

Fe₃O₄.CeO₂/SiO₂ oxide nanocomposite as a Fenton-like catalyst for degradation of Congo red

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Abstract— Congo red (CR) was broken down by a heterogeneous Fenton oxidation process using a catalyst that concurrently contained cerium dioxide and ferromagnetic oxide on a silicon dioxide substrate (Fe₃O₄.CeO₂/SiO₂). CeO₂ was prepared from Ce(NO₃)₃.6H₂O with a carrier SiO₂ generated from rice husks; Fe₃O₄ catalyst was prepared from FeCl₃.6H₂O and FeCl₂.4H₂O. X-ray diffraction (XRD), scanning electron microscopy (SEM-EDX), specific surface area (BET), and Fourier transform infrared (FTIR) spectroscopy were used to investigate the catalyst's characteristics. The oxidation of Congo red was used to measure the catalytic activity. Other factors examined included the amount of catalyst, the pH, the H₂O₂ ratio, and the decomposition duration.

I. INTRODUCTION

The textile dyeing industry is one of many traditional industries and has a long development history. According to statistics, the entire textile industry releases an average of about 70 million m³ of wastewater into the environment per year [1]. Typical pollutants are vital dyes, organic substances, or inorganic salts [2]. The Fenton system is considered the most effective in treating dyes, aromatic amines, etc. In particular, the heterogeneous Fenton reaction uses iron catalysts or combined iron catalysts on different support substrates. At the same time, other multivalent metals have been researched and developed strongly in recent years.

Cerium is a typical rare earth metal with a redox cycle between 3⁺ and 4⁺ oxidation states, providing high oxygen storage capacity [3]. Accordingly, Juan Liu et al. [3] reported that Fe₃O₄-CeO₂/activated carbon (AC) can remove ofloxacin and total organic carbon (TOC) with efficiencies of 95% and 54%, respectively. Aniruddha and colleagues [4] synthesized Fe₃O₄-CeO₂ that can help

decompose 89.2% of catechol in the catalytic system. SiO₂ material has long been known for many applications, such as catalytic materials, dielectric materials, gas adsorbents, heavy metal ion adsorbents, and inorganic carriers [5]. SiO₂ in amorphous form has inert properties, high durability, and a large specific surface area > 100 m²/g [6]. With these properties, SiO₂ helps increase the durability of catalytic materials and the efficiency of organic matter treatment, especially colored organic substances.

In this study, a catalyst containing combined Fe₃O₄ and CeO₂ carried on SiO₂ was synthesized and used for the Fenton process to decompose Congo Red dye. Influential factors for Congo red oxidation were studied, such as catalyst amount, H₂O₂ amount, pH, and time.

II. EXPERIMENTS

2.1. Chemical

FeCl₃.6H₂O ≥98.5%, FeCl₂.4H₂O ≥98.5%,
Ce(NO₃)₃.6H₂O ≥98%, HCl 36%, H₂O₂ 30%, HNO₃ 68%,

NH₃ 25%, Congo red (3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid)) received from Macklin (China).

2.2. Preparation of SiO₂ from rice husk

SiO₂ is prepared from rice husk using the sol-gel method according to the following process [7]:

The rice husk is collected, washed with water, and allowed to dry naturally. Rice husks continue to be pretreated with a precisely measured 1 M HCl solution for a scientifically determined 2 hours at a controlled temperature of 105 °C. They are then washed with HCl acid and dried at 105 °C for 4 hours. The calcination process is carried out in an air environment at a scientifically determined temperature of 600 °C to altogether remove organic compounds. The ivory-white solid obtained after calcination is called rice husk ash, a scientifically proven precursor for SiO₂ preparation.

