Effective Photocatalytic Degradation of Nitrobenzene by Magnetite Modified Titania Composite

E.S. Kunarti[*], R. Roto, S. Sutarno, I.S. Budi and M. Mardiansyah

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia

*Corresponding author: Tel./Fax: +62 274 545188; E-mail: eko_kunarti@ugm.ac.id

Magnetic photocatalyst of magnetite modified titania composite Fe_3O_4/TiO_2 was prepared by co-precipitation and sol-gel methods followed by calcination at 450 °C. The produced material was confirmed by XRD, FTIR spectrophotometer, vibrating sample magnetometer and transmission electron microscope. The solid material was tested as a photocatalyst for degradation of nitrobenzene under UV light irradiation. The progress of degradation of nitrobenzene was monitored by using a UV-visible spectrophotometer. The photodegradation of nitrobenzene could be best realized at a medium pH of 7 and 120 min of irradiation. The reaction rate constant of nitrobenzene degradation catalyzed by TiO_2 and Fe_3O_4/TiO_2 solids were found to be 0.0058 min^{-1} and 0.0092 min^{-1}, respectively. The photocatalyst was recoverable by use of a magnetic bar and reusable.

Keywords: Titania, Magnetite, Degradation, Nitrobenzene.

INTRODUCTION

Nitrobenzene is a highly toxic and carcinogenic organic pollutant and also known as the main contaminant in the aquatic ecosystems [1,2]. Various methods have been proposed for the treatment of nitrobenzene contamination in wastewater such as advanced oxidation processes (AOPs) [3], biodegradation using microorganisms [4], photocatalysis [5], *etc*. The photo-catalytic treatment is one of the easy techniques, which works based on applying light irradiation to the reaction mixture [6].

The use of photocatalysts such as titanium dioxide (TiO_2) materials for the reduction of nitrobenzene to aniline is increasingly popular among researchers due to its high selectivity and activity [6,7]. Makarova *et al.* [8] and Kominami *et al.* [9] also reported that TiO_2 solids work well as photocatalysts in the photoreduction of nitrobenzene to aniline. However, the effectiveness of TiO_2 photocatalyst did not go along with its relatively difficult separation from a liquid medium [10]. To avoid the use of such materials in large quantities, modifiers which exhibit magnetic properties were applied in order to recover the solid material and also can be reused repeatedly [11]. Among the magnetic materials, magnetite (Fe_3O_4) is commonly chosen as a modifier for photocatalysts [12,13].

Magnetite (Fe_3O_4) has been studied largely for its strong magnetic properties, low toxicity, ease of production and high separation efficiency in liquid media [14,15]. Further, magnetite can adsorb metal ions [16] and organic substances [17], which is often beneficial for photocatalytic reactions [12,13].

Based on the previous work on the development of TiO_2 photocatalyst materials and their use in the degradation of organic wastes, this study reports on the synthesis of magnetite modified TiO_2 composite as a catalyst in the photodegradation reaction of nitrobenzene. The effect of magnetite upon addition on TiO_2 on the degradation reaction of nitrobenzene in aqueous media was evaluated.

EXPERIMENTAL

The chemicals *viz.* iron(II) sulfate heptahydrate ($FeSO_4$·$7H_2O$), iron(III) chloride hexahydrate, ($FeCl_3$·$6H_2O$), titanium tetraisopropoxide, trisodium citrate dihydrate ($Na_3C_6H_5O_7$·$2H_2O$), ethanol, ammonia solution (25%), nitrobenzene used were of analytical grade and purchased from Merck, USA.

The equipment for product characterization was Fourier transform infrared spectrophotometer (Shimadzu Prestige-21), X-ray diffractometer (Shimadzu XRD 6000), transmission electron microscope (JEOL-1400 120 kV) and vibrating sample magnetometer (Oxford VSM 1.2H). The degradation progress was monitored by using a UV-vis spectrophotometer (Genesys 10S).

Preparation of Fe_3O_4/TiO_2: The catalyst Fe_3O_4/TiO_2 was prepared according to previous work with slight modifications

[18]. The molar ratio of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ in 1:2 was dissolved in 100 mL of deionized water under purging of N_2 gas and ultrasonicated followed by the dropwise addition of 25% NH_3 solution. The produced black solid was washed with deionized water to neutrality and soaked into 0.5 M of 100 mL sodium citrate solution for 1 h. The precipitate was separated from the liquid by using an external magnetic bar, washed with deionized water and dried at 80 ºC overnight in the oven. The Fe_3O_4 solids from the previous step weighing 0.10 g were dispersed into 30 mL of 98% ethanol. About 1.3 mL of titanium tetraisopropoxide 97% and 0.20 mL of distilled water were added slowly and sonicated for 0.5 h for forming a sol. The formed sol was mixed with Fe_3O_4 suspension and stirred for 1 h. The precipitate was separated and calcined at 450 ºC for 3 h.

