sub>2</sub>·6H<sub>2</sub>O was dispersed in 10 mL of DEG for 30 minutes at room temperature using a water bath sonicator, followed by adding 0.5 g of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and 10 mL of 0.0025 M NH<sub>4</sub>HCO<sub>3</sub> solution under stirring for 15 minutes. The mixture was transferred to a Teflon autoclave and heated at 120 for 5 hours. The precipitate was washed using distilled water and ethanol. The obtained product was dried in an oven at 70°C for 3 hours. Finally, it is calcined at a temperature of 300°C for 2 hours.

### 2.5. Characterization

The product obtained was identified using an X-ray diffractometer (XRD Panalytical), operated at 40 kV and 30 mA, Cuα (λ = 1.542 Å) as a radiation source, and a range of 2θ at 10-90°. The bond formation was analyzed with Fourier Transform Infra-Red spectroscopy (FTIR, Prestige 21, Shimadzu) at wave numbers of 400-4000 cm<sup>-1</sup> using the KBr pellet technique. Furthermore, the specific surface areas were evaluated with N<sub>2</sub> adsorption-desorption using the BET (Quantachrome QuadraWin) method. Scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS JSM 6510) was used to observe surface morphology and elemental composition. Additionally, magnetic properties were evaluated using a Vibrating Sample Magnetometer (VSM Oxford Type 1.2 T). UV-Vis Diffuse Reflectance Spectroscopy (Pharmaspec, UV-1700) was used to determine the band gap at 200-800 nm wavelengths. The concentration of methylene blue dye was determined using a UV-Vis spectrophotometer (Type Orion Aquamate 8000).

### 2.6. Photocatalytic activity

Photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO against methylene blue dye under UV light irradiation source (15-W x 3, Philips). In the experiment, 50 mL methylene blue dye at a concentration of 20 mg/L with a 0.5 g/L catalyst dose, the pH of the solution was varied at 5, 6, 7, 8, 9, and 10 using 0.1 M HCl or NaOH. The mixture was stirred in a dark room for 40 minutes to reach equilibrium, followed by a photocatalytic degradation process for 120 minutes (20 minutes intervals). Other variables are catalyst dose (0.25, 0.5, 0.75 and 1.0 g/L) and the dye concentration (10, 20, 30, and 40 mg/L).

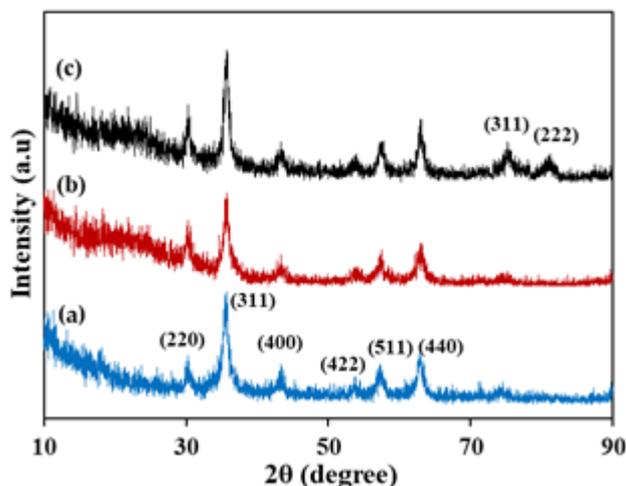
The reusability of the catalyst was assessed by magnetically separating it following photocatalytic degradation under optimal conditions. It was then washed using deionized water and dried in an oven for 3 hours at 70°C. Calcination was carried out at 300°C for ± 2 hours to remove organic substances (Prasad *et al.*, 2022). Finally, the catalyst is reused for photocatalytic degradation and repeated up to 5 times.

### 3. Results and discussion

#### 3.1. Catalyst characterization

Fe<sub>3</sub>O<sub>4</sub> as the core was synthesized and coated SiO<sub>2</sub> using the coprecipitation and the sol-gel methods, respectively. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO was synthesized using the hydrothermal technique. Figure 1 shows that the crystal structure of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO were determined using XRD. According to the cubic spinel phase (JCPDS card no. 74-0748), the diffraction characteristics of Fe<sub>3</sub>O<sub>4</sub> were observed at  $2\theta = 30.39^\circ$ ,  $35.69^\circ$ ,  $43.35^\circ$ ,  $53.87^\circ$ ,  $57.65^\circ$ , and  $62.97^\circ$ . This was appropriate for the planes (220), (311), (400), (422), (511), and (440). After coating with SiO<sub>2</sub>, a broad peak was observed at  $2\theta$  around  $23^\circ$ . This peak is a characteristic of amorphous SiO<sub>2</sub> (Chen *et al.*, 2014).

