DOI: https://doi.org/10.20535/2218-93002722020209587

PHOTOCATALYTIC ACTIVITY OF TiO_2-Eu_2O_3 SYSTEMS FOR PHENOL DECOMPOSITION IN AQUEOUS SOLUTIONS

[1]Van Tien Mai, [1]Le Thi Hai Le*

[1]Department of Environment - Hanoi University of natural resources and environment, Ha Noi City, ZIP 10000, Vietnam.

Corresponding authors: maitienvhcn@gmail.com

Abstract

TiO_2-Eu_2O_3 is a photocatalytic material synthesized from tetra-n-butylorthotitanate and rare earth oxide Eu_2O_3 by sol-gel method with polyvinyl alcohol. The morphology, chemical composition, and structure of the catalysts were characterized by infrared (IR) spectrometry, X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray (EDX) fluorescence spectroscopy. The photocatalytic activity of TiO_2-Eu_2O_3 was studied for the decomposition of phenol in an aqueous medium (initial phenol concentration was 10 ppm) in the visible light range, and its degree decomposition reached more than 90%. The obtained photocatalytic material can be used in the field of water treatment, namely as a catalyst for the photochemical decomposition in the visible range of light of organic pollutants for the purification of textile wastewater, and moreover to create a bactericidal effect in solutions.

Key words: photocatalysis; oxide of TiO_2-Eu_2O_3; phenol; aqueous solutions; visible light range.

Introduction

TiO_2 nanosized is a material much more studied nowadays, it is less toxic, chemically sustainable, and low priced. TiO_2 is a semiconductor with the bandgap at 3.05 eV for rutile and 3.25 eV for anatase; it is able to initiate a sustainable photocatalyst decomposition reaction of organic compounds in water (Wu 2012, Wang 2012, Tachikawa 2007 and Hu 2008). The photocatalytic ability of TiO_2 can be realised in several ways: photocatalytic dehydration on TiO_2 electrodes, creation of a super-permeable surface, and photocatalytic decomposition of organic substance in ultraviolet light λ <380 nm. However, the amount of ultraviolet radiation in the solar spectrum near the Earth's surface is only 3.5 ~ 4%, so the utilization of this radiation source for the photocatalytic action of TiO_2 is limited (Lee 2013 and Kebede 2013). To expand the use of solar radiation energy to the region of visible light for photocatalytic reactions, the bandgap of TiO_2 should be smaller (Zhang

2011, Kamegawa 2014 and Diker 2011). Therefore, to achieve this goal, many researchers have synthesized TiO_2 nanostructures by introducing metal and non-metal ions on its surface or into its structure. Currently, there are four directions for studying the creation and application of photocatalytic materials based on pure TiO_2: modification of TiO_2 with non-metals, modification of TiO_2 with metals, and mixing of metal and non-metal oxides (Crake 2017 and Teng 2012).

Rare earth oxides are widely used for various applications, such as the synthesis of optoelectronic devices, catalysts, and electro-chemicals. At present, mixed oxide systems based on CeO_2, Nd_2O_3, Eu_2O_3, Y_2O_3 oxides are used. In addition, titanium oxide is also of particular interest to many scientists due to its unique properties and wide applicability. Many studies show that the combination of Eu_2O_3 and TiO_2 forms photocatalytic systems with strong catalytic activity in the visible light area (Feng 2007 and Zhang 2008).

Phenol is a very toxic aromatic compound that is difficult to decompose, it spreads an unpleasant odour, affects agricultural production, and causes many diseases that are dangerous for humans even at very low concentrations (Bao 2016). Since the end of the twentieth century, there have been many questions regarding the content of phenolic compounds in the environment, especially in water. The main source of natural water pollution with phenol is industrial wastewater after petrochemical treatment, phenol production, pharmaceuticals, coal, and steel production (Lu 2016 and Gami 2014). Therefore, the removal of phenol from wastewater is an urgent problem today. Many methods, such as adsorption, biology treatment, catalytic oxidation in a water medium, etc are used to remove phenol from water. However, it is often necessary to combine two or more different methods to completely remove phenol from the wastewater (Cheng 2018). It should be noted that photochemical nanocatalysts significantly increase the efficiency of phenol decomposition in water (Wang 2017 and Hamza 2015).

In this study TiO_2-Eu_2O_3, photocatalytic catalyst composite was synthesized by the sol-gel method, because this is a simple method that is easy to implement. During the sintering of the sol-gel, mixed nano-oxide crystals can be formed at a lower temperature in a short time, and the final product can be obtained without the formation of an intermediate phase. The effects of the TiO_2/Eu_2O_3 ratio, sintering temperature and initial phenol concentration on the structure, morphology of TiO_2-Eu_2O_3, as well as the ability of phenol to photocatalytic decomposition in the range of visible light radiation are discussed in this paper.

Materials and Methods

Chemicals

All the reagents and chemicals were of analytical grade and used without further purification. Tetra-n-butyl orthotitanate ($Ti(OC_4H_9)_4$, Merck), Eu_2O_3 (Merck), nitric acid (HNO_3,

DOI: https://doi.org/10.20535/2218-93002722020209587

Merck), alcohol (C_2H_5OH, Merck), acetone (C_3H_6O, Merck), PVA 205 ($M_w \approx 10.000$ g/mol (Japan) were used for synthesising of TiO_2-Eu_2O_3 photocatalytic catalyst composite materials. The original standard phenol solution (1000 ppm, Merck) $NH_4Cl \geq 99.5\%$ (China), Kali hexaxynoferat ≥ 99% (China), 4-aminoantipyrin ≥ 99% (China) were used to develop analytical calibration curve for phenol in water by an optical measurement method according to the ISO 6439: 1990.

Equipment

Devices used for the research:

- the catalysts were obtained by the sol-gel method and sintered in a Naberthem WSC furnace (Germany);
- Optical Absorption Meter Dr 500 (Hach, USA) was used to analyse phenol concentration in accordance with the ISO 6439: 1990 method;
- X-ray analyser EDX-D8 Advance (Bruker, Germany) was used to analyse and evaluate the Ti and Eu content in the catalyst samples;
- the capture device TEM-Tecnai G20 (Shimadzu, Japan) was used to determine the microstructure of the catalyst particles;
- the image of the morphology and structure of the catalyst particle surface was obtained using an SEM Jeol JMS 6490 electron microscope (Edax, Japan);
- the infrared (IR) spectrometer (Bruker-Tensor instrument (Bruker, Germany)) was used to analyse functional groups on the catalyst surface.