Photocatalytic degradation of nitrobenzene: A 20 mg photocatalyst of either TiO_2 or Fe_3O_4/TiO_2 was added to 20 mL of nitrobenzene solution 20 mg L^{-1} and pH was adjusted to 4, 5, 6, 7, 8 and 9. The mixture was stirred for 10, 20, 30, 60, 90, 120 and 150 min and was irradiated with UV light. After the reaction ceased, the photocatalyst was separated by a centrifugation for TiO_2 and by an external magnetic bar for Fe_3O_4/TiO_2. The supernatant was analyzed by UV-vis spectrophotometer to determine the remaining nitrobenzene.

RESULTS AND DISCUSSION

Characterization of Fe_3O_4/TiO_2: The X-ray patterns of Fe_3O_4 and Fe_3O_4/TiO_2 materials are presented in Fig. 1. The peaks at 2θ of 30.62º, 36.02º, 43.84º, 54.50º, 57.76º and 63.32º are observed (Fig. 1a) and correspond to that of magnetite (Fe_3O_4) and match well with JCPDS No. 19-0629 [19]. In Fig. 1b, new peaks were detected at 2θ of 25.38º, 38.00º, 48,24º, 55.14º, 70.59º and 75.40º, which are appropriate to the diffraction patterns of anatase TiO_2 in JCPDS No. 21-1272 [12].
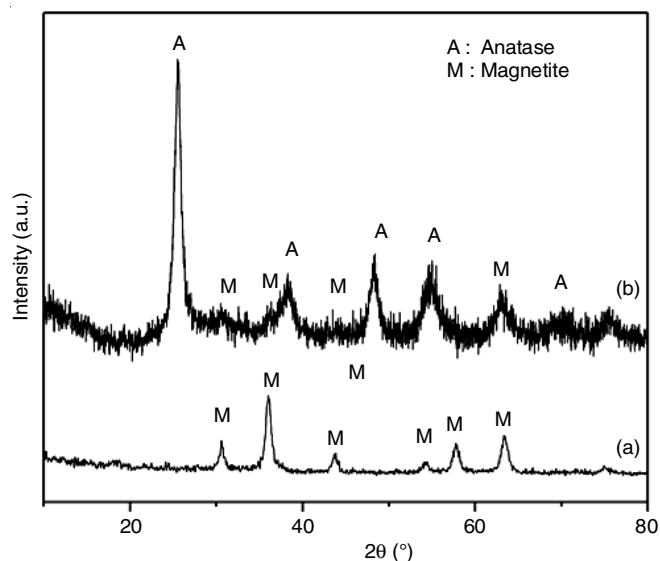

Fig. 1. Diffractogram of Fe_3O_4 (a) and Fe_3O_4/TiO_2 (b)

Fig. 2 shows infrared absorption bands at a wavenumber of 594.08, 1396.4 and 1589.34 cm^{-1}. The band at 594.08 cm^{-1} may be attributed to the stretching vibration of the Fe-O bond in Fe_3O_4. The absorption bands at 1396.4 and 1589.34 cm^{-1}

are attributed to the presence of a citrate group (Fig. 2a). Fig. 2b displays the infrared spectrum of Fe_3O_4/TiO_2. The presence of a broad absorption band from 477 to 795 cm^{-1} could be assigned as the Ti-O band of TiO_2 [13,20]. In Fig. 2b, it can also be seen that the absorption band intensity at the wavelengths of 1396.4 and 1589.34 cm^{-1} is reduced. It suggests that the citrate anion is completely lost due to the calcination at high temperatures.
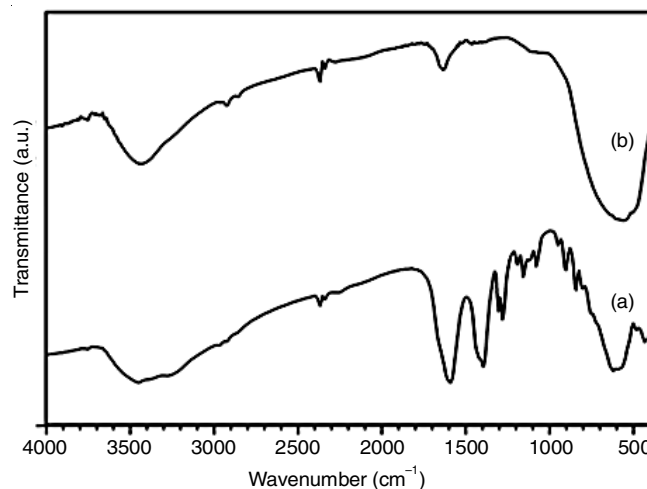