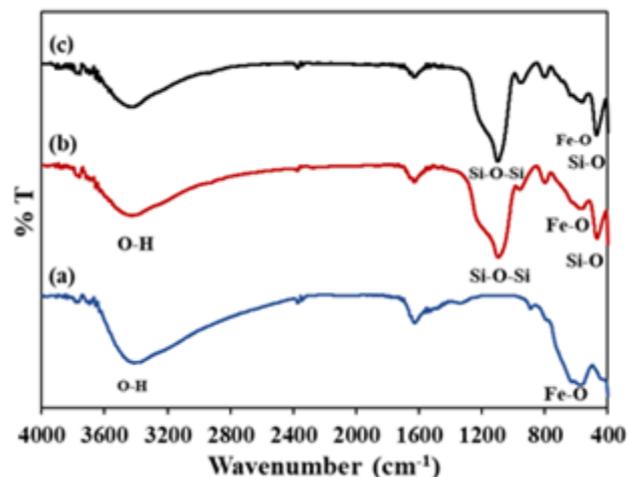
The new peaks in Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO were observed at  $2\theta = 76.01^\circ$  (311) and  $80.05^\circ$  (222). Meanwhile, other peaks overlapped those of Fe<sub>3</sub>O<sub>4</sub>, including  $37.21^\circ$  (111),  $43.45^\circ$  (200), and  $62.95^\circ$  (220), according to the structure of JCPDS card no. 78-0423 (NiO). Using the Debye-Scherrer equation, the crystal size of Fe<sub>3</sub>O<sub>4</sub> was calculated to be 7.0 nm, while those of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO were 8.2 nm. Another research showed that coating Fe<sub>3</sub>O<sub>4</sub> with SiO<sub>2</sub> increased the crystal size from 22.60 to 38.0 nm (Reman *et al.*, 2021).



**Figure 1.** XRD diffraction pattern of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and (c) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

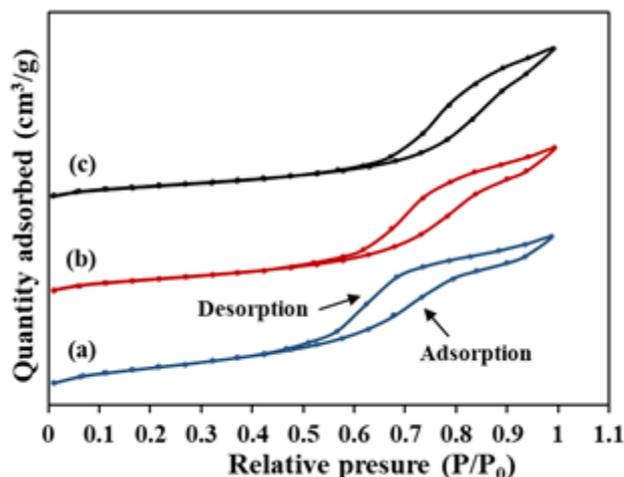
Figure 2 shows the FTIR spectra of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO. The wave numbers between  $3400\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  appear in all peaks, indicating the presence of O-H groups from free water, which is absorbed by the catalyst (Hariani *et al.*, 2021; Elzahrani 2017; Ojemaye *et al.*, 2017). In Figure 2(a), Fe-O stretching vibration is observed at a wave of  $557.43\text{ cm}^{-1}$ . Meanwhile, no other peak was observed apart from water absorption. Figure 2b shows an additional peak at  $464.84$  and  $804.31\text{ cm}^{-1}$ , which indicates symmetrical and asymmetrical Si-O terminals (Reman *et al.*, 2021). A strong peak at  $1089.78\text{ cm}^{-1}$  is an asymmetric Si-O-Si and Si-O-H vibrational bond observed at a wave number of  $950.60\text{ cm}^{-1}$  (Fu *et al.*, 2019; Han and An, 2021). The wave number for metal-oxygen stretching vibration was observed in the  $400\text{--}700$

$\text{cm}^{-1}$  range. The absorption band in the  $600\text{--}700\text{ cm}^{-1}$  indicates absorptions of Ni-O stretching vibration. This study appears at  $670.32\text{ cm}^{-1}$ , even though it is not sharp (Qiao *et al.*, 2009).



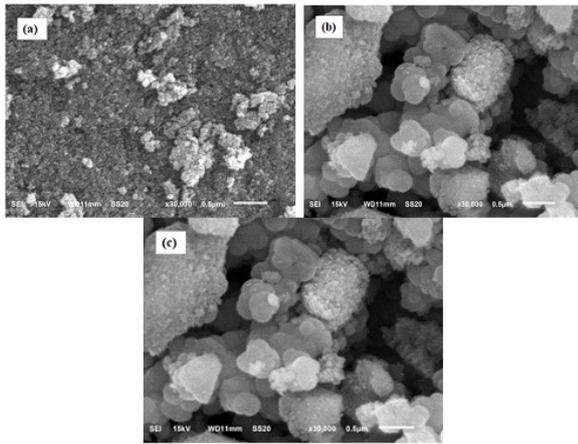
**Figure 2.** FTIR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and (c) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

The surface area affects the catalyst's ability in the degradation process (Kalam *et al.*, 2018). Based on the N<sub>2</sub> gas adsorption-desorption curve shown in Figure 3, the specific surface area ( $S_{\text{BET}}$ ) of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO were determined using BET analysis. According to the classification IUPAC, all BET curves showed compliance with the Type IV isotherm, namely mesoporous materials. The specific surface area of Fe<sub>3</sub>O<sub>4</sub> ( $S_{\text{BET}}$ ) is  $88.4\text{ m}^2/\text{g}$ , but after coating with SiO<sub>2</sub>, it becomes  $124.2\text{ m}^2/\text{g}$ . SiO<sub>2</sub> protects it from agglomeration processes, thereby increasing the surface area (Li *et al.*, 2017; Wu *et al.*, 2020). Another research showed that coating Fe<sub>3</sub>O<sub>4</sub> with graphene oxide (GO) produces a larger surface area than Fe<sub>3</sub>O<sub>4</sub> and GO (Thy *et al.*, 2020). In this study, the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO has a larger surface area than Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, which are  $128.8\text{ m}^2/\text{g}$ . These results are similar to CoFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>, which have a larger surface area than CoFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub> (Zielińska-Jurek *et al.*, 2017).

