**Chimica et Natura Acta**
p-ISSN: 2355-0864 e-ISSN: 2541-2574
Homepage: http://jurnal.unpad.ac.id/jcena

# Effectiveness of Magnetic Nanocomposites Modified with Reduced Graphene Oxide Derived from Spent Coffee Grounds for Pharmaceutical Waste Remediation

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DOI: https://doi.org/10.24198/cna.v13.n2.57812

**Abstract:** The Covid-19 pandemic significantly inflluenced the growth of the pharmaceutical industry in Indonesia, leading to environmental challenges, particularly with the discharge of pharmaceutical wastewater. Traditional treatment methods, such as flocculation and coagulation, hav limitations as they produce large volumes of activated sludge. An alternative approach for remediating this wastewater is the use of magnetite nanocomposites modified with reduced graphene oxide. This material leverages the unique properties of reduced graphene oxide, enhancing the separation and transfer of electron-hole pairs generated in the photogeneration process and significantly reducing charge carrier recombination in the photocatalytic system. This study aims to determine the degradation precentage of pharmaceutical wastewater using magnetic nanocomposite materials synthesized via in-situ chemical co-precipitation. The degradation percentage achieved through photocatalytic testing was 38.34% in basic conditions, with a band gap value of 2.03 Ev, operating under visible light. The characterization techniques used in this research include XRD, TM-EDS, FTIR, and UV-vis-DRS.

**Keywords:** reduced Graphene Oxide, magnetite nanocomposite, photocatalytic

***Abstrak:*** *Pandemi Covid-19 memberikan pengaruh yang signifikan terhadap pertumbuhan industri farmasi di Indonesia sejalan dengan timbulnya permasalahan lingkungan berupa air limbah dari industri farmasi tersebut. Metode pengolahan limbah seperti flokulasi dan koagulasi memiliki kekurangan karena menghasilkan lumpur aktif dalam volume yang besar. Salah satu metode yang dapat digunakan untuk remediasi limbah farmasi adalah dengan menggunakan material magnetik nanokomposit termodifikasi reduced Graphene Oxide yang memanfaatkan karakteristik unik yang dimiliki reduced Graphene Oxide dapat membantu pemisahan dan perpindahan pasangan electron-hole yang dihasilkan melalui proses fotogenerasi serta secara signifikan mengurangi rekombinasi pembawa muatan dalam sistem fotokatalitik. Tujuan dari penelitian ini adalah untuk mengetahui persentase degradasi limbah farmasi menggunakan material magnetik nanokomposit. Metode yang digunakan pada penelitian ini adalah in-situ chemical co-precipitation. Persentase degradasi limbah farmasi yang diperoleh dengan menggunakan material magnetik nanokomposit melalui uji fotokatalitik sebesar 38,34% pada material kondisi basa dengan nilai celah pita sebesar 2,03 eV yang bekerja pada sinar tampak. Karakterisasi yang digunakan pada penelitian ini berupa XRD, TM-EDS, FTIR, dan UV-vis-DRS.*

***Kata kunci:*** *fotokatalisis, magnetik nanokomposit, reduced Graphene Oxide*

## INTRODUCTION

Garbage management poses a significant difficulty in industrial sectors, and inadequate garbage disposal without effective treatment can result in detrimental environmental effects. The pharmaceutical industry is notably proficient in generating trash. This industry generates liquid effluent that may exhibit toxic and dangerous characteristics, including metformin. Metformin is utilised for diabetes management and facilitates weight reduction (Shurrab & Arafa 2020); furthermore, it has been administered in several nations to support COVID-19 patients (Samuel *et al*. 2021). Water contaminated with metformin waste is dangerous to organisms upon consumption, as it may disrupt the endocrine system and elevate cancer risk with prolonged exposure (Endeshaw 2024; Balakrishnan *et al*. 2022). Conventional wastewater treatment techniques are ineffective in entirely removing metformin due to its distinctive physical

and chemical properties, such as high solubility, slow biodegradation, considerable mobility in water, and a low octanol-water partition coefficient (Mahmoud *et al*. 2020).