Fig. 2. Infrared spectra of Fe_3O_4 (a) and Fe_3O_4/TiO_2 (b)

After the Fe_3O_4/TiO_2 structure was confirmed, the microanalysis of the sample was carried out by TEM. The TEM images (Fig. 3) revealed the morphology and size of the obtained material. Fig. 3 shows that Fe_3O_4/TiO_2 has a spherical shape, with the dark part being the magnetite and the light colour being the titania coating. It could also be noticed that the average particle diameter of Fe_3O_4/TiO_2 nanomaterials is in the range of 14-24 nm. It indicates that the Fe_3O_4/TiO_2 nanostructured material is successfully prepared.

The magnetic property of Fe_3O_4/TiO_2 composite was determined by VSM instruments. Conventionally, the study of magnetic properties was also carried out by dispersing the synthesized material into distilled water in a container and a magnetic bar was applied outside the container. Fig. 4a-b shows that the separation time of Fe_3O_4 material was faster than that of the Fe_3O_4/TiO_2 composite (Fig. 4c-d). It implies a decrease in the magnetic susceptibility of Fe_3O_4/TiO_2 from that of the native Fe_3O_4. The VSM results show that the magnetic moment of Fe_3O_4/TiO_2 composite is lower than that of unmodified solid. The magnetic moment of Fe_3O_4/TiO_2 and Fe_3O_4 was 21 emu/g and 72 emu/g, respectively (Fig. 4e).

It has been reported that the coating of magnetite core by titania leads to a decrease in the magnetic susceptibility [21]. Although there is an observed decrease in the magnetic moment, the Fe_3O_4/TiO_2 composite could be still separated from the liquid medium with the use of an external magnetic bar.