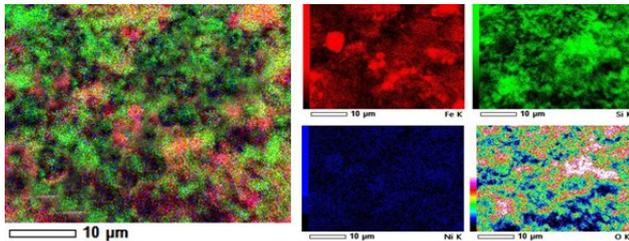


**Figure 3.** N<sub>2</sub> adsorption-desorption isotherm of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and (c) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

Figure 4 presents the morphology of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO analyzed using SEM. The Fe<sub>3</sub>O<sub>4</sub> surface appears to be small, dense, and agglomerated, while the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO appear to be a granular molecule with reasonably large sizes coating Fe<sub>3</sub>O<sub>4</sub>. The SEM mapping of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO in Figure 5 shows the distribution of elements on the composite surface. Some parts of the surface indicate the agglomeration of Fe<sub>3</sub>O<sub>4</sub> (red). Meanwhile, Ni (blue) appears to be distributed on the surface of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>.



**Figure 4.** Morphology of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and (c) Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO



**Figure 5.** SEM Mapping of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

Table 1 shows the composition of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO as a result of EDX analysis. The composition of Fe<sub>3</sub>O<sub>4</sub> consists of Fe and O, which indicates its purity. The addition of Si to Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> indicates that SiO<sub>2</sub> has successfully coated Fe<sub>3</sub>O<sub>4</sub>, while the addition of Ni shows that the element was distributed on the surface of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>.

Figure 6 shows the magnetic properties of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO. The Fe<sub>3</sub>O<sub>4</sub> saturation magnetization of 83.26 emu/g is classified as strong magnetization. Previous research showed that nanomagnetic coating ferrite with non-magnetic materials reduces saturation magnetization. Subsequently, coating Fe<sub>3</sub>O<sub>4</sub> with SiO<sub>2</sub> blocks the interaction of the magnetic dipole between adjacent magnetic particles and isolates them from the magnetic field (Kotutha *et al.*, 2019). In

**Table 1.** EDX analysis of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

Materials	Elements (%)			
	O	Fe	Si	Ni
Fe <sub>3</sub> O <sub>4</sub>	29.70	70.30	-	-
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub>	53.51	18.60	27.89	-
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /NiO	53.28	14.64	23.97	8.11

general, SiO<sub>2</sub> is non-magnetic, which implies that it is insulating and inert. In this research, the saturation magnetization values of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO were 61.96 and 53.84 emu/g, respectively. The presence of NiO reduces the properties of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>. This is related to the surface effect and anisotropy of the particles (Zhao *et al.*, 2015; Sadeghi *et al.*, 2012). The magnetization curve shows a mixture of ferromagnetic and superparamagnetic properties. Therefore, the magnetic properties allow for the easy separation of the composite from the solution after being used for photocatalytic degradation.

The energy absorbed by the catalyst depends on the optical band gap energy, namely the difference between the valence and conduction bands (Kalam *et al.*, 2018). Figure 7 shows plots  $(\alpha h\nu)^2$  versus Energy (eV) to obtain band gap values of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO. The broad spectrum indicates that Fe<sub>3</sub>O<sub>4</sub> dominates the phase in the material. Finally, the band gap value is obtained from Tauc's plot according to the following equation.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

Where  $\alpha$ ,  $A$ ,  $h$ ,  $\nu$ , and  $E_g$  are the absorption coefficient, proportionality constant, Planck's constant, vibrational frequency, and energy band gap. NiO was absorbed in a wavelength of 320 nm. Another research showed that NiO and Fe<sub>3</sub>O<sub>4</sub> were observed at 330 nm and 440 nm, respectively (Barzinjy *et al.*, 2020). In this research, the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO band gap was 2.83 eV, which is smaller than the band gap of NiO  $\sim$  3.5 eV and larger than the band gap of ferrite compounds  $\sim$  2 eV (Hariani *et al.*, 2021). The formation of the core-shell-shell, namely the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO, successfully reduced the band gap.

### 3.2. Photocatalytic activity

Figure 8a shows the effect of pH on the efficiency of photocatalytic degradation. The dye concentration was 20 mg/L, and the catalyst dose was 0.5 g/L with a pH varying from 5 to 10. The pH solution contributes to the degradation of dyestuffs and gives a charge to the catalyst's surface. Photocatalytic degradation of methylene blue dye using several catalysts, namely TiO<sub>2</sub>, ZnO, Co<sub>3</sub>O<sub>4</sub>, CdS, and MnTiO<sub>3</sub>, was optimum at a pH range of 9 to 11 (Alkaykh *et al.*, 2020; Alkaim *et al.*, 2014). Methylene blue dye is a cationic dye at alkaline pH, the dye has a positive charge, and the interaction is more effective with a negatively charged catalyst. Furthermore, there are many OH<sup>-</sup> ions at the pH of alkaline solutions. The catalyst absorbs irradiation to produce holes ( $h\nu_{\text{ph}}$ ) which then react with OH<sup>-</sup> to form hydroxyl radicals ( $\bullet\text{OH}$ ). At high pH, hydroxyl radicals are quickly scavenged, giving them no opportunity to react with dyes (Alkaim *et al.*, 2014).