A method for degrading metformin in pharmaceutical waste is photocatalysis using magnetic nanocomposites. Photocatalysis is a process whereby metal oxides, semiconductors, and organic molecules demonstrate catalytic capabilities upon exposure to light, hence facilitating the acceleration of chemical reactions by light energy. Metformin degradation can be improved by applying magnetic nanocomposites, as their magnetic characteristics enable more efficient and rapid separation in the concluding phase of the process (Zaki *et al*. 2023).

Magnetic nanocomposites are solid, multiphase materials with one magnetic and various additional phases. This combination facilitates the creation of novel materials with characteristics different from conventional nanoparticles (Popova *et al*. 2022). Magnetic nanocomposites demonstrate excellent chemical stability, reduced cost, and can be separated via magnetic means. Magnetic oxides or semiconductor composites augment photocatalytic efficacy. An instance of a magnetic nanocomposite suitable for application is $Fe_3O_4$ and $TiO_2$ modified with reduced graphene oxide (rGO).

A poll by Snapcart in September 2023 reveals that 79% of the Indonesian population consumes coffee, leading to a rise in biomass output, especially in the form of spent coffee grounds. Improper disposal of spent coffee grounds, particularly from Arabica coffee, can elevate soil acidity, harm aquatic ecosystems, and release methane gas into the atmosphere (Mukherjee *et al*. 2021). A viable way to alleviate these consequences is to employ the spent coffee grounds in liquid waste treatment. Due to their high carbon content, spent coffee grounds can be a precursor in synthesizing rGO. The increased carbon content is primarily attributable to their composition, mainly cellulose, hemicellulose, and lignin (Challa *et al*. 2023).

rGO exhibits distinctive characteristics, including an extensive surface area, significant chemical adaptability, and superior electron absorption proficiency. In this magnetic nanocomposite, rGO can augment light absorption capacity and specific surface area, both critical for photocatalysis (Khavar *et al*. 2019).

## MATERIALS AND METHOD

### Materials

The majority of the reagents employed were pro-analysis grade items from Merck.

### The Instrument

In this study, several tools and instruments were used, including laboratory glassware, a visible light lamp (Philips, 125 W), magnetic stirrer and hotplate (IKA C-MAG HS 7), analytical balance (Sartorius Entris 224-1S), oven (Carbolite S30 2RR), photocatalytic reactor, centrifuge (Thermo Scientific Heraeus Labofuge 200 Centrifuge), Tabletop Microscope-Energy Dispersive X-Ray Spectroscopy (TM-EDS, Hitachi Tabletop Microscope-1000, Tokyo, Japan), sonicator Aczet Cub-10, spectrophotometer UV-vis (Shimadzu 1800), furnace (Nabertherm LT5/11/B410), spectrophotometer UV-vis diffuse reflectance spectroscopy (UV-vis-DRS, Jasco V-550, Tokyo, Japan), and X-ray diffraction (XRD, Rigaku/Miniflex 600, Tokyo, Japan).

### Synthesis of Graphene Oxide (GO)

All synthesis methods in this work were derived from the strategy established by Nada *et al*. (2018). Graphene oxide was produced using a modified Hummers technique. Initially, 2 g of coffee grounds, previously carbonized via pyrolysis, were combined with 50 mL of sulfuric acid in an ice bath, followed by 1 g of sodium nitrate, and the mixture was agitated for 4 hours. Subsequently, 6 g of $KMnO_4$ was included in the solution, and the mixture was agitated for an additional hour at 35°C. Subsequently, 100 mL of deionized water was incorporated, and the solution was stirred at 90°C for 1 hour. The solution was subsequently supplemented with 200 mL of deionized water and 10 mL of 30% $H_2O_2$.

### Synthesis of $Fe_3O_4$/rGO (*Magnetite Reduced Graphane Oxide)*

Magnetite Reduced Graphene Oxide (MRGO) was synthesized using the in-situ chemical co-precipitation method. Ferrous sulfate ($FeSO_4$) was mixed with ferric chloride ($FeCl_3$) in a molar ratio of 1:2. The solution was then dissolved in 80 mL of distilled water and stirred for 30 minutes. The homogeneous solution was afterward heated to 30°C and stirred for 30 minutes. A 20 wt.% graphene oxide (GO) solution was formulated by dissolving GO in 50 mL of distilled water, followed by sonication for 15 minutes. The sonicated suspension was then added to the $Fe_3O_4$ solution and stirred for 10 minutes. The pH of the GO/$Fe_3O_4$ solution was adjusted to 7 and 10 through the incorporation of ammonia solution (30% w/v). Sodium borohydride ($NaBH_4$) was added to the solution and stirred for 10 minutes. The mixture was separated using vacuum filtering and washed with distilled water and ethanol. The filtered residue was then dried in an oven at 60°C for 12 hours. The produced $Fe_3O_4$/rGO composite was analyzed using FTIR and TEM-EDS methods.