Photocatalytic degradation of nitrobenzene

Effect of pH: To determine the reaction condition, the nitrobenzene degradation reaction was carried out at various pH solutions. For this, the plot of $C_o/C_t \times 100\%$ *versus* pH solution was developed, where C_o is the initial, C_t the final
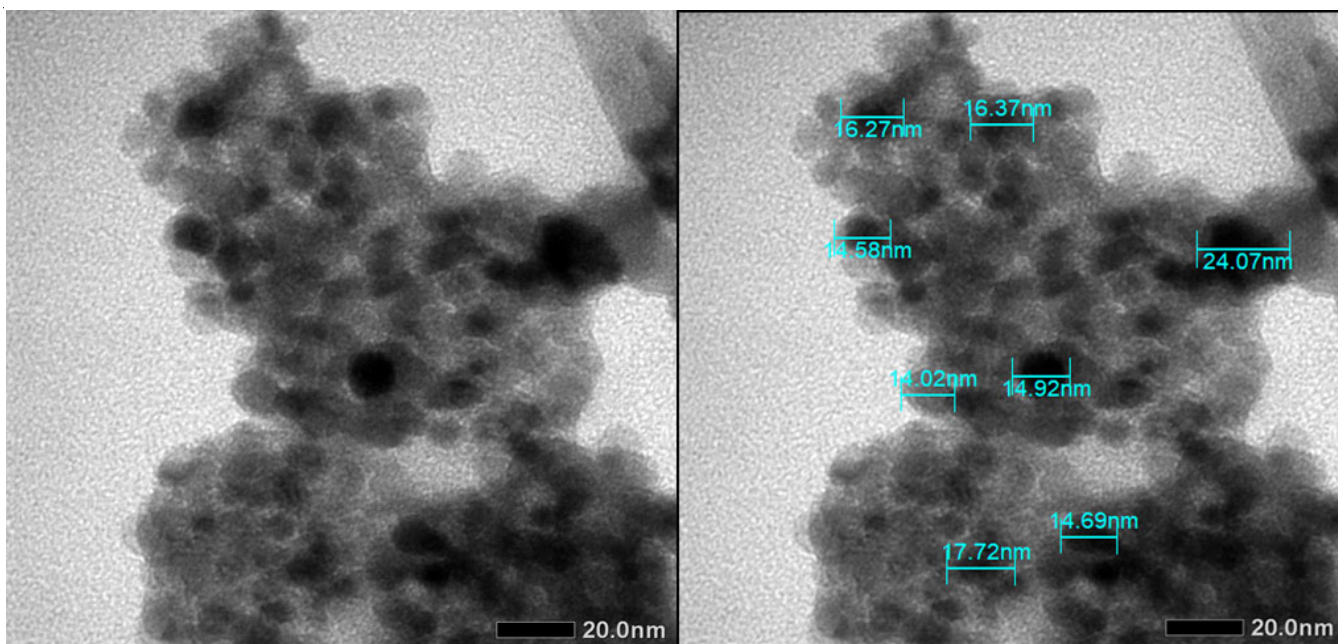
Fig. 3. TEM images of Fe_3O_4/TiO_2 composite
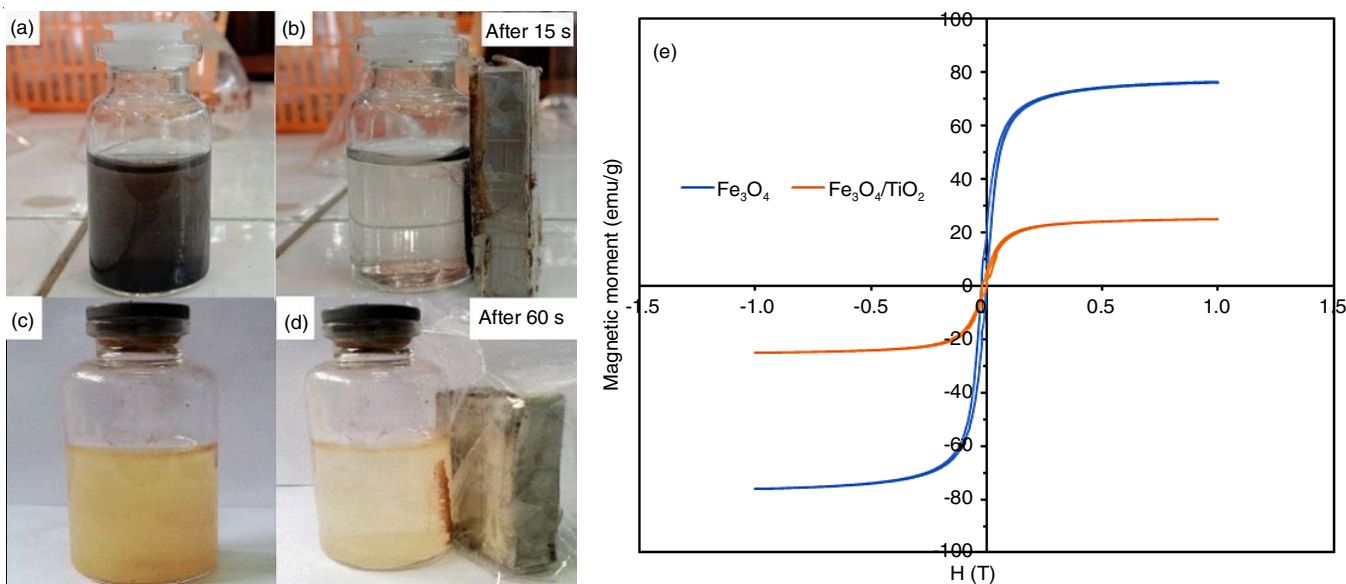
Fig. 4. Appearance of magnetic properties of Fe_3O_4 (a,b) and Fe_3O_4/TiO_2 (c,d) before and after interaction with a magnetic bar and the data of the VSM measurements (e)

concentration of nitrobenzene after photodegradation at the time (mg/L). In acidic and alkaline conditions, both catalysts have similar profiles. The Fe_3O_4/TiO_2 photocatalyst has a higher degradation of nitrobenzene than that of unmodified TiO_2. For Fe_3O_4/TiO_2 photocatalyst, at pH 7 the unreacted nitrobenzene decreases from 100% to 26% (Fig. 5). On the other hand, for TiO_2 photocatalyst, the unreacted nitrobenzene decreases from 100% to 40% (Fig. 5).

In an acidic medium (*e.g.* pH < 4), the photodegradation reaction occurs very slowly, which may be due to the dissolution of both photocatalysts and unfavourable conditions. The degradation of nitrobenzene increases with increasing pH, which is optimum at pH 7. In this condition, hydroxyl radicals

are directly generated from OH^- ions, which interact with the holes (eqn. 1) [15,22]:

$$h^+_{vb} + OH^- \longrightarrow {}^\bullet OH \qquad (1)$$

Therefore, in conditions where the amount of H^+ is equivalent to OH^-, more hydroxyl radicals (${}^\bullet OH$) will be produced and the degradation reaction progresses well. Meanwhile, in acidic conditions (pH < 7), the H^+ will interact with the electrons produced from photocatalysis to form $H^\bullet$ radicals. The ${}^\bullet H$ radicals will react with ${}^\bullet OH$ to form H_2O (eqn. 2):