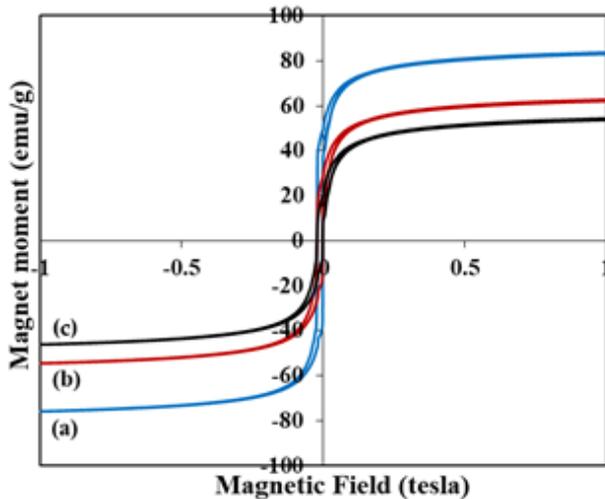


Figure 6. The magnetization of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  and (c)  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NiO}$

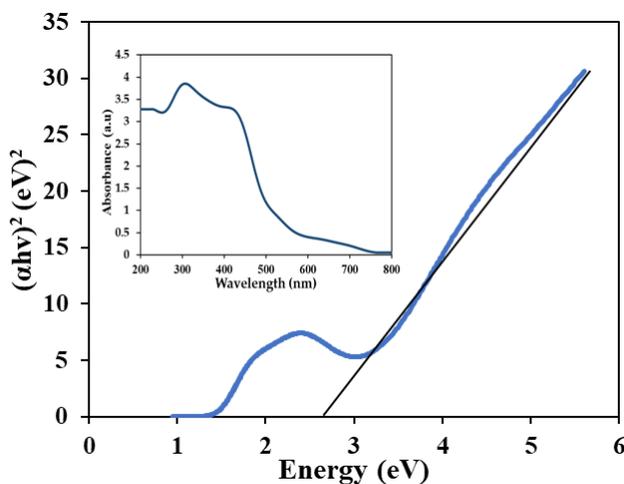


Figure 7. Wood-Tauc plot for  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NiO}$

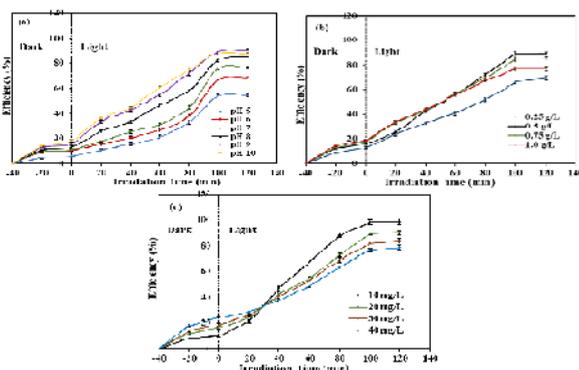


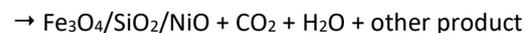
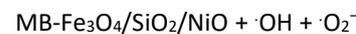
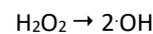
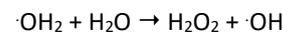
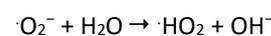
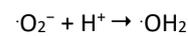
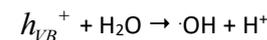
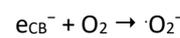
Figure 8. Effect of (a) pH solution, (b) catalyst dose, and (c) initial concentration of dye on the photocatalytic degradation of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NiO}$

The effect of catalyst doses was conducted with variations of 0.25, 0.5, 0.75, and 1.0 g/L, while the concentration was 20 mg/L at a pH of 9. Figure 8b shows that the higher the amount of catalyst, the more the dye degraded. In addition to being observed at 100 minutes, doses of 0.5 and 0.75 g/L had nearly the same degradation rate. However, there was a decrease at 1.0 g/L. At higher doses, there is a reduction in the reaction

rate due to catalyst loading, which causes the deactivation of activated molecules by collision with ground state catalysts (Herman, 1995). Furthermore, the optimum dose was at 0.5 g/L with a dye reduction efficiency of 89.77% in 100 minutes.

The effect of the initial dye concentration was analyzed using 10 to 50 mg/L. Figure 8c shows that the dye reduction efficiency increased directly with the initial dye concentration after 100 min. It also increases with the number of dye molecules adsorbed on the catalyst surface. This prevents photons from reaching the catalyst surface as they are blocked by the dye (Hariani *et al.*, 2022; Makeswari and Saraswathi, 2020). Therefore, the photocatalytic degradation of methylene blue dye was better at a low concentration of 10 mg/L with an efficiency of 98.51%. This indicates that the catalyst plays a significant role in dye degradation.

The mechanism of photocatalytic degradation of methylene blue (MB) dye using  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NiO}$  composite according to the reaction: (Ammar *et al.*, 2020).