### Synthesis of $TiO_2$

Titanium dioxide ($TiO_2$) was produced via the hydrolysis process. Initially, 7 mL of titanium (IV) isopropoxide was dissolved in 100 mL of isopropyl alcohol and agitated for 1 hour. Subsequently, 400 mL of distilled water was incorporated into the homogenous solution and stirred for 3 hours. The resultant homogeneous mixture was filtered via

vacuum filtration and rinsed with distilled water and ethanol. The filtrate residue was dried at 40°C for 6 hours in an oven, then calcined at 400°C for 2 hours.

**Synthesis of $Fe_3O_4$/rGO/$TiO_2$**

The synthesized $TiO_2$ and $Fe_3O_4$/rGO, at a mass ratio 1:1, were suspended in 50 mL of ethanol and subjected to sonication for 10 minutes. The two suspensions were combined and separated using vacuum filtering and drying in an oven at 60°C. The synthesized $Fe_3O_4$/rGO/$TiO_2$ composite was further studied via FTIR, XRD, and UV-Vis DRS techniques.

**Photocatalytic Test**

The synthesized $Fe_3O_4$/rGO/$TiO_2$ magnetic nanocomposite (MRGT) was employed for photocatalytic evaluation by including it in 100 mL of a 10 ppm metformin solution. The mixture was agitated for 60 minutes in darkness to attain adsorption-desorption equilibrium. The solution was subsequently exposed to visible light for 120 minutes. Sample analysis was conducted with a UV-Vis spectrophotometer at 30-minute intervals.

**RESULT AND DISSCUSION**

Characterization with the Tabletop Microscope (TM) was conducted to examine the morphology of the synthesized MRG. Figure 1 illustrates that the morphology of MRG at pH 7 exhibits a spherical form with a diameter range of 29.8 µm, whereas MRG at pH 10 displays a diameter range of 56.3 µm.

The functional groups of the MRG and MRGT materials can be detected using FTIR. The FTIR results of the magnetic nanocomposite in Figure 1 reveal peaks that signify the existence of functional groups, including OH, C-O-C (epoxide), and C=C (alkene) in MRG at pH 7 and 10, aligning with the structure of rGO. A prominent peak with a wavenumber of 3438 $cm^{-1}$ signifies the reduction of the C=O functional group to the C-OH group. Ti-O-C and Ti-O-Ti functional groups indicate the practical synthesis of MRGT.

The crystal structure of MRGT can be analyzed with an X-ray diffractometer (XRD). The XRD study results in Figure 2 indicate that the anatase phase of $TiO_2$ in MRGT at pH 7 displays crystallographic planes (112) and (022), but at pH 10, the crystallographic planes are (011), (112), (020), (015), and (004).

The crystallographic planes adhere to the ICSD standard 98-020-0392, and $TiO_2$ possesses a tetragonal crystal structure. The rGO diffraction peak at 2θ was undetected in the study due to its overlap with the diffraction peak of the anatase phase of $TiO_2$, which occurs at 24.5° (Nada *et al*. 2018).

Figure 2 illustrates that $Fe_3O_4$ in MRGT at pH 7 displays crystallographic planes (111), (022), (135),

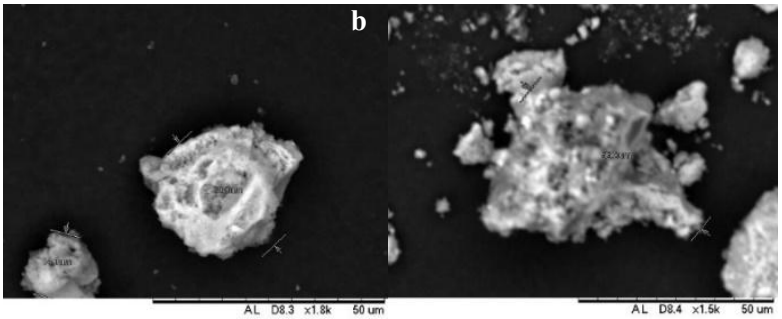


**Figure 1.** The characterisation outcomes of MRG ($Fe_3O_4$/rGO) using the TM instrument are as follows: (a) pH 7 at a magnification of 1800×; (b) pH 10 at a magnification of 1500×