$$e^- + H^+ \longrightarrow H^\bullet$$
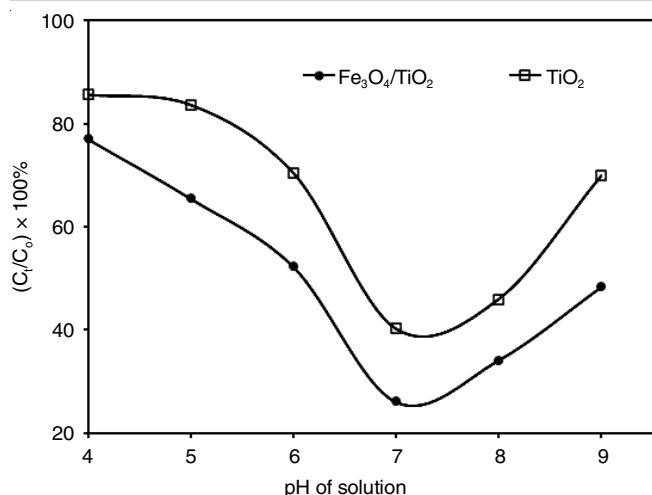
$$H^\bullet + {}^\bullet OH \longrightarrow H_2O \qquad (2)$$
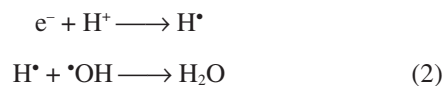
Fig. 5.　Effect of pH on nitrobenzene degradation catalyzed by TiO$_2$ and Fe$_3$O$_4$/TiO$_2$

Decreasing the number of hydroxyl radicals ($^{•}$OH) reduces the ability of photocatalyst, which results in the lowering of nitrobenzene degradation efficiency. However in the alkaline media (pH > 8), a large number of OH$^-$ ions present and the photocatalyst surface will be negatively charged due to the deprotonation and repel one another. It leads to a reduced generation of reactive species and slows down the degradation reaction.

Effect of irradiation time: Fig. 6 exhibits the effect of irradiation time on the nitrobenzene degradation catalyzed by the two-photocatalyst materials. There is no significant difference in the degradation pattern of nitrobenzene using TiO$_2$ or Fe$_3$O$_4$/TiO$_2$ after 10-30 min UV irradiation time. The undegraded nitrobenzene was 72% and 63%, respectively by TiO$_2$ and Fe$_3$O$_4$/TiO$_2$, respectively. This indicated that the absorbed photons energy is not optimal, hence, the number of electron-hole pairs produced to react with OH$^-$ ions have not shown a difference for both photocatalyst materials.
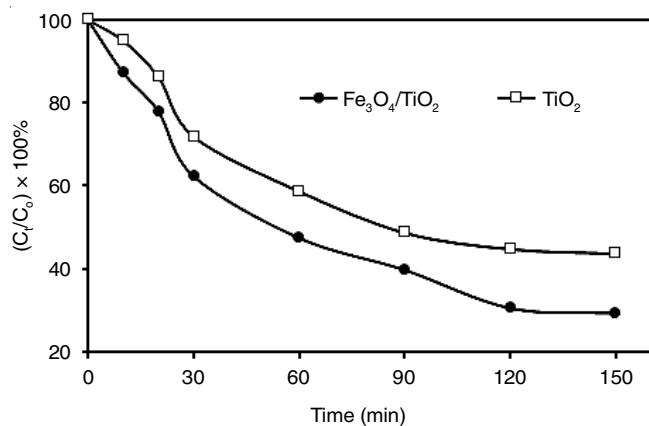

Fig. 6.　Effect of UV irradiation time on nitrobenzene degradation catalyzed by TiO$_2$ and Fe$_3$O$_4$/TiO$_2$

On the contrary, when the UV irradiation time increases to over 90 min, there is a difference in the degradation results. The results showed that the remaining undegraded nitrobenzene after 120 min UV irradiation time was 26% and 45% by using

Fe$_3$O$_4$/TiO$_2$ and TiO$_2$, respectively. It suggests that Fe$_3$O$_4$/TiO$_2$ is a better catalyst than TiO$_2$ for the nitrobenzene photodegradation. It could be explained by the fact that the magnetite material has better adsorption capability which could facilitate the photocatalytic degradation process.