Synthesis of photocatalytic TiO_2-Eu_2O_3 nanosized system

The preparation of photocatalytic TiO_2-Eu_2O_3 nanomaterials by the sol-gel method using $Ti(OC_4H_9)_4$ and Eu_2O_3 as a raw material source is presented in Figure 1.

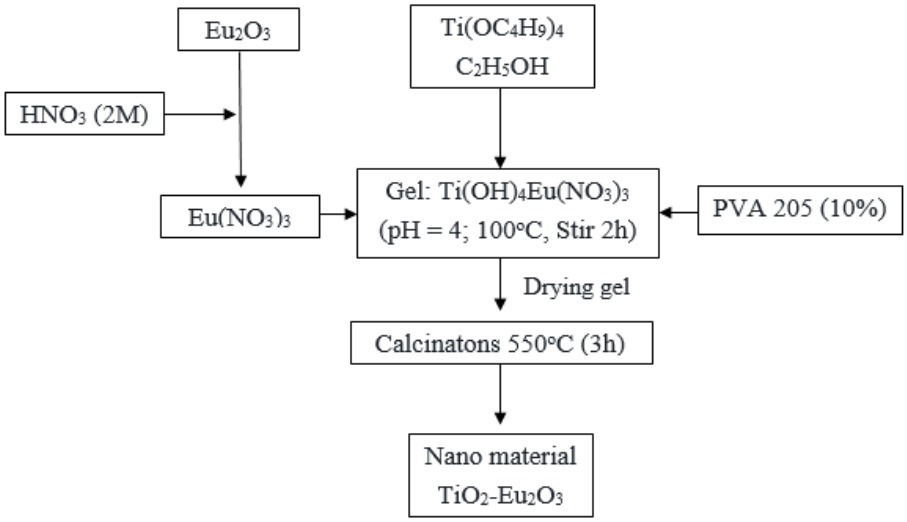

Fig. 1. Scheme of preparation of TiO_2/Eu_2O_3 nanostructured materials by sol-gel method.

First, the oxide Eu_2O_3 was converted to the form $Eu(NO_3)_3$ by the complete dissolution of Eu_2O_3 with an excess of HNO_3 (2M). Excess acid was evaporated by boiling in a water bath at 80°C ÷ 95°C until a wet salt was obtained. Then distilled water was added and the excess acid continued to evaporate. This process was repeated three to five times until pure salt crystals of the $Eu(NO_3)_3$ were obtained, after which it was dried at 80°C under vacuum to constant weight.

Further, the preliminary calculated masses of $Ti(OC_4H_9)_4$; $Eu(NO_3)_3$ and PVA (10%) were introduced into a 250 mL reactor. The PH was adjusted to 4 with HNO_3 (2%), stirring for gelation was carried out at 100°C for 2 hours. The formed gel was dried at 105°C for 8 hours to obtain a dry light pink white powder. Samples of mixed oxide TiO_2-Eu_2O_3 nanomaterial with different TiO_2/Eu_2O_3 ratios were sintered at 500-600°C for 3 hours, then analysed using XRD, SEM, IR and TEM to determine any changes in the crystal structure, phase composition and average size particles of material. To determine the content of the material ingredients, EDX spectra of TiO_2-Eu_2O_3 samples were used.

Activity of TiO_2-Eu_2O_3 system for phenol decomposition

The assessment of the photochemical catalytic activity of the material for the decomposition of phenol in water using a wastewater sample with an expected phenol concentration of 10 ppm was carried out as follows: photochemical catalysts TiO_2/Eu_2O_3 with different TiO_2/Eu_2O_3 ratios (by weight) were weighed with an accuracy of 0.05 ± 0.001 g and was placed in a 500 mL chemical flask, labelled in accordance with the experiments. Then, 100 mL of an already prepared phenol solution with a concentration of 10 ppm was added to each flask. The pH was adjusted to 4 with HCl and NaOH. The flasks were placed in the correct position of the model device. The samples were illuminated with visible or ultraviolet light or shaded with thin aluminium plates with slow stirring during testing.

Then the solutions were transferred to centrifuge tubes and centrifuged at 6000 rpm for 10 minutes. After the completion of the centrifugation process, 1 mL of each solution was placed in a 25 mL volumetric flask with necessary reagents and buffers and left to stabilize for 15 minutes. The absorption spectrum was determined at a wavelength of 510 nm. The calibration curve for phenol is constructed spectroscopically in accordance with ISO 6439:1990.

The percentage of degradation of phenol (η) was calculated according to the initial, C_o (ppm), and the final, C (ppm), concentrations of phenol in the solution following this equation:

$$\eta = 100 \times (C_o - C)/C_o.$$

The influence of the TiO_2 / Eu_2O_3 ratio by weight on the activity of the phenol decomposition catalyst

50 mg of TiO_2/Eu_2O_3 catalyst samples at with various TiO_2/Eu_2O_3 ratios (by weight), namely: 1/0; 5/1; 10/1; 15/1, 20/1, were accurately weighed and placed in conical flasks containing 100 mL phenol

DOI: https://doi.org/10.20535/2218-93002722020209587

10 ppm. The solution was radiated using a tungsten lamp at a distance of 20 cm from the surface of the solution by continuously stirred at 30°C. The reaction time was 2 hours. At the end of the experiment, the concentration of phenol was determined by spectrophotometric measuring the optical density at 510 nm.

The influence of the calcination temperature on the activity of the phenol decomposition catalyst

The catalytic synthesis process was performed as above. The sintering temperature was selected to make the mixture of catalyst materials according to the documents (Wang 2012 and Tachikawa 2007). The sintering temperature was selected at 500°C, 550°C, 600°C, sintering time was 3 hours, and the TiO_2/Eu_2O_3 ratio (by wt) was 15/1.

The assessment of the photocatalytic activity of TiO_2-Eu_2O_3 nanomaterials using different lighing conditions (natural light, no light and UV light)

The photocatalytic activity of TiO_2-Eu_2O_3 materials with a ratio Eu_2O_3/TiO_2 = 1/15 was conducted in UV, visible light and in the absence of light:

- For UV radiation, two 15 W UV lamps were used, located in parallel symmetrically on both sides of the reaction flask;
- For visible light, a 165 W tungsten lamp was used, placed directly above the reaction solution;
- In the absence of light, aluminium foil was used to seal the reaction flask.