Weigh 10 g of rice husk ash into a 250 ml flask. Add 200 ml of 1 M NaOH solution and heat the mixture to 110 °C for 2 hours. At the end of the reaction, the mixture was allowed to cool to room temperature, the residue was removed, and the remaining liquid was collected. Add 200 ml of distilled water to the rice husk ash extract and stir well under stable temperature conditions of 30 °C. Adjust the solution pH to pH = 6 with 1M HCl to form a gel. The gel was aged 24 hours and washed with water until all Cl⁻ ions were gone. The gel was dried at 60 °C for 24 hours and calcined at 600 °C for 5 hours in an ambient atmosphere. The resulting SiO₂ is white and porous at the end of the process.

2.3. Preparation of Fe₃O₄.CeO₂/SiO₂ catalyst

Fe₃O₄.CeO₂/SiO₂ catalyst is prepared by co-precipitation method as follows:

Dissolve 0.6487g of FeCl₃.6H₂O in 20 mL of distilled water with 2 mL of 36% HCl solution (solution A). Do the same with 0.2386g FeCl₂.4H₂O (solution B). Continue to dissolve 0.6210g of Ce(NO₃)₃.6H₂O and 1 mL of 68% HNO₃ solution in 20 mL of distilled water (solution C).

4g of SiO₂ derived from rice husks was evenly dispersed in 150 mL of distilled water. The prepared solutions A, B, and C were added to the SiO₂ suspension under circular stirring for 30 minutes. Next, 2 M NH₃ solution was added to the suspension until the pH reached ~ 7. The mixture continued to be stirred for 60 minutes and filtered to collect the residue. The solid was washed with distilled water several times (3 to 5 times) and dried at 105 °C for 24 hours. Finally, the solid was calcined at 400 °C for 5 hours and reddish brown Fe₃O₄.CeO₂/SiO₂ was obtained.

2.4. Characterization of materials

The phase structure of the sample was examined by X-ray diffraction (XRD PANalytical X' Pert Powder, Netherlands) using Cu K α radiation. The scanning electron microscope characterized the microstructure and morphology (SEM HITACHI S-4800). The chemical states and compositions of the sample were performed by energy dispersive X-ray spectroscopy with mapping (EDX, HITACHI S-4800). The Brunauer–Emmett–Teller (BET) specific surface area and porosity of the samples were determined by nitrogen adsorption-desorption (NOVATouch LX2, QUANTACHROME, USA) at 77 K. Thermal gravimetric analysis (TGA/DTG NETZSCH STA 409 PC/PG, Germani) investigated the sample's thermodynamic property.

2.5. Congo Red catalytic oxidation

The Fenton oxidation of CR in solution by the Fe₃O₄.CeO₂/SiO₂ catalyst is meticulously conducted at room temperature. The substances are carefully placed into a 250 mL glass beaker containing 100mL of CR solution with a concentration of 100mg/L. The reaction time is precisely measured from the moment of H₂O₂ addition. We thoroughly investigate influential factors, including: Catalyst amount 0.05-0.25 g/100mL; pH 2-10; the volume of H₂O₂ (30%) 0.5-2.5/100 (V/V); Processing time is performed to determine the appropriate conditions for CR decomposition, samples are taken at 5-180 minute intervals then the optical density of the solution is measured on a G10S UV-Vis Spectrophotometer.

Efficiency (H %) of CR decomposition according to the formula:

$$H(\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

C₀ and C_t are the initial and remaining CR concentrations after time t (mg/L), respectively.

III. RESULT AND DISCUSSION

3.1. Characteristics of Cu-BTC

The results of the XRD spectrum of SiO₂ and the catalyst sample are presented in Fig. 1a. The results show that the XRD pattern of SiO₂ has only one diffraction peak with a reasonably broad base at about 23-26 ° and no cristobalite or tridymite crystalline phase peak. Thus, SiO₂ has the structure of amorphous silica material. In addition, on the XRD chart of the catalyst, peaks appear at positions corresponding to the scanning angle 2 θ including 30.2, 35.6, 57.1, and 62.8°, characterizing the existence of Fe₃O₄, similar to the study of Guaqiang Gan and colleagues [8]. Peaks at 28.6, 33.1, 47.5, and 56.4°, which are characteristic of CeO₂, were also obtained on the diffraction pattern and are consistent with the research of Keyan Li and colleagues

[9]. The existence of Fe_3O_4 and CeO_2 on SiO_2 has been confirmed through these results.