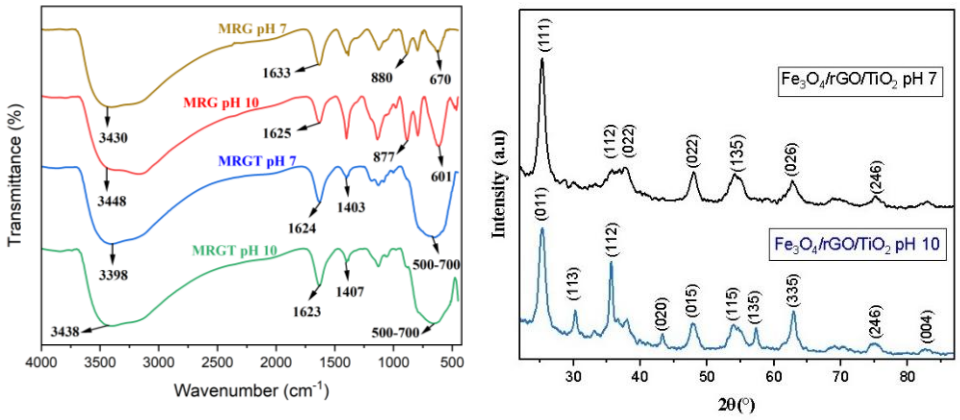


**Figure 2.** FTIR spectra (left) and XRD diffraction pattern

**Table 1.** The FTIR characterization results of MRG and MRGT at pH 7 and 10

| MRG pH 7 and 10 | | MRGT pH 7 and 10 | |
|---|---|---|---|
| Wavenumber ($cm^{-1}$) | Assumption | Wavenumber ($cm^{-1}$) | Assumption |
| 3448-3430 | O-H | 3438-3398 | O-H |
| 1633-1625 | C=C (alkene) | 1624-1623 | C=C (alkene) |
| 880-877 | C-O-C (epoxide) | 1407 | Ti-O-C |
| 607-601 | Fe-O | 700-500 | Ti-O-Ti |