The decomposition of phenol was conducted at room temperature at pH = 4, the phenol concentration was 10 ppm. The concentration (optical density) of the remaining phenol in the solution after centrifugation of the reaction mixture samples was measured at 510 nm.

Results and discussion

Characteristics of the photocatalytic activity of TiO_2-Eu_2O_3 nanomaterials

** IR spectra of Eu_2O_3, TiO_2 and TiO_2-Eu_2O_3*

Infrared spectra of Eu_3O_2 TiO_2 and TiO_2-Eu_2O_3 are presented on Figure 2. There are peaks of oscillation for Eu_3O_2 observe at: 1486.83 cm^{-1}, 1384.7 cm^{-1}, 535.45 cm^{-1} and 477.87 cm^{-1}. Infrared spectra of TiO_2 show peaks of oscillation at: 1631.3 cm^{-1}, 979.82 cm^{-1}, 751.38 cm^{-1}. Infrared spectra of TiO_2-Eu_2O_3 show peaks of oscillation for TiO_2 at: 1631.3 cm^{-1}, 979.82 cm^{-1}, 751.38 cm^{-1}. The peaks are at 1486.83 cm^{-1}, 1384.7 cm^{-1}, 535.45 cm^{-1}, 477.87 cm^{-1}, characteristic of oscillation of Eu_2O_3 links with the same width with difference < 50 cm^{-1}: 1487cm^{-1}, 93 cm^{-1}, 1388 cm^{-1}, 509.79 cm^{-1}, 464.07 cm^{-1}. This indicates that the combination of TiO_2 and Eu_2O_3 leads to the formation of a compound, which can be characterized by a change and displacement of the Ti-O and Eu-O bonds.

DOI: https://doi.org/10.20535/2218-93002722020209587

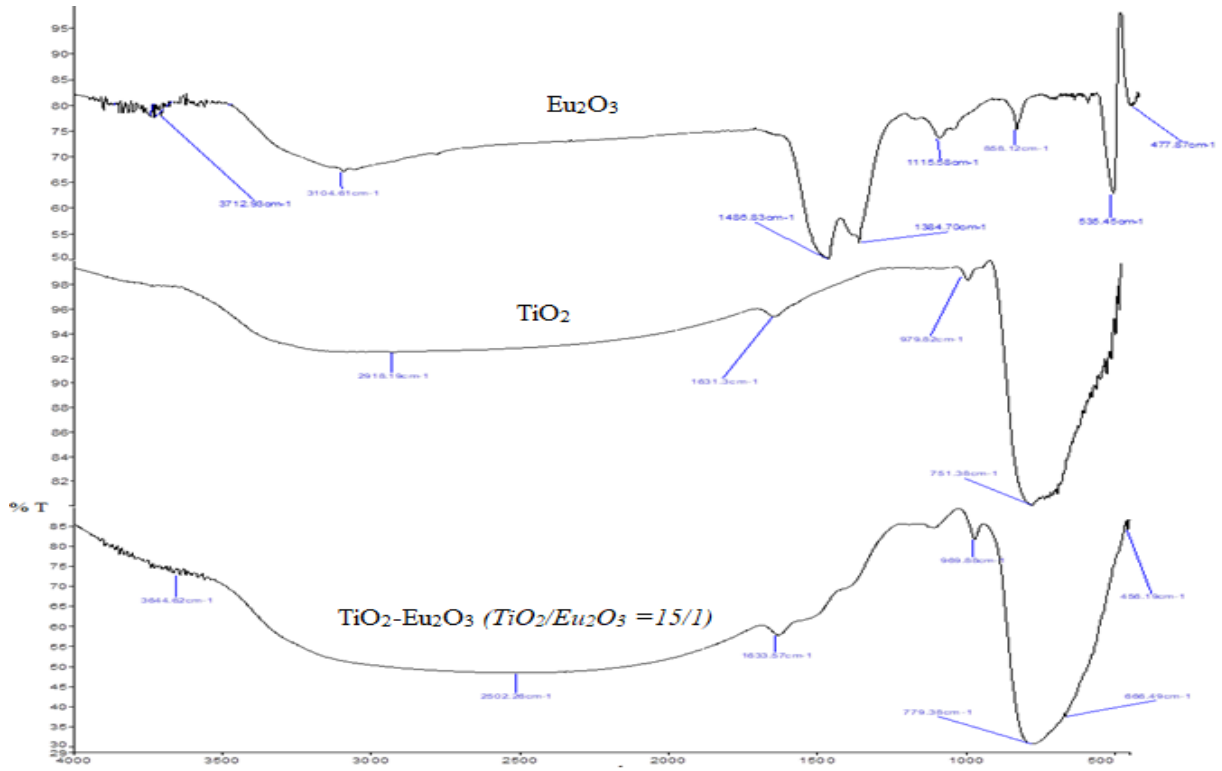

Fig. 2. IR spectra of Eu_2O_3, TiO_2 and TiO_2-Eu_2O_3 (TiO_2/Eu_2O_3=15/1).