The FTIR spectrum (Fig. 1b) shows a peak at 544 cm^{-1} assigned to the stretching vibration of Fe-O in Fe_3O_4 . The appearance of a leading band in the region below 500 cm^{-1} is indicated for the stretching vibrations of Ce-O, similar to the study of D. Channei and colleagues [10]. The presence of SiO_2 is observed through two characteristic bands of the Si-O-Si bond (1086 and 795 cm^{-1}) and of Si-OH (984 cm^{-1}) [11].

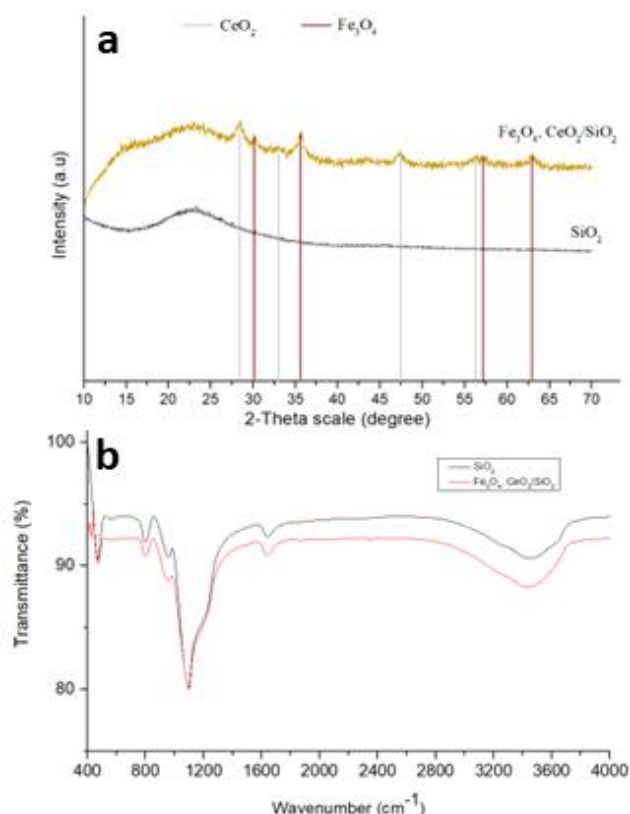


Fig. 1: XRD patterns (a) and FTIR spectrum (b) of SiO_2 and prepared $\text{Fe}_3\text{O}_4.\text{CeO}_2/\text{SiO}_2$

From Fig. 2a,b, $\text{Fe}_3\text{O}_4.\text{CeO}/\text{SiO}_2$ catalyst is spherical particles clustered together, with a uniform particle size $<250\text{ nm}$ and an average size of 150 nm . The EDX diagram with the elemental composition of the $\text{Fe}_3\text{O}_4.\text{CeO}_2/\text{SiO}_2$ catalyst is shown in Figure 2c. The catalyst was mainly silicon, ferromagnetic, and cesium oxides mixture. The Fe content is about 7.48% by mass (corresponding to 2.84% of the element). Meanwhile, the Ce content is about 5.71% by mass (corresponding to 0.86% element). The remaining SiO_2 accounts for 32.88% of the mass (corresponding to 24.33% of the component). Analysis results also show that the material is free of other impurities.