### 3.3. Kinetic for photodegradation

The following formula expresses the kinetic model of photocatalytic degradation on methylene blue dye using pseudo-first-order:

$$\ln C_0 / C_t = kt \quad (2)$$

Where  $C_0$  and  $C_t$  are the initial concentration at each time (a certain time) (mg/L),  $t$  is the irradiation time (min), and  $k$  is the rate constant ( $\text{min}^{-1}$ ). The  $k$  value is obtained from the slope of the linear fitting graph  $\ln C_0/C_t$  Versus  $t$ . This research determined the kinetics of photocatalytic degradation using a methylene blue dye concentration of 10 mg/L, a catalyst dose of 0.5 g/L, and a solution pH of 9 (Figure 9). The coefficient of determination value ( $R^2 = 0.990 > 0.9$ ) indicates that the kinetic model is compatible (Van *et al.*, 2019). Therefore, the  $k$  value obtained is  $1.1 \cdot 10^{-4} \text{ min}^{-1}$ .

### 3.4. Reusability of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NiO}$

Reusability is essential for the remediation process as it aims to see the cost-effectiveness and feasibility of catalysts (Gebrezgiabher *et al.*, 2019; Moosavi *et al.*, 2020). Its performance uses methylene blue dye

concentration of 10 mg/L, a dose of 0.5 g/L, and a solution of pH 9. Figure 10 shows the efficiency of photocatalytic degradation after 5 cycles. Subsequently, the efficiency of photocatalytic degradation decreased from 98.02 to 94.97% (< 5%). The photocatalyst properties, such as surface area, number of active sites, and the presence of impurities, could change during reuse, but those with approximately 5 cycles continue to show good performance. It can be believed that the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO exhibits excellent photocatalyst stability.

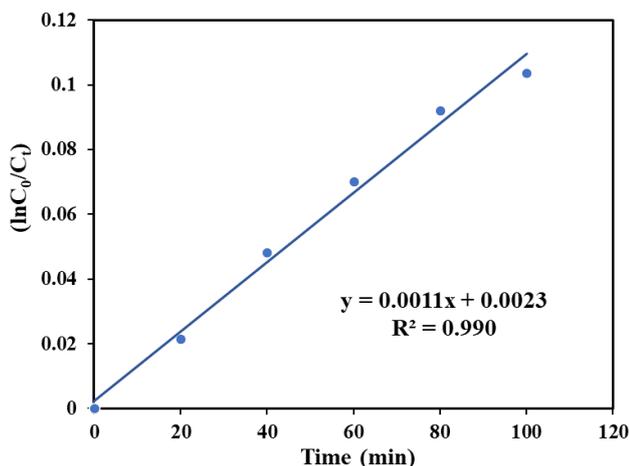


Figure 9. The plot of the pseudo-first-order for photocatalytic degradation on methylene blue dye

Table 2 shows a degradation efficiency comparison of methylene blue dye using several catalysts. The results of this research have high degradation efficiency with the same initial concentration and relatively fast time.

#### 4. Conclusion

Table 2. Photocatalytic degradation efficiency of some catalysts againsts methylene blue dye

Catalyst	Initial concentration (mg/L)	Irradiation time (min)	Efficiency(%)	References
Cu-TiO <sub>2</sub> /ZnO	35	120	64.72	Khaki <i>et al.</i> (2017)
SnS <sub>2</sub> -SiO <sub>2</sub> @ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	5	100	96.0	Balu <i>et al.</i> (2018)
ZnO-SnO <sub>2</sub>	10	60	96.53	Lin <i>et al.</i> (2018)
TiO <sub>2</sub> /Alg/FeNPs	5	120	97.6	Kanakaraju <i>et al.</i> (2018)
CoFe <sub>2</sub> O <sub>4</sub> /H <sub>2</sub> O <sub>2</sub>	10	140	82.0	Kalam <i>et al.</i> (2018)
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @CeO <sub>2</sub>	10	50	98.0	Ziaadini <i>et al.</i> (2019)
CoFe <sub>2</sub> O <sub>4</sub> @SiO <sub>2</sub> @DyCe <sub>2</sub> O <sub>7</sub>	20	30	94.5	Zinatloo-Ajabshir and Salavati-Niasari (2019)
Fe <sub>2</sub> TiO <sub>5</sub>	10	250	97.0	Vasiljevic <i>et al.</i> (2020)
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /NiO	10	100	98.51	Present study

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#### References

Ali M., Sarkar A., Pandey M.D., and Pandey S. (2006). Efficient precipitation of dyes from dilute aqueous solutions of ionic liquids. *Analytical sciences*, **22**, 1051–1053.

The core-shell-shell composite Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO has been successfully synthesized, with Fe<sub>3</sub>O<sub>4</sub> as the core, SiO<sub>2</sub> as the interlayer, and NiO spread on the composite surface. The composite has magnetic properties with a saturation magnetization value of 53.84 emu/g. Furthermore, the optimum conditions for photocatalytic degradation of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO against methylene blue dye were pH 9, catalyst dose of 0.5 g/L, 10 mg/L dye concentration, and irradiation time of 100 minutes, the degradation efficiency of 98.51%. This composite has high stability, and reusability of approximately 5 cycles decreases the removal efficiency by < 5%. Therefore, the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO composite has the potential to reduce water pollution. Further research needs to be developed for the photocatalytic degradation of wastewater containing other pollutants.