** The EDX and X- ray diffraction:*

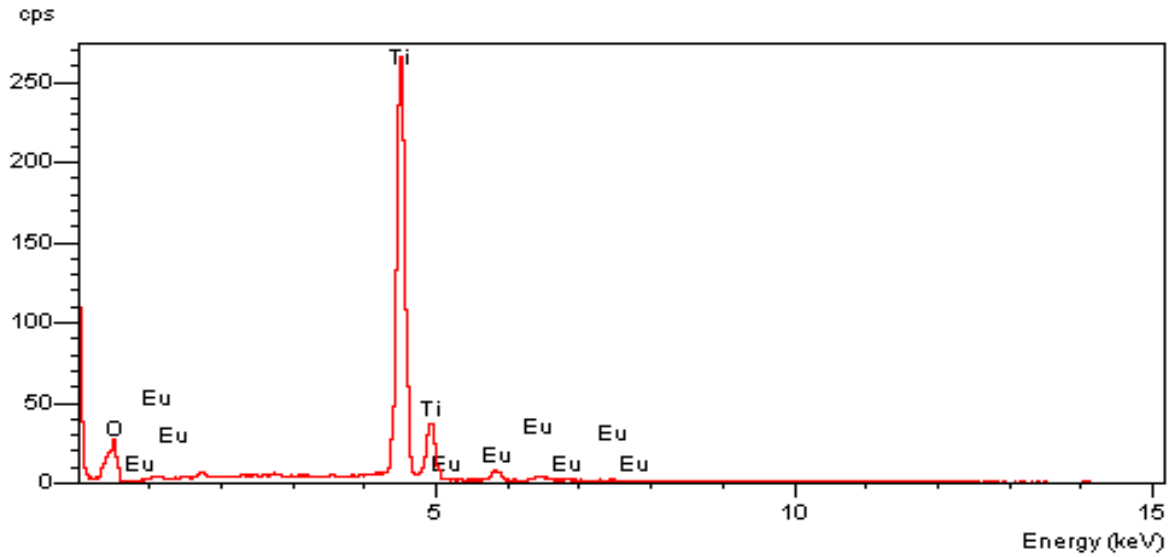

Fig. 3. EDX scattering spectrum of TiO_2-Eu_2O_3.

The presence of oxide TiO_2 and Eu_2O_3 in material samples were found by x-ray energy scattering analysis (Fig. 3). Element Eu were found at 1-2 keV và 5-7 keV, while element Ti appeared at around 4.5-5 keV. Comparison with some of the previous research results (Feng 2007 and Zhang 2008) shows quite a lot in common.

DOI: https://doi.org/10.20535/2218-93002722020209587

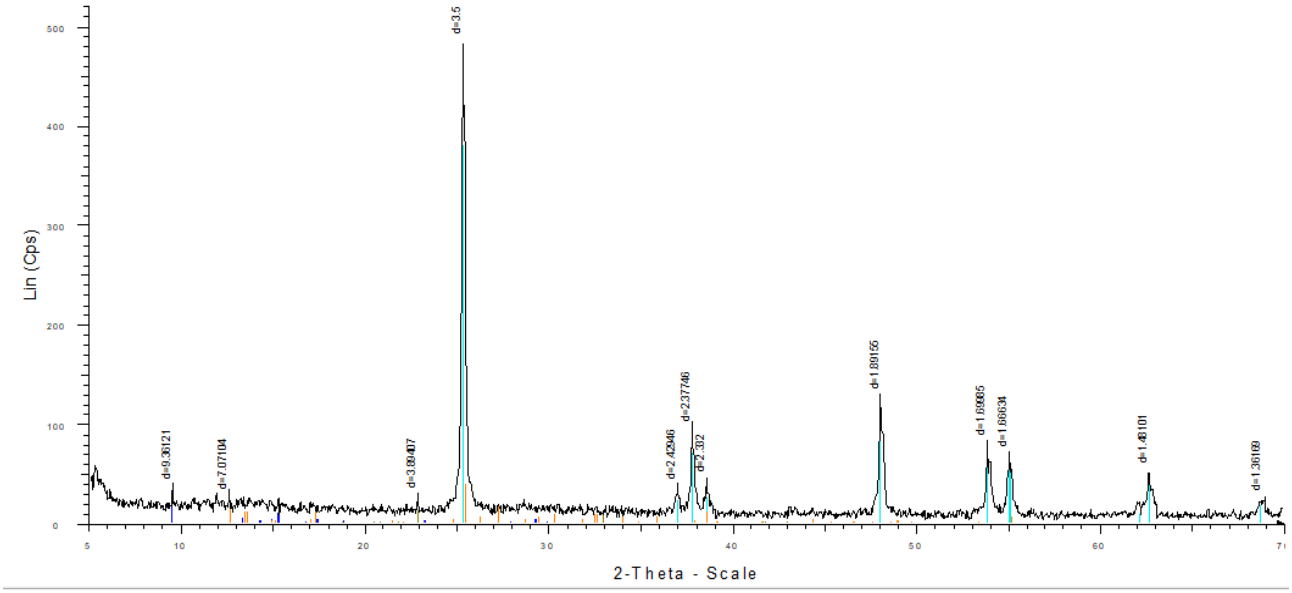

Fig. 4. X-ray diffraction diagram of TiO_2-Eu_2O_3.

The X-ray diffraction pattern of a TiO_2-Eu_2O_3 sample (Fig. 4) with a TiO_2/Eu_2O_3 ratio of 15/1 (by mass) shows peaks at position 2^{θ} = 25.4°, 36.9°, 37.85°, 48.0°, 53.9°, 55.05°, 62.7°, 68.8°, which characterize the TiO_2 structure in the form of anatase. This proves that the phase structure of TiO_2-Eu_2O_3 does not change. In addition, the peak at position 22.9° characterizes the crystal structure of Eu_2O_3.