Isotherm studies: The Langmuir-Hinshelwood model is commonly used model to explain the kinetics of photocatalytic degradation for the organic compounds [22,23]. The Langmuir-Hinshelwood kinetics is represented as follows:

$$\ln \frac{C_o}{C_t} = k_r t \tag{3}$$

where C$_o$ is the initial concentration of nitrobenzene (mg/L), C$_t$ is the nitrobenzene concentration after photodegradation at time t and k$_r$ is degradation rate constant. The rate constant can be extracted from the plot of ln C$_o$/C$_t$ *versus* t. Fig. 7 displays the Langmuir-Hinshelwood plot of the reaction. An increase in the efficiency of degradation of nitrobenzene with Fe$_3$O$_4$/TiO$_2$ photocatalyst was clearly observed. The rate constant (k$_r$) of nitrobenzene degradation reaction was 0.0058 min^{-1} by TiO$_2$ and 0.0092 min^{-1} by Fe$_3$O$_4$/TiO$_2$, respectively. These results suggest that magnetite (Fe$_3$O$_4$) has a major role in increasing the photoactivity of TiO$_2$ catalyst in nitrobenzene degradation.
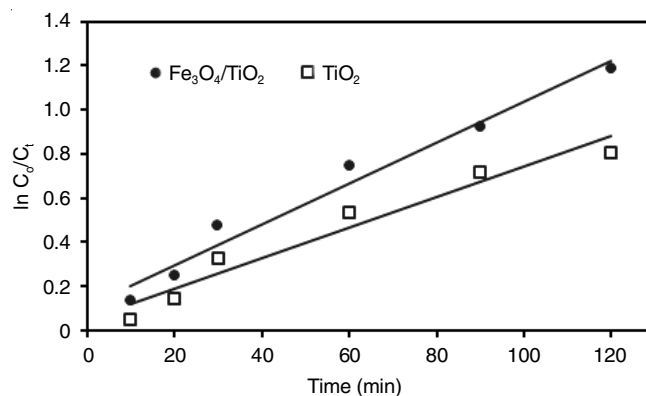

Fig. 7. Langmuir-Hinshelwood plot of nitrobenzene degradation

XRD studies: There was no structural change as indicated by the X-ray diffraction pattern. The XRD patterns are still similar to the reference of JCPDS No. 19-0629 for magnetite and JCPDS No. 21-1272 for TiO$_2$ anatase (Fig. 8). The diffraction patterns of the two materials did not change appreciably (Fig. 8a and b), except only that of a slight diminishing in the peak intensity. It implies that Fe$_3$O$_4$/TiO$_2$ photocatalyst was reusable after the successful separation from the reaction medium.

Comparison studies: The activity performance of the prepared photocatalytic material was compared with the most relevant reported photocatalysts for the degradation of nitrobenzene is shown in Table-1. The percentage of degradation was 74% and achieved within 2 h in the present work.

Conclusion

Magnetite modified titania composite of Fe$_3$O$_4$/TiO$_2$ was prepared and used as a catalyst for photocatalytic degradation of nitrobenzene. The results suggested that Fe$_3$O$_4$/TiO$_2$ catalysts

TABLE-1
COMPARISON OF PHOTOACTIVITY OF Fe_3O_4/TiO_2 WITH THE REPORTED PHOTOCATALYSTS
FOR THE DEGRADATION OF NITROBENZENE (NB) FOR 2 h IRRADIATION TIME