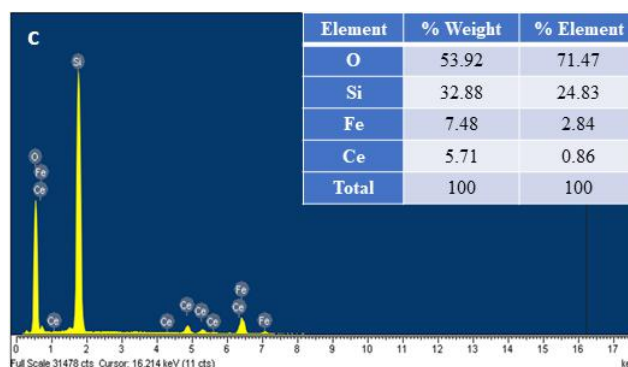
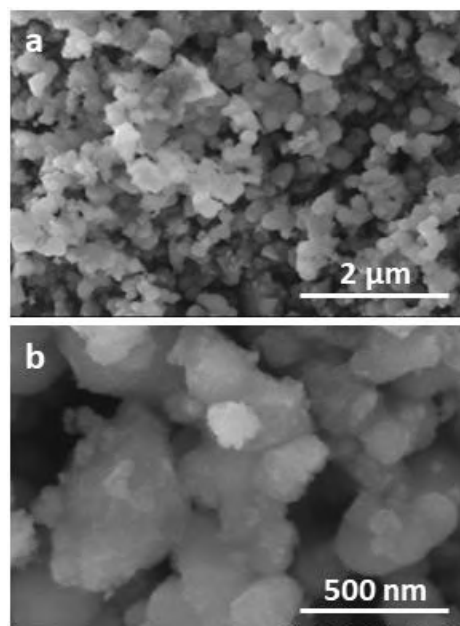


Fig. 2: SEM images (a, b) and EDX spectra (c) of SiO_2 and prepared $\text{Fe}_3\text{O}_4.\text{CeO}_2/\text{SiO}_2$.

Surface characteristics of the SiO_2 substrate (Figure 3a) show that it is a porous material with a specific surface area of $368.615\text{ m}^2/\text{g}$ and a large pore volume from $0.291 - 0.334\text{ cm}^3/\text{g}$. Therefore, adding metal oxides Fe_3O_4 and CeO_2 to SiO_2 does not change the material's pore structure and capillary size (Figure 3b). The pore volume value of the catalyst ranges from $0.276 - 0.317\text{ cm}^3/\text{g}$. However, the specific surface area of the catalyst decreased compared to the SiO_2 support from $368.615\text{ m}^2/\text{g}$ of SiO_2 to $299.68\text{ m}^2/\text{g}$ of the catalyst. The reason may be that Fe_3O_4 and CeO_2 particles, when placed on the SiO_2 substrate, will displace some of the SiO_2 pores, leading to a decrease in the specific surface area of the catalyst. The isothermal adsorption-desorption diagram of SiO_2 and catalyst (Figure 2a) shows that a hysteresis loop appears at the relative pressure range p/p_0 from 0.4 to 1.0 and is characteristic of medium capillary material. The pore sizes of SiO_2 and the catalyst are $3,505-4,208\text{ nm}$ and $4,216 - 4,642\text{ nm}$, respectively.