** SEM and TEM images*

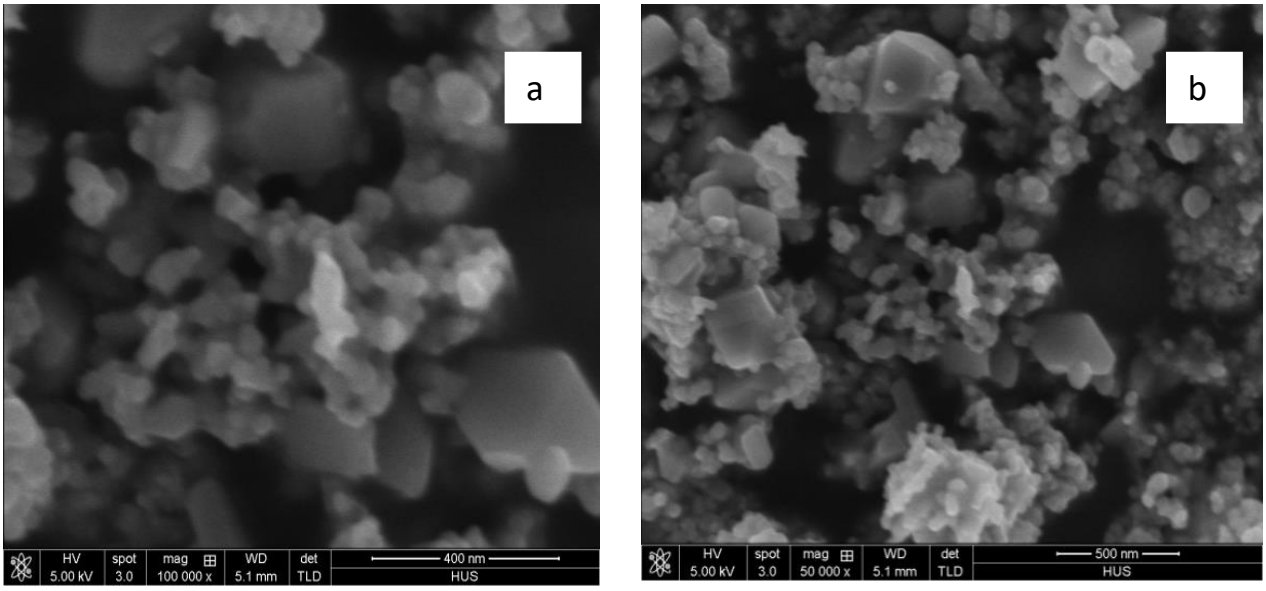

Fig. 5. SEM *(a), (b)* images of TiO_2-Eu_2O_3 nanostructures.

DOI: https://doi.org/10.20535/2218-93002722020209587

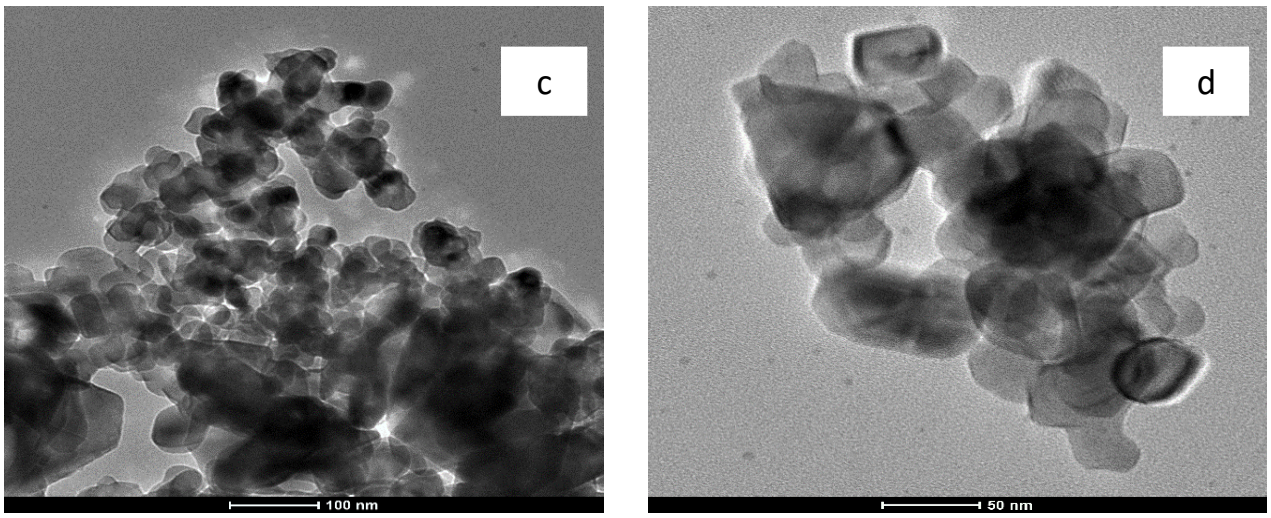

Fig. 5. TEM *(c), (d)* images of TiO_2-Eu_2O_3 nanostructures.

Particle size has a large influence on the catalytic performance of photocatalytic materials. The smaller the particle size, the larger the surface area and the higher the efficiency of electrons received from light.

The results of SEM and TEM of TiO_2-Eu_2O_3 show that the surface structure of the material is spongy, the particles are uniform in size, have a spherical shape, and are evenly distributed along the TiO_2 nanoparticles. The shape and size (20 nm to 50 nm) of TiO_2-Eu_2O_3 nanoparticles are shown in Figure 5 (c) and (d).

***** *UV-Vis spectrum*

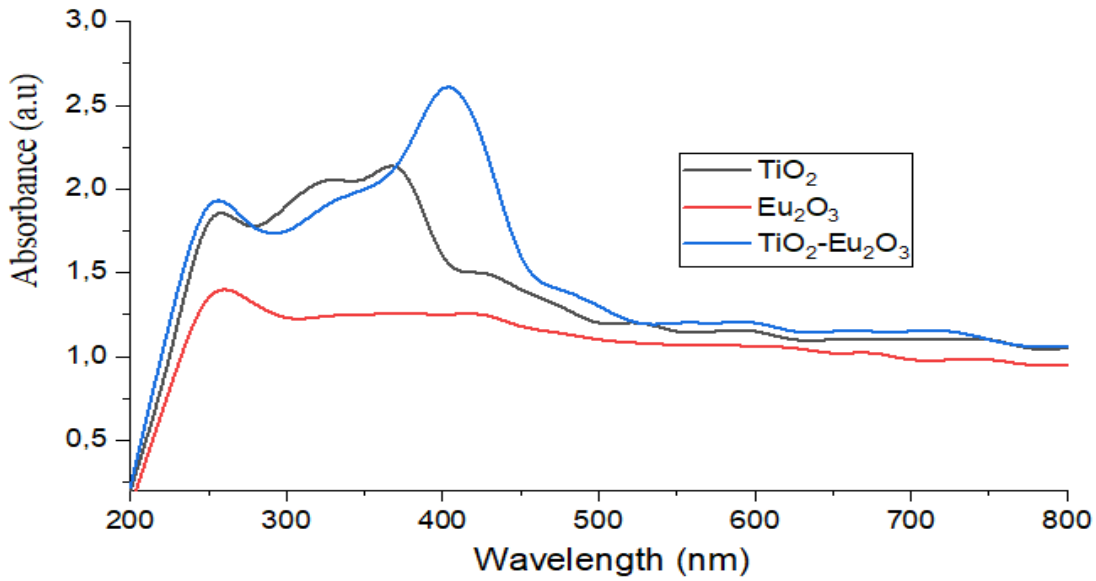

Fig. 6. Light absorption TiO_2; Eu_2O_3 and TiO_2-Eu_2O_3 in the UV/visible region.