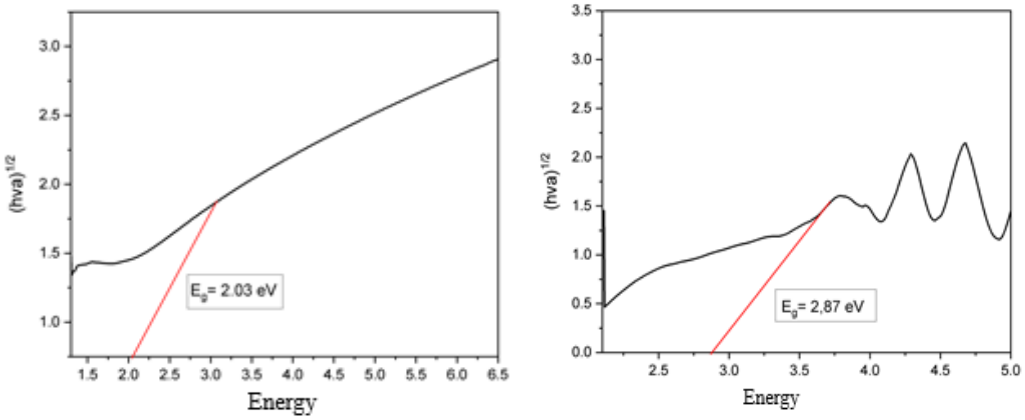


**Figure 3.** UV-DRS spectrum of MRGT pH 7 (left) and pH 10 (right)

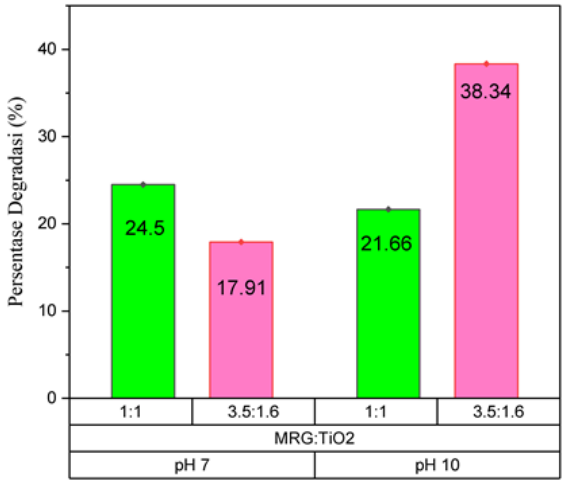


**Figure 4.** Percentage of metformin degradation

(026), and (246). In MRGT at pH 10, the crystallographic planes are (113), (115), (135), (335), and (246). The crystallographic planes adhere to the ICSD norm 98-002-9129, and $Fe_3O_4$ exhibits a cubic crystal structure.

The band gap of $Fe_3O_4$/rGO/$TiO_2$ can be evaluated using Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS). Titanium dioxide nanoparticles ($TiO_2$ NPs) exhibit a band gap of 3.2 eV, enabling photocatalytic activity when exposed to ultraviolet light (Suhaimi *et al*. 2024). $Fe_3O_4$ has a band gap of 1.64 eV, making it responsive to visible light excitation. The band gap of $Fe_3O_4$/rGO/$TiO_2$ can be calculated via the Tauc equation as described by Jubu *et al*. (2022):

$$(\alpha hv)^{1/n} = C(hv\text{-}E_g)$$

In this context, α denotes the absorption coefficient of the semiconductor, which is energy-dependent (hv), h signifies Planck's constant, v indicates the photon frequency, Eg represents the band gap energy, C is a constant, and n refers to the electron transition. This study employs a value of n equal to 2 in the calculations, as the absorption of $TiO_2$ adheres to an indirect allowed transition. Figure 4.4 illustrates that the band gap value of $Fe_3O_4$/rGO/$TiO_2$ (MRGT) at pH 7, determined by the Tauc equation, is 2.87 eV, exhibiting a blue shift, whereas at pH 10, the band gap is 2.03 eV, signifying a redshift. The red shift in MRGT results from the presence of hydroxyl groups attributable to the surplus addition of ammonia, which renders the solution basic.

**Photocatalytic Activity Test of MRGT Against Metformin**

The photocatalytic activity test involved comparing the pH of MRGT ($Fe_3O_4$/rGO/$TiO_2$) synthesized under neutral and basic conditions, along with the mass ratio of $Fe_3O_4$/rGO to $TiO_2$ in the synthesis of $Fe_3O_4$/rGO/$TiO_2$. The experiment indicated that the produced substance effectively decomposed metformin. The findings suggested that an increase in the mass of $Fe_3O_4$ in relation to $TiO_2$ corresponded with a rise in the percentage of metformin degradation. This increase in degradation can be attributed to the 1.64 eV band gap of $Fe_3O_4$, which enables its functionality under visible light.

The influence of the synthesis environment, namely under basic and neutral conditions, on metformin degradation is evident in the mass ratio of $Fe_3O_4$/rGO to $TiO_2$ at 1:1. The findings indicated that pH 7 yielded a more significant degradation percentage than pH 10, as at pH 5-8, the carboxyl and hydroxyl groups on $Fe_3O_4$/rGO convert into –COO− and –O− functional groups, thereby augmenting the electrostatic interaction between the adsorbent surface and the pollutant (Ghasemi & Azimi-Amin 2022). The diminished deterioration percentages of metformin in both versions can be attributed to its commendable stability in water, exhibiting a degradation rate of merely 10% after 8 days at temperatures ranging from 30°C to 80°C (Prajaputra & Isnaini 2023).

## CONCLUSION

$Fe_3O_4$/rGO/$TiO_2$ (MRGT) with a spherical morphology was effectively synthesized via the modified Hummer process and in-situ chemical co-precipitation. This material serves as a photocatalyst in the photodegradation of metformin waste in water. It attains a degradation rate of 38.34% in alkaline circumstances, with a band gap of 2.03 eV, enabling its operation under visible light.

**Acknowledgement**

Special thanks to Belmawa for providing material funding, enabling this research to proceed smoothly in participating in the PKM-RE 2024 program.

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