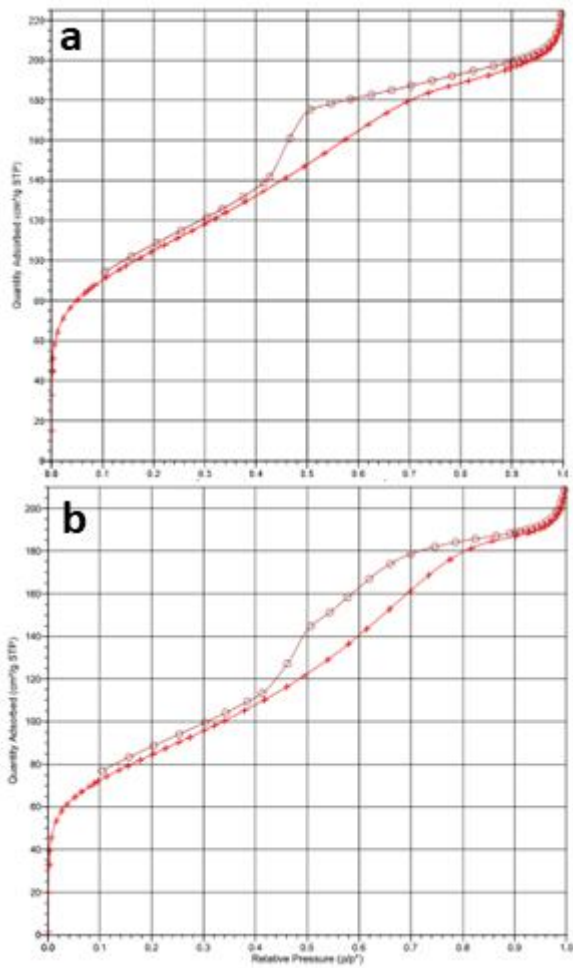


Fig .2: BET diagram of SiO₂ (a) and prepared Fe₃O₄.CeO₂/SiO₂ (b).

3.2. Congo Red catalytic oxidation

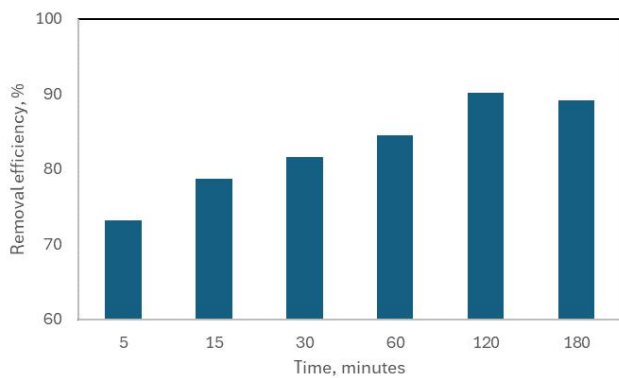


Fig .2: The effect of time on Congo red removal efficiency with Fe₃O₄.CeO₂/SiO₂.

Figure 3 presents the effect of time on Congo red removal efficiency of Fe₃O₄.CeO₂/SiO₂. The process efficiency increased rapidly from about 73.19% after 5 minutes to about 90.22% after 120 minutes of reaction. At this time, the Congo red catalytic oxidation process

occurred almost wholly. Thus, under the conditions and scope of the survey, the appropriate reaction time was 120 minutes.

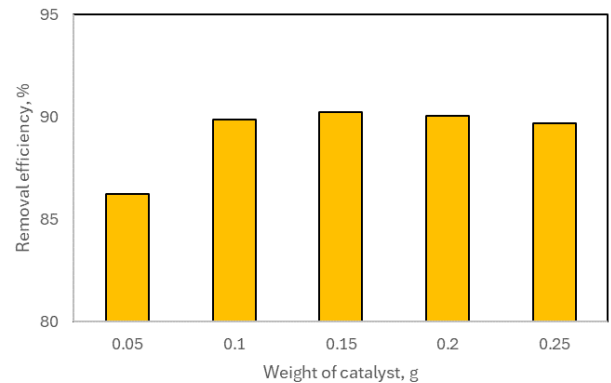


Fig .3: The effect of catalyst's weight on Congo red removal efficiency with Fe₃O₄.CeO₂/SiO₂.

The results of the influence of the amount of Fe₃O₄.CeO₂/SiO₂ catalysts are shown in Figure 3. The results show that increasing the amount of catalyst increases Congo red treatment efficiency, as demonstrated by the practical value. The H% yield increased and reached the highest catalytic ratio at 0.15 g/100 mL, reaching 90.22 %. However, when adding a catalyst, the processing efficiency does not increase. A slight decrease to 90.04 % corresponds to a catalyst amount of 0.2 g/100 mL. The cause may be due to the reaction of *HO and Fe²⁺ produced during the reaction [12]. From there, the most appropriate catalyst content ratio is 0.15 g/100 mL.