DOI: https://doi.org/10.20535/2218-93002722020209587

The results of the light absorption study (Fig. 6) demonstrate that the TiO_2 nanostructure has the maximum absorption at 370 nm, and the Eu_2O_3 nanostructure has the maximum adsorption at 240 nm. In the case of the nanostructure of the TiO_2-Eu_2O_3 mixed oxide, the maximum absorption of the UV-visible spectrum passes into the region of visible light and it is 410-425 nm. This proves that the combination of Eu_2O_3 and TiO_2 leads to a shift in the maximum absorption, widening the TiO_2 bandgap towards visible light.

The influence of TiO_2/Eu_2O_3 ratios on catalytic activity in photocatalytic degradation of aqueous phenol solutions

The following ratios TiO_2/Eu_2O_3 (by weight) for the synthesis of samples were investigated: 1/0; 5/1; 10/1; 15/1 and 20/1. The conditions for the synthesis and study of the catalysts were constant: the temperature of gel sintering was 550°C; the sintering time was 3 hours; the amount of catalyst for catalytic studies was 0.05 g; the volume of a phenol solution with a concentration of 10 ppm was 100 ml; the holding time was from 60 to 150 minutes at natural light for all experiments. The results are presented in Figure 7.

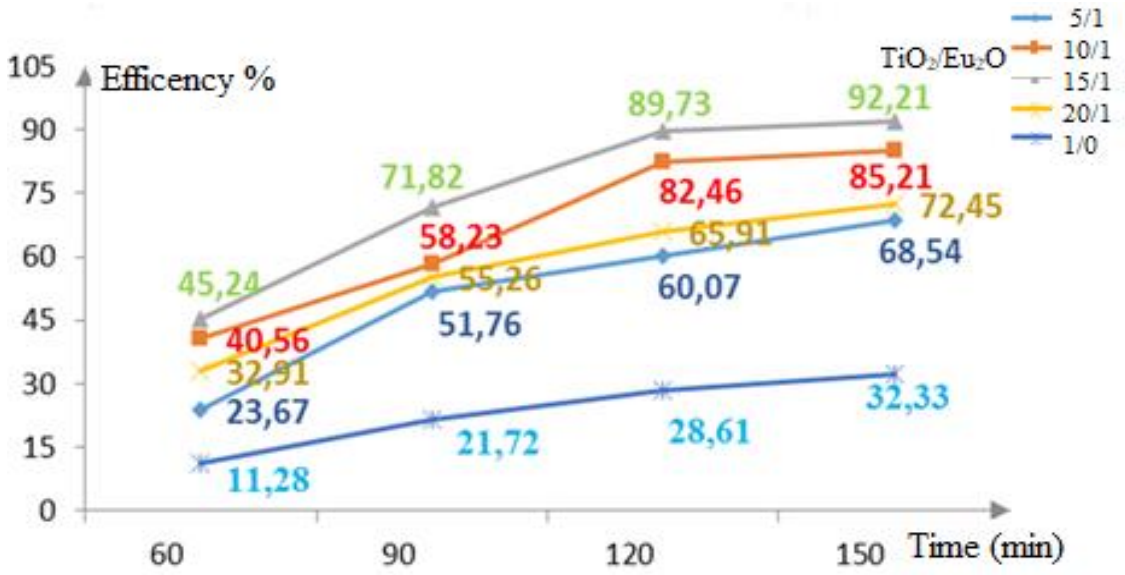

Fig. 7. The influence of the TiO_2/Eu_2O_3 ratio and time on the photodegradation of phenol in aqueous solutions.

TiO_2 nanocatalyst has the lowest efficiency for the phenol photodegradation process. At the same time, for nano catalytic systems TiO_2-Eu_2O_3 with different ratios of TiO_2-Eu_2O_3 (by mass), the efficiency of photodegradation of phenol is much higher, as shown in Figure 7. The highest decomposition efficiency is observed at a TiO_2-Eu_2O_3 ratio of 15/1 and with an increase in the processing time to 120 minutes the efficiency reaches 92.21%.

The influence of catalyst sintering temperature on phenol decomposition

Based on the results of the above experiment and the results of other researchers (Wang 2012 and Tachikawa 2007), the temperature conditions for sintering the catalysts were chosen as follows: 500°C, 550°C, 600°C for 3 hours. The TiO_2/Eu_2O_3 ratio (by weight) was chosen 15/1. The effect of the sintering temperature on the photocatalytic decomposition of phenol is presented in Table 1.

Table 1. The effect of catalyst sintering temperature on phenol degradation

Sintering temperature, °C	500	550	600
Initial phenol concentration C_o, ppm	10	10	10
Phenol concentration after catalysis C_t, ppm	2.31	0.73	1.36
Efficiency, %	76.9	92.7	86.4

The results in Table 1 demonstrate that a catalyst sintering temperature of 550°C provides maximum efficiency of 92.7%. It is known (Wang 2012 and Tachikawa 2007) that at 550°C titanium dioxide is converted into anatase with better photocatalytic activity compared to other crystalline polyforms, which was explained on the basis of the energy band structure of the TiO_2 nanomaterial.

Photocatalytic activity assessment of TiO_2-Eu_2O_3 photocatalyst under different visible light, dark light and UV light

The photocatalytic activity of the TiO_2-Eu_2O_3 catalyst under different lighting conditions is different (Fig. 8). In the absence of light (in the dark), the phenol decomposition efficiency is low, only 38.94% after 150 minutes.

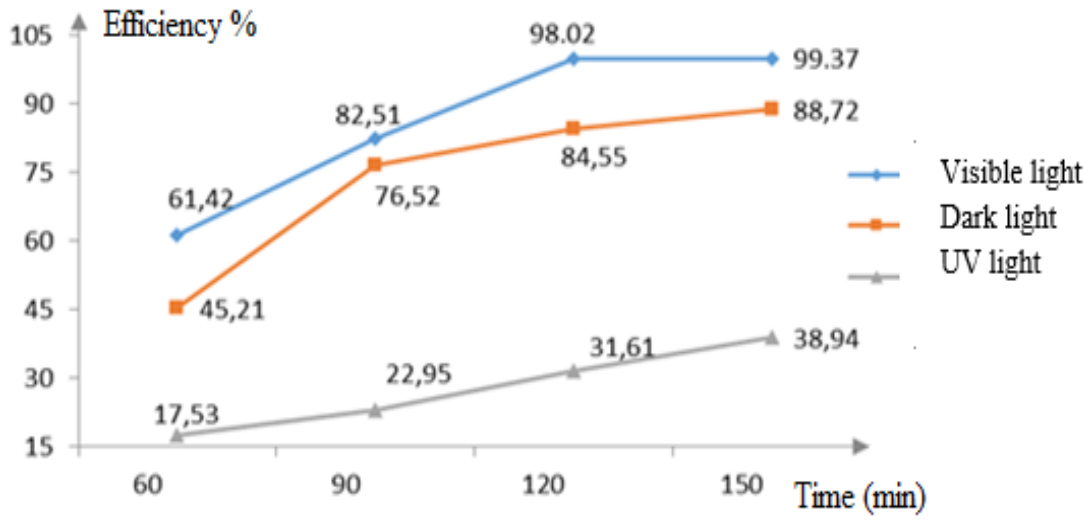

Fig. 8. The influence of different lighting conditions on the process of the phenol photodegradation.