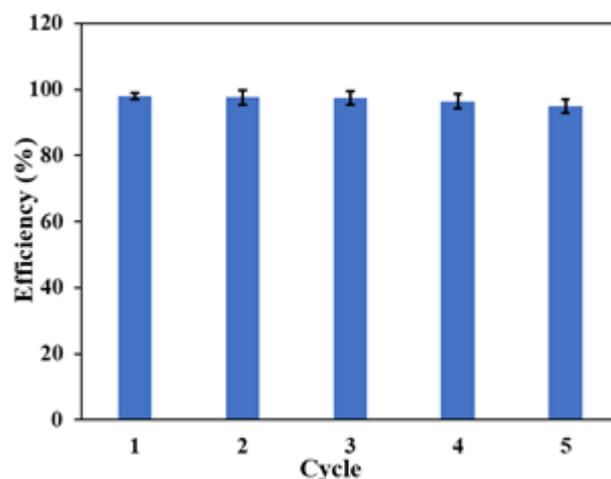


Figure 10. Reusability of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/NiO

Alkaim A.F., Aljeboree A.M., Alrazaq N.A., Baqir S.J., Hussein F.H., and Lili A.J. (2014). Effect of pH on adsorption and photocatalytic degradation efficiency of different catalyst on removal of Methylene blue, *Asian Journal of Chemistry*, **26**, 8445–8448.

Alkaykh S., Mbarek A. and Ali-Shattle E.E. (2020). Photocatalytic degradation of methylene blue dye in aqueous solution by MnTiO<sub>3</sub> nanoparticles under sunlight irradiation, *Heliyon*, **6**, 1–6.

Ammar S.H., Elaibi A.I., and Mohamme I.S. (2020). Core/shell Fe<sub>3</sub>O<sub>4</sub>@Al<sub>2</sub>O<sub>3</sub>-PMo magnetic nanocatalyst for photocatalytic