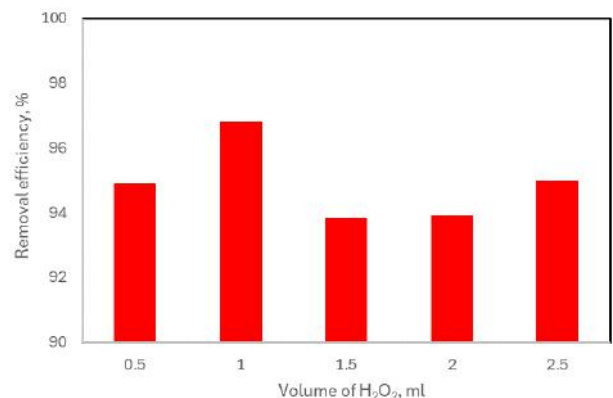
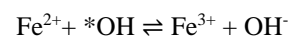
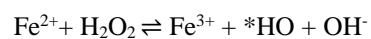
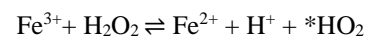
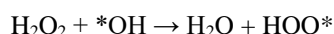


Fig .4: The effect of H₂O₂'s volume on Congo red removal efficiency with Fe₃O₄.CeO₂/SiO₂.

The results of studying the influence of H₂O₂ amount on Congo red oxidation efficiency are shown in Figure 4. The

results show that when the proportion of H_2O_2 (30%) increases, the decomposition efficiency increases. Specifically, when the H_2O_2 ratio is 0.5 mL/100 mL at 120 min, and the amount of catalyst added is 0.15g, the Congo red treatment efficiency reaches about 94.90%. Then, it increased and reached the highest efficiency of 96.79% at the ratio of 1 mL/100 mL. The reason is that an increase in H_2O_2 concentration leads to an increase in $\cdot\text{OH}$ free radicals and increases the efficiency of the Congo red decomposition process [13]. However, when the amount of H_2O_2 is in excess, it will create $\cdot\text{OOH}$ radical according to the reaction:



The oxidation property of $\cdot\text{OOH}$ radical is weaker than that of $\cdot\text{OH}$ radical, leading to a slight decrease in Congo red oxidation efficiency. Thus, the appropriate H_2O_2 ratio is 1 mL/100 mL.

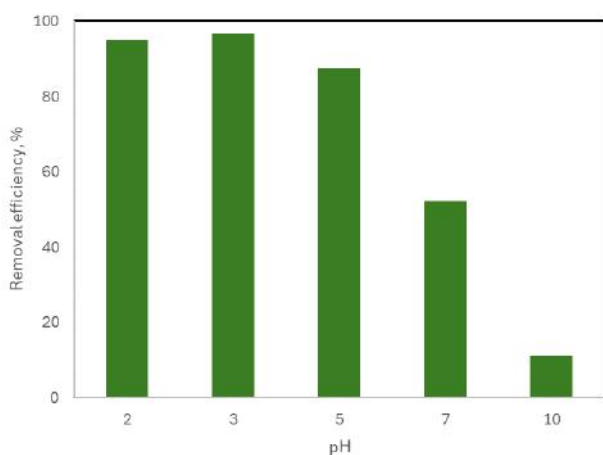


Fig .6: The effect of pH on Congo red removal efficiency with $\text{Fe}_3\text{O}_4.\text{CeO}_2/\text{SiO}_2$.

The results of studying the influence of pH on the Congo red decomposition process are presented in Figure 6. The results show that at pH range 2-3, the Congo red decomposition efficiency has a stable value of 95 ~ 97% and reaches the highest efficiency at pH = 3. However, at pH > 3, Congo red decomposition efficiency drops sharply. In an acidic environment, the catalytic reaction with H_2O_2 creates high oxidation properties, and hydroxyl radicals have the effect of quickly decomposing organic pollutants [4]. Therefore, the pH value chosen is 3.