Under UV light and natural light, the photodegradation efficiency of phenol reaches 88.72%, and after 150 minutes of treatment it is 99.37%. It demonstrates the shift of the bandgap of the TiO_2-Eu_2O_3 material towards visible light, which increases the photocatalytic activity of the TiO_2-Eu_2O_3 system.

Conclusions

The results obtained on the preparation of mixed oxide photocatalysts TiO_2-Eu_2O_3 showed that: the catalyst particles have a spherical shape, the average size of the catalyst particles is in the range of 20-50 nm. The synthesized TiO_2-Eu_2O_3 photocatalysts showed good photocatalytic activity of the phenol decomposition in aqueous solution under visible light irradiation. The photocatalytic system was able to decompose 98% phenol (10 ppm starting concentration) in aqueous solutions after 150 minutes. The results of this study will contribute to the improvement of the use of modified TiO_2 photocatalytic materials in environmental cleaning, especially in the decomposition of phenol in aqueous solutions.

Conflict of interests

The authors declare that they have no conflict of interest.

Acknowledgement

This research was funded by the Hanoi University of Natural resources and Environment. The authors would like to thank Rohan Project for instrument usage.

References

Bao, Q.; Hui, K. S; Duh, J. G. “Promoting catalytic ozonation of phenol over graphene through nitrogenation and Co_3O_4 compositing”, *Journal of Environmental Sciences (China)*, **2016**, *vol. 50,* 38-48.

Cheng, W.; Quan, X.; Li, R.; Wu, J.; Zhao, Q. “Ozonation of Phenol Containing Wastewater Using O_3/$Ca(OH)_2$ System in a Micro Bubble Gas-Liquid Reactor, Ozone”, *Science and Engineering*, **2018,** *vol. 40*, no. 3, 173-182.

Cheng, Y.; Zeng, F. S.; Liu, L.; Zhang, L.Q. “Preparation and luminescence performance of rare earth agriculture-used light transformation composites”, *Journal of materials science*, **2008**, *vol 43* (5), 1681-1687.

Crake, A.; Christoforidis, K. C.; Kafizas, A.; Zafeiratos, S.; Petit, C. “CO_2 capture and photocatalytic reduction using 8 Journal of Chemistry bifunctional TiO_2/MOF nanocomposites under UV–vis irradiation,” *Applied Catalysis B: Environmental*, **2017**, *vol. 210*, 131–140.

Diker, H.; et al. "Characterizations and photocatalytic activity comparisons of N-doped ncTiO$_2$ depending on synthetic conditions and structural differences of amine sources", *Energy*, **2011**, *36*, 1243-1254.

Feng, J. "Europium-containing nanoparticle material useful for solar and thermal ennergy conversion and related uses", *WIPO Patent Application WO/2007/130671*, **2007**.

Gami, A. A.; Shukor, M. Y.; Khalil, K. A.; Dahalan, F. A. "Phenol and its toxicity", *Journal of Environmental Microbiology and Toxicology*, **2014**, *vol. 2*, no 1. January 11-24.

Hamza, M. A. A.; Asmaly, A.; Abussaud, B.; Tawfik, A. "Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: From synthesis to enhanced removal of phenol", *Journal of Saudi Chemical Society*, **2015,** *Volume 19*.

Hu, H.; Xiao,W. J.; Yuan, J.; Shi, J. W.; Chen, M. X.; ShangGuan, W. F. "High photocatalytic activity and stability for decomposition of gaseous acetaldehyde on TiO$_2$/Al$_2$O$_3$ composite films coated on foam nickel substrates by sol-gel processes", *Journal of Sol-Gel Science and Technology*, **2008**, *45* (1) 1-8.

Kamegawa, T.; Ishiguro,Y.; Kido, R.; Yamashita, H. "Design of composite photocatalyst of TiO$_2$ and Y-zeolite for degradation of 2-propanol in the gas phase under UV and visible light irradiation," *Molecules*, **2014**, *vol. 19*, no. 10, 16477–16488.

Kebede, M. A.; Varner, M. E.; Scharko, N. K.; Gerber, R. B.; Raff, J. D. "Photooxidation of ammonia on TiO$_2$ as a source of NO and NO$_2$ under atmospheric conditions," *Journal of the American Chemical Society*, **2013**, *vol. 135*, no. 23, 8606–8615.

Lachheb, H.; Ahmed,O.; Houas, A.; Nogier, J. P. "Photocatalytic activity of TiO$_2$–SBA-15 under UV and visible light," *Journal of Photochemistry and Photobiology A: Chemistry*, **2011**, *vol. 226*, no. 1, 1–8.

Lee, S. Y.; Park, S. J. "TiO$_2$ photocatalyst for water treatment applications," *Journal of Industrial and Engineering Chemistry*, **2013**, *vol. 19*, no. 6, 1761–1769.

Liang, B.; Zhu, M. X. "Synthesis and Photoluminescence of New Europium Complex Eu(DBM)$_3$(DPPZ) with Dipyridophenazine Ligand", *Chinese Chemical Letters*, **2003**, *Vol 14* (1), 43-46.

Lu, D.; Ouyang, S.; Xu, H.; Li, D.; Zhang, X.; Li, Y. "Designing Au surface-modified nanoporous-single-crystalline SrTiO$_3$ to optimize diffusion of surface plasmon resonanceinduce photoelectron toward enhanced visible-light photoactivity," *ACS Applied Material and Interfaces*, **2016**, *vol. 8*, no. 14, 9506–9513.