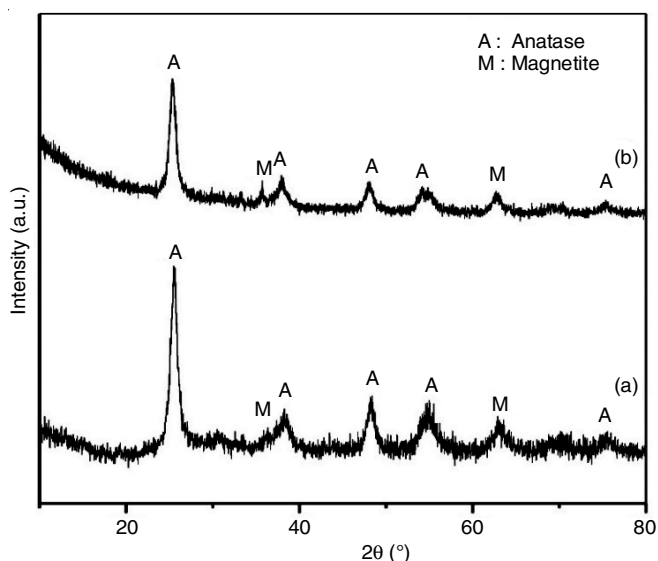| Photocatalyst	[Photocatalyst]	[Nitrobenzene]	Type of irradiation	Degradation (%)	Rate constant	Recoverability and reusability	Ref.
Coupled grafted cassava-ZnO	1 g/L	50 ppm	Visible light	87	NA	NA	[24]
Uncoupled ZnO	1 g/L	50 ppm	Visible light	67	NA	NA	
Tyrosine-modified CdS-TiO₂	0.1 g/100 mL	0.0136 M	125 W-visible lamp	75	0.024 min⁻¹	Reusable	[25]
Cobalt modified-ZnO	0.75 g	20 ppm	8 W-visible lamp	80	NA	NA	[26]
ZnO₂ nanoparticles	30 ppm	15 ppm	UV lamp (254 nm)	90	NA	NA	[27]
Nanocrystalline TiO₂/Zn²⁺		15 ppm	254 nm	99	0.035 min⁻¹	NA	[28]
Nanocrystalline TiO₂	50 mg/250 mL	50 ppm	125-W Mercury vapour lamp	76	NA	NA	[29]
				99.5 (with an air purge)	NA	NA	
TiO₂ doped Fe 0.5%	250 mg/L	2.52×10^{-4} M	Mercury lamp (320-500 nm)	85	2.54×10^{-4} (s⁻¹)	NA	[30]
TiO₂ doped Co 1%	250 mg/L	2.52×10^{-4} M	Mercury lamp (320-500 nm)	81	2.24×10^{-4} (s⁻¹)	NA	
TiO₂ doped Ni 1%	250 mg/L	2.52×10^{-4} M	Mercury lamp (320-500 nm)	78	2.19×10^{-4} (s⁻¹)	NA	
Undoped TiO₂	250 mg/L	2.52×10^{-4} M	Mercury lamp (320-500 nm)	54	1.08×10^{-4} (s⁻¹)	NA	
TiO₂/single-walled carbon nanotube	100 mg	50 ppm	20 W UV lamp (365 nm)	74	NA	Reusable	[31]
				100 (4 h)	NA	Reusable	
Fe₃O₄/TiO₂ composite	20 mg/20 mL	20 ppm	40 W UV lamp (260 nm)	74	0.0092 min⁻¹	Recoverable and reusable	This work

Fig. 8.　X-ray diffraction pattern of the photocatalyst of Fe_3O_4/TiO_2 before (a) and after used (b)

could improve reaction efficiency. The photocatalytic degradation of nitrobenzene catalyzed by TiO_2 and Fe_3O_4/TiO_2 exhibits a rate constant of 0.0058 min⁻¹ and 0.0092 min⁻¹, respectively. It proves that the modification of TiO_2 with the magnetic material of Fe_3O_4 improves the rate constant and facilitates the separation. Concisely, synthesized Fe_3O_4/TiO_2 composite could work as an excellent photocatalyst for the degradation of nitrobenzene

even better then the other reported catalysts in terms of both removable efficiency and re-useable.

ACKNOWLEDGEMENTS

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A. Wang, H. Cheng, B. Liang, N. Ren, D. Cui, N. Lin, B.H. Kim and K. Rabaey, *Environ. Sci. Technol.*, **45**, 10186 (2011);
https://doi.org/10.1021/es202356w

2. H. Fu and D. Zhu, *Environ. Sci. Technol.*, **47**, 4204 (2013);
https://doi.org/10.1021/es304872k

3. W.K. Jo, Y.S. Won, I. Hwang and R.J. Tayade, *Ind. Eng. Chem. Res.*, **53**, 3455 (2014);
https://doi.org/10.1021/ie500245d

4. T. Li, Z. Zhou and L. He, *Int. Biodeter. Biodegr.*, **123**, 63 (2017);
https://doi.org/10.1016/j.ibiod.2017.06.004

5. Y. Zhang, K. Zhang, C. Dai and X. Zhou, *Chem. Eng. Sci.*, **111**, 135 (2014);
https://doi.org/10.1016/j.ces.2014.02.029

6. S. Chen, H. Zhang, X. Yu and W. Liu, *Chin. J. Chem.*, **29**, 399 (2011);
https://doi.org/10.1002/cjoc.201190094

7. S.O. Flores, O. Rios-Bernij, M.A. Valenzuela, I. Córdova, R. Gómez and R. Gutiérrez, *Top. Catal.*, **44**, 507 (2007);
https://doi.org/10.1007/s11244-006-0098-2

8. O.V. Makarova, T. Rajh, M.C. Thurnauer, A. Martin, P.A. Kemme and D. Cropek, *Environ. Sci. Technol.*, **34**, 4797 (2000);
https://doi.org/10.1021/es001109+

9. H. Kominami, S. Iwasaki, T. Maeda, K. Imamura, K. Hashimoto, Y. Kera and B. Ohtani, *Chem. Lett.*, **38**, 410 (2009);
https://doi.org/10.1246/cl.2009.410

10. M. Abbas, B.P. Rao, V. Reddy and C. Kim, *Ceram. Int.*, **40**, 11177 (2014);
https://doi.org/10.1016/j.ceramint.2014.03.148

11. X. Feng and X. Lou, *Sep. Purif. Technol.*, **147**, 266 (2015);
https://doi.org/10.1016/j.seppur.2015.04.036

12. A. Banisharif, S.H. Elahi, A.A. Firooz, A.A. Khodadadi and Y. Mortazavi, *Int. J. Nanosci. Nanotechnol.*, **9**, 193 (2013).