- degradation of organic pollutants in an internal loop airlift reactor, *Journal of Water Process Engineering*, **37**, 1–11
- Balu S, Uma K., Pan G.T., Yang T.C. and Ramaraj S.K. (2018). Degradation of methylene blue dye in the presence of visible light using  $\text{SiO}_2/\alpha\text{-Fe}_2\text{O}_3$  nanocomposites deposited on  $\text{SnS}_2$  flowers, *Materials*, **6**, 1030.
- Barakat A., Al-Noaimi M., Suleiman M. *et al.* (2013). One Step Synthesis of NiO Nanoparticles via Solid-State Thermal Decomposition at Low-Temperature of Novel Aqua (2,9-dimethyl-1,10-phenanthroline)  $\text{NiCl}_2$  Complex, *International Journal of Molecular Sciences*, **14**, 23941–23954.
- Barzinjy A.A., Hamad S.M., Aydin S., Ahmed M.H., and Hussain F.H.S. (2020). Green and eco-friendly synthesis of Nickel oxide nanoparticles and its photocatalytic activity for Methyl orange degradation, *Journal of Materials Science: Materials in Electronics*, **31**, 11303–11316.
- Behzadi S., Nonahal B., Royae S.J., and Asadi A.A. (2020).  $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$  magnetic nanoparticles synthesis and application in Methyl orange UV photocatalytic removal, *Water Science and Technology*, **11**, 2432–2445.
- Chaneei D., Inceesungvorn B., Wetchakun N., and Phanichphant S. (2014). Synthesis of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CeO}_2$  core-shell magnetic and their application as photocatalyst, *Journal of Nanoscience and Nanotechnology*, **14**, 7756–7762.
- Chen F., Yan F., Chen Q., Wang Y., Han L., Chen Z., and Fang S. (2014). Fabrication of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanoparticles supported by graphene oxide sheets for the repeated adsorption and photocatalytic degradation of rhodamine B under UV irradiation, *Dalton Transactions*, **43**, 13537–13544.
- Chen X., Wu Z., Liu D., and Gao. (2017). Preparation ZnO photocatalyst for the efficient and rapid photocatalytic degradations of azo dyes, *Nanoscale Research Letters*, **12**, 143.
- David P.S., Karananithi A. and Fathima N.N. (2020). Improved filtration for dye removal using keratin-polymide blend nanofibrous membranes, *Environmental Science and Pollution Research*, **27**, 45629–45638.
- Dias N.C., Bassin J.P., and Sant'Anna G.L. (2019). Ozonation of the dye reactive red 239 and biodegradation of ozonation products in a moving-bed biofilm reactor: revealing reaction products and degradations pathways, *International Biodeterioration & Biodegradation*, **144**, 1–9.
- D'Amario L., Fohlinger J., Boschloo G., and Hammarstrom L. (2018). Unveiling hole trapping and surface dynamics of NiO nanoparticles, *Chemical Science*, **9**, 223–230.
- Elzahrani E. (2017). Photodegradation of binary azo dyes using core-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$  nanospheres, *American Journal of Analytical Chemistry*, **8**, 95–115.
- Fu C., Liu X., Wang Y., Li L., and Zhang Z. (2019). Preparation and characterization of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2\text{-Co/rGO}$  magnetic visible light photocatalyst for water treatment, *RSC Advances*, **9**, 20256–20265.
- Gao P., Liu J., Sun D.D., and Ng W. (2013). Graphene oxide-CdS composite with high photocatalytic degradation and disinfection activities under visible light irradiation, *Journal of Hazardous Materials*, **250**, 412–2420.
- Gebrezgiabher M., Gebreslassie G., Gebretsadik T., Yeabyo G., Elemo F., Bayeh Y., Thomas M. and Linert W. (2019). AC-Doped  $\text{TiO}_2/\text{Fe}_3\text{O}_4$  nanocomposite for photocatalytic dye degradation under natural sunlight irradiation, *Journal of Composites Science*, **3**, 75.
- Girginova P.I., Daniel-da-Silva A.L., Lopes C.B., Figueira P., Otero M., Amaral V.S., Pereira E., and Trindade T. (2010). Silica coated magnetite particles for magnetic removal of  $\text{Hg}^{2+}$  from water, *Journal of Colloid and Interface Science*, **345**, 234–240.
- Han J.S., and An G.S. (2021). Preparation of Dual-Layered Core-Shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  nanoparticles and their properties of plasmid DNA purification, *Nanomaterials*, **11**, 3422.
- Hariani P.L., Said M., Rachmat A., Riyanti F., Pratiwi H.C., and Rizki W.T. (2021). Preparation of  $\text{NiFe}_2\text{O}_4$  nanoparticles by solution combustion method as photocatalyst of congo red, *Bulletin of Chemical Reaction Engineering & Catalysis*, **16**, 481–490.
- Hariani P.L., Said M., Salni, Aprianti N. and Naibaho Y.A.L.R. (2022). 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, *Journal of Ecological Engineering*, **23**, 118–128.
- Herman J.M. (1995). Heterogeneous photocatalysis; an emerging discipline involving multiphase system, *Catalyst Today*, **24**, 157–164.
- Hosny N.M. (2011). Synthesis, characterization and optical band gap of NiO nanoparticles derived from anthranilic acid and precursors via a thermal decomposition route, *Polyhedron*, **30**, 470–476.
- Hou C., Hu B., and Zhu J. (2018). Photocatalytic degradation of methylene blue over  $\text{TiO}_2$  Pretreated with varying concentrations of NaOH, *Catalysts*, **8**, 575.
- Jarariya R. (2022). A review based on spinel ferrite nanomaterials  $\text{MgFe}_2\text{O}_4$  - synthesis of photocatalytic dye degradation in visible light response, *Journal of Environmental Treatment Techniques*, **10**, 149–2156.
- Kanakaraju D., Shahdad N.R.M., Lim Y., and Pace. A. (2018). Magnetic hybrid  $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{FeNPS}$  triads for the efficient removal of Methylene blue from water, *Sustainable Chemistry and Pharmacy*, **8**, 50–62.
- Kalam A., Al-Sehemi A.G., Assiri M. *et al.* (2018), Modified solvothermal synthesis of cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) magnetic nanoparticles photocatalysts for degradation of Methylene blue with  $\text{H}_2\text{O}_2$ /visible light, *Results in Physics*, **8**, 1046–1053.
- Khaki M.R.D., Shafeeyan M.S., Raman A.A.A. and Daud W.M.A.W. (2017), Evaluating the efficiency of nano-sized Cu doped  $\text{TiO}_2/\text{ZnO}$  photocatalyst under visible light irradiation, *Journal of Molecular Liquids*, **258**, 354–365.
- Khan N.A., Saeed K., Khan I. *et al.* (2022). Efficient photodegradation of orange II dye by nickel oxide nanoparticles and nanoclay supported nickel oxide nanocomposite, *Applied Water Science*, **12**, 1–10.
- Khodai M., Ghasemi N., Moradi B., and Rahimi M. (2013). Removal of methylene blue from wastewater by adsorption onto  $\text{ZnCl}_2$  activated corn husk carbon equilibrium studies, *Journal of Chemistry*, **3**, 1–7.
- Kotutha I., Duangchuen T., Swatsitang K., Meewasana W., Khajonrit J., and Maensiri S. (2019). Electrochemical properties of  $\text{rGO}/\text{CoFe}_2\text{O}_4$  nanocomposites for energy storage application, *Ionics*, **25**, 5401–5409.
- Kuang Y., Zhang X., and Zhou S. (2020). Adsorption of methylene blue in water onto activated carbon by surfactant modification, *Water*, **12**, 587.
- Lett J.A., Sagadevan S., Weldegebräel G.K., and Fatimah I. (2022). Hydrothermal synthesis and photocatalytic activity of