Lu, L. S.; Pei. "A study on phenol migration by coupling the liquid membrane in the ionic liquid" *International Journal of Hydrogen Energy*, **2016**, *vol. 41* (35), 15.

Shipeng, W.; Xiaoping, Z. "Fluorescence and Judd-Ofelt analysis of rare earth complexes with maleic anhydride and acrylic acid", *Journal of rare earths*, **2008**, *vol 26* (6), 787-791.

Son,.S.; Hwang, S. H.; Kim, C.; Yun, J. Y.; Jang, J. "Designed synthesis of SiO_2/TiO_2 core/shell structure as light scattering material for highly efficient dye-sensitized solar cells," *ACS Applied Materials and Interfaces*, **2013**, *vol. 5*, no. 11, 4815–4820.

Tachikawa, T.; Fujitsuka, M.; Majima, T. "Mechanistic insight into the TiO_2 photocatalytic reactions: design of new photocatalysts", *The Journal of Physical Chemistry*, **2007**, *C 111* (14) 5259-5275.

Tasic, Z.; Gupta, V. K.; Antonijevic, M. M. "The mechanism and kinetics of degradation of phenolics in wastewaters using electrochemical oxidation", *International Journal of Electrochemical Science*, **2014**, *vol. 9*, no. 7, 3473–3490.

Teng, Z.; Su, X.; Chen, G.; Tian,C.; Li, H.; Ai, L. "Superparamagnetic high-magnetization composite microspheres with $Fe_3O_4@SiO_2$ core and highly crystallized mesoporous TiO_2 shell," Colloid and Surface A: *Physicochemical Engineering Aspects*, **2012**, *vol. 402*, 60–65.

Wang, B.; Xiong, X.; Ren, H.; Huang, Z. "Preparation of MgO nanocrystals and catalytic mechanism on phenol ozonation", *RSC Advances*, **2017**, *vol. 7*, no. 69, 43464–43473.

Wang, M. C.; et al. "Effects of annealing temperature on the photocatalytic activity of N-doped TiO_2 thin films", *Ceramics International*, **2012,** *38* (1) 195-200.

Wu, D.; et al. "Low-temperature synthesis of N-TiO_2 sol and characterization of N-TiO_2 coating on cotton fabrics", *Surface & Coatings Technology*, **2012**, *206*, 3196-3200.

Xu, L.; Steinmiller, E. M. P.; Skrabalak, S. E. "Achieving synergy with a potential photocatalytic Z-scheme: synthesis and evaluation of nitrogen-doped TiO_2/SnO_2 composites," *Journal of Physical Chemistry C*, **2012**, *vol. 116*, no. 1, 871–877.

Zhang, Z.; Zhang, C.; Fan, M.; Yan, W. "Synthesis and complexation mechanism of europium ion (Eu^{3+}) with spiro[indoline-phenanthrolineoxazine] ", *Dyes and Pigment*s, **2008**, *vol 77* (2), 469-473.

Zhang, Q.; Joo, J. B.; Lu, Z.; et al. "Self-assembly and photocatalysis of mesoporous TiO_2 nanocrystal clusters," *Nano Research*, **2011**, *vol. 4*, no. 1, 103–114.

Zhang, Y.; Wang, T.; Zhou, M.; Wang, Y.; Zhang, Z. "Hydrothermal preparation of Ag-TiO_2 nanostructures with exposed {001}/{101} facets for enhancing visible light photocatalytic activity," *Ceramics International*, **2017**, *vol. 43*, no. 3, 3118–3126.

Received 07.08.2020
Revised 28.09.2020
Accepted 12.10.2020

ФОТОКАТАЛІТИЧНА АКТИВНІСТЬ СИСТЕМ TiO_2-Eu_2O_3 В ПРОЦЕСІ РОЗКЛАДАННЯ ФЕНОЛА У ВОДНИХ РОЗЧИНАХ

[1]Ван Тьєн Май, [1]Ле Тхі Хай Ле*

[1]Департамент навколишнього середовища Ханойський університет природних ресурсів та довкілля, місто Ханой, ZIP 10000, В'єтнам.

[*]Автор для листування: maitienvhcn@gmail.com

Реферат

У роботі досліджено композитний фотокаталітичний матеріал TiO_2-Eu_2O_3, що є синтезованим із тетра-н-бутилортотитанату та рідкоземельного оксиду Eu_2O_3 золь-гель методом з використанням полівінілового спирту. Морфологія, хімічний склад та структура каталізаторів охарактеризовано методами інфрачервоної (ІЧ) спектрометрії, рентгенівської дифракції, скануючої електронної мікроскопії (SEM), а також просвічувальною електронною мікроскопією (TEM) та енергетично дисперсійною рентгенівською (EDX) флуоресцентною спектроскопією. Фотокаталітичну активність TiO_2-Eu_2O_3 вивчали в процесі розкладання фенолу у водному середовищі (початкова концентрація фенолу становила 10 ppm). У роботі розглянуто вплив співвідношення Eu/Ti (а саме: 1/0; 5/1; 10/1; 15/1 та 20/1), температури спікання та початкової концентрації фенолу на структуру, морфологію TiO_2-Eu_2O_3, а також здатність фенолу до фотокаталітичного розкладання в діапазоні випромінювання видимого світла у присутності TiO_2-Eu_2O_3. Найвища ефективність розкладання спостерігається у TiO_2-Eu_2O_3 з співвідношенням активних компонентів 15/1. Актуальність досліджень зумовлено тим, що фенол є дуже токсичною ароматичною сполукою, яка важко розкладається, поширює неприємний запах, впливає на сільськогосподарське виробництво та викликає безліч хвороб, небезпечних для людини навіть при дуже низьких концентраціях. Основним джерелом забруднення природних вод фенолом є промислові стічні води після нафтохімічної очистки, виробництво фенолу, фармацевтика, виробництво вугілля та сталі. Виявлено, що максимальний ступінь розкладання фенолу сягав понад 90% вже через 150 хвилин. Отже, отриманий фотокаталітичний матеріал може бути використаний у галузі водопідготовки, а саме як каталізатор для фотохімічного розкладання у видимому діапазоні світла органічних забруднювачів для очищення текстильних стічних вод, а також для створення бактерицидного ефекту в розчинах.

Ключові слова: фотокаталітична активність; нанокомпозит TiO_2-Eu_2O_3; фенол; водні розчини; діапазон видимого світла.