13. I.S. Budi, I. Kartini and E.S. Kunarti, *Key Eng. Mater.*, **840**, 79 (2020);
https://doi.org/10.4028/www.scientific.net/KEM.840.79

14. S. Tong, R. Shi, H. Zhang and C. Ma, *J. Environ. Sci. (China)*, **22**, 1623 (2010);
https://doi.org/10.1016/S1001-0742(09)60298-9

15. E. Alzahrani, *Am. J. Anal. Chem.*, **8**, 95 (2017);
https://doi.org/10.4236/ajac.2017.81008

16. A.S. Maylani, T. Sulistyaningsih and E. Kusumastuti, *Indo. J. Chem. Sci.*, **5**, 130 (2016).

17. J.S.T. Hernandez, A.A. Muriel, J.A. Tabares, G.A.P. Alcazar and A. Bolanos, *J. Phys. Conf. Ser.*, **614**, 012007 (2015);
https://doi.org/10.1088/1742-6596/614/1/012007

18. E.S. Kunarti, I. Kartini, A. Syoufian and K.M. Widyandari, *Indones. J. Chem.*, **18**, 403 (2018);
https://doi.org/10.22146/ijc.26831

19. B.Y. Yu and S.Y. Kwak, *J. Mater. Chem.*, **20**, 8320 (2010);
https://doi.org/10.1039/c0jm01274b

20. X. Li, D. Wang, G. Cheng, Q. Luo, J. An and Y. Wang, *Appl. Catal. B*, **81**, 267 (2008);
https://doi.org/10.1016/j.apcatb.2007.12.022

21. X. Huang, G. Wang, M. Yang, W. Guo and H. Gao, *Mater. Lett.*, **65**, 2887 (2011);
https://doi.org/10.1016/j.matlet.2011.06.005

22. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995);
https://doi.org/10.1021/cr00033a004

23. K.V. Kumar, K. Porkodi and F. Rocha, *Catal. Commun.*, **9**, 82 (2008);
https://doi.org/10.1016/j.catcom.2007.05.019

24. H.S. Aliyua, J. Yusuf and M.I. Mohammed, *Int. J. Sci. Basic Appl. Res.*, **15**, 25 (2014).

25. M. Padervand, A. Rahmani, S. Rahimnejad and M.R. Gholami, *Nanochem. Res.*, **2**, 109 (2017);
https://doi.org/10.22036/NCR.2017.01.010

26. M.G. Liman, A.H. Abdullah, M.Z. Hussein and Z. Zainal, *Asian J. Chem.*, **26(Suppl.)**, S287 (2014);
https://doi.org/10.14233/ajchem.2014.19067

27. J.I.D.L. Ramírez, V.A.R. Villegas, S.P. Sicairos, E.H. Guevara, M.D.C. Brito Perea and B.L. Sánchez, *Catalysts*, **10**, 1041 (2020);
https://doi.org/10.3390/catal10091041

28. E.A. Reynoso-Soto, S. Pérez-Sicairos, A.P. Reyes-Cruzaley, C.L. Castro-Riquelme, R.M. Félix-Navarro, F. Paraguay-Delgado, G. Alonso-Núñez and S.W. Lin-Hoa, *J. Mex. Chem. Soc.*, **57**, 298 (2013).

29. R.J. Tayade, R.G. Kulkarni and R.V. Jasra, *Ind. Eng. Chem. Res.*, **45**, 922 (2006);
https://doi.org/10.1021/ie051060m

30. I. Nitoi, P. Oancea, M. Raileanu, M. Crisan, L. Constantin and I. Cristea, *J. Ind. Eng. Chem.*, **21**, 677 (2015);
https://doi.org/10.1016/j.jiec.2014.03.036

31. W. Zhou, K. Pan, Y. Qu, F. Sun, C. Tian, Z. Ren, G. Tian and H. Fu, *Chemosphere*, **81**, 555 (2010);
https://doi.org/10.1016/j.chemosphere.2010.08.059