- NiO nanoparticles under visible light illumination, *Bulletin of Chemical Reaction Engineering & Catalysis*, **17**, 2, 340–349.
- Lin J., Luo Z., Liu J., and Li P. (2018). Photocatalytic degradation of methylene blue in aqueous solution by using ZnO-SnO<sub>2</sub> nanocomposites, *Materials Science in Semiconductor Processing*, **87**, 24–31.
- Li Q., Lu C., Chen C., Xie L., Liu Y., Li Y., Kong Q., and Wang H. (2017). Layered NiCo<sub>2</sub>O<sub>4</sub>/ reduced graphene oxide composite as an advanced electrode for supercapacitor, *Energy Storage Materials*, **8**, 59–67.
- Loan N.T.T., Hien Lan N.T.H., Hang N.T.T. *et al.* (2019). CoFe<sub>2</sub>O<sub>4</sub> nanomaterials: effect of annealing temperature on characterization, magnetic, photocatalytic, and photo-Fenton properties, *Processes*, **7**, 885.
- Makeswari M. and Saraswathi P. (2020). Photocatalytic degradation of methylene blue and methyl orange from aqueous solution using solar light onto chitosan bi-metal oxide composite, *SN Applied Sciences*, **2**, 336.
- Moghaddam S.S., Moghaddam M.R.A. and Arami M. (2010). Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology, *Journal of Hazardous Materials*, **175**, 651–657.
- Moosavi S., Li R.Y.M., Lai C.W. *et al.* (2020). Methylene blue dye photocatalytic degradation over synthesized Fe<sub>3</sub>O<sub>4</sub>/AC/TiO<sub>2</sub> nano-catalyst: degradation and reusability studies, *Nanomaterials*, **10**, 2360.
- Ojemaye M.O., Okoh O.O., and Okoh A.I. (2017). Performance of NiFe<sub>2</sub>O<sub>4</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> photocatalyst for the effective photocatalytic re-duction of Cr(VI) from aqueous solutions, *Journal of Nanomaterials*, **2017**, 1–18.
- Pham T.D., Bui T.T., Nguyen V.T. *et al.* (2018). Adsorption of polyelectrolyte onto nanosilica synthesized from rice husk: characteristics, mechanisms, and application for antibiotic removal, *Polymers*, **10**, 220.
- Prasad K.S., and Shamshuddin S.Z.M. (2022). Highly efficient conversion of glycerol and t-butanol to biofuel additives over AIPO solid acid catalyst under microwave irradiation technique: kinetic study, *Comptes Rendus Chimie*, **25**, 149–170.
- Qiao H., Wei Z., Yang H., Zhu L., and Yan X. (2009). Preparation and characterization of NiO nanoparticles by anodic arc plasma method, *Journal of Nanomaterials*, **2009**, 1–5.
- Reman G U., Tahir M., Goh P.S., Ismail A.F., Hafeez A., and Khan I.U. (2021). Enhancing the photodegradation of phenol using Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> binary nanocomposite mediated by silane agent, *Journal of Physics and Chemistry of Solids*, **153**, 110022.
- Sadeghi S., Azhdari H., Arabi H., and Moghaddam A.Z. (2012). Surface modified magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a selective sorbent for solid phase extraction of uranyl ions from water samples, *Journal of Hazardous Materials*, **215**, 208–216.
- Salomon R.V., Lydia I.S., Merlin J.P., and Venuvalingam P. (2012). Enhanced photocatalytic degradation of azo dye using nano Fe<sub>3</sub>O<sub>4</sub>, *Journal of the Iranian Chemical Society*, **9**, 101–109.
- Thy L.T.M., Cuong P.M., Tu T.H., Nam H.M., Hieu N.H., and Phong M.T. (2020). Fabrication of magnetic iron oxide/graphene oxide nanocomposite for removal of lead ions from water, *Chemical Engineering Transactions*, **78**, 277–282.
- Vandevivere P.C., Bianchi R., and Verstraete W. (1998). Treatment and reuse of wastewater from textile wet-processing industry: review of emerging technologies, *Journal of Chemical Technology and Biotechnology*, **72**, 289–302.
- Van Tran T., Nguyen D.T.C., Le H.T.N. *et al.* (2019). A hollow mesoporous carbon from metal-organic framework for robust adsorbability of ibuprofen drug in water, *Royal Society Open Science*, **6**, 190058.
- Vasiljevic Z.Z., Dojcinovic M.P., Vujanec J.D. *et al.* (2020). Photocatalytic degradation methylene blue, under natural sunlight using iron titanate nanoparticles prepared by a modified sol-gel method, *Royal Society Open Science*, **7**, 1–15.
- Wan X., Yuan M., Tie S., and Lan S. (2013). Effect of catalyst characters on photocatalytic activity and process of NiO nanoparticles in the degradation of methylene blue, *Applied Surface Science*, **277**, 40–46.
- Wu Y., Shu R., Shan X., Zhang J., Shi J., Liu Y., and Zheng M. (2020). Facile design of cubic-like cerium oxide nanoparticles decorated reduced graphene oxide with enhanced microwave absorption properties, *Journal of Alloys and Compounds*, **817**, 152766.
- Zhao P., Mo Z., Zhang P., Zhu X., and Guo R. (2015). Synthesis of graphene/Fe<sub>3</sub>O<sub>4</sub>/NiO magnetic nanocomposites and its application in photocatalytic degradation the organic pollutants in wastewater, *Journal of Porous Materials*, **22**, 1245–1253.
- Ziaadini F., Mostafavia A., Shamsputra T., and Fathirad F. (2019). Photocatalytic degradation of Methylene blue from aqueous solution using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@CeO<sub>2</sub> core-shell magnetic nanostructure as an effective catalyst, *Advances in Environmental Technology*, **2**, 127–132.
- Zielińska-Jurek A., Bielan Z., Dudziak S. *et al.* (2017). Design and application of magnetic photocatalysts for water treatment. The effect of particle charge on surface functionality, *Catalysts*, **7**, 360.
- Zinatloo-Ajabshir S., and Salavati-Niasari M. (2019). Preparation of magnetically retrievable CoFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Dy<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> nanocomposites as novel photocatalyst for highly efficient degradation of organic contaminants. *Composites Part B: Engineering*, **174**, 106930.