IV. CONCLUSION

The materials $\text{Fe}_3\text{O}_4.\text{CeO}_2/\text{SiO}_2$ was synthesized by the co-precipitation method from $\text{FeCl}_3.6\text{H}_2\text{O}$, $\text{FeCl}_2.4\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3.6\text{H}_2\text{O}$ with atomic ratio 5%Fe: 4%Ce on support of SiO_2 (from rice husk ash). The specific surface area of the material reaches $299.68 \text{ m}^2/\text{g}$, with an average pore size.

The material was used as a catalyst for the Fenton process to degrade Congo red with appropriate conditions: catalyst amount 0.15g/100ml Congo red solution; pH = 3; volume ratio H_2O_2 30%/100ml Congo red solution = 1mL; Decomposition time was 120 minutes with efficiency reaching 96.79%.

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REFERENCES

- [1] Pham Van Liem, "Prioritize the development of clean technology in Vietnam's textile and dyeing industry", Industry and Trade Magazine, 2020.
- [2] Dang Thi Thom, Nguyen Thanh Duong, Nguyen Chi Thanh, Tran Manh Hai, Do Van Manh, Nguyen Hoai Chau, Trinh Van Tuyen, "Research on the ozonation process to treat Methyl Orange dye in textile wastewater", Conference Proceedings: Basic Research in "Earth and Environmental Sciences" 2019.
- [3] Juan Liu, Xia Wu, Jingjing Liu, Conglu Zhang, Qi Hu, Xiaohong Hou, "Ofloxacin degradation by $\text{Fe}_3\text{O}_4\text{-CeO}_2/\text{AC}$ Fenton-like system: Optimization, kinetics, and degradation pathways", *Molecular Catalysis* 465 (2019) 61–67.
- [4] Aniruddha Gogoi, Madhukar Navgire, Kanak Chandra Sarma, Parikshit Gogoi, " $\text{Fe}_3\text{O}_4\text{-CeO}_2$ metal oxide nanocomposite as a Fenton-Like heterogeneous catalyst for degradation of catechol", *Chemical Engineering Journal* (2016).
- [5] J. F. Chen, H. M. Ding, J. X. Wang, L. Shao, "Preparation and characterization of porous hollow silica nanoparticles for drug delivery application", *Biomaterials*, 25(3), 723-727 (2003).
- [6] Nguyen Thi Ha Chi, Doan Trung Dung, Pham Ngoc Chuc, Duong Thi Lim, Dao Ngoc Nhiem, "Synthesis of nanometer-sized CeO_2 materials on SiO_2 substrate and study of their photocatalytic ability", *Journal of Chemistry*, 2018, 56(1),117-121.
- [7] Nguyen Manh Ha, Tran Thi Huong & Ninh The Son (2023), "Synthesis of the $\text{MnO}_2\text{-Fe}_3\text{O}_4$ catalyst support on amorphous silica: a new Fenton's reagent in the degradation of the reactive blue-19 in aqueous solution", *Journal of Environmental Science and Health, Part A*, 58:5, 506-514.
- [8] Keyan Li, Yongqin Zhao, Chunshan Song, Xinwen Guo, "Magnetic ordered mesoporous $\text{Fe}_3\text{O}_4/\text{CeO}_2$ composites with synergy of adsorption and Fenton catalysis", *Applied Surface Science* Volume 425, 15 December 2017, Pages 526-534.
- [9] Yang Wang, Haoran Sun, Tong Zhang, Yuhua Shen, Jian Zhang, Jialing Xia; "Synthesis and Property of Multifunctional $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{CeO}_2@/\text{Au}$ Composite Microspheres", *Brief Reports and Reviews* Vol. 7, No. 6 (2012) 1250042.
- [10] D. Channei, B. Inceesungvorn, N. Wetchakun, and S. Phanichphant, "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*, Vol. 14, 7756–7762, 2014.
- [11] Guoqiang Gan, Juan Liu, Zhixi Zhu, Ziran Yang, Conglu Zhang, Xiaohong Hou; “A novel magnetic nanoscaled $\text{Fe}_3\text{O}_4/\text{CeO}_2$ composite prepared by oxidation-precipitation process and its application for degradation of orange G in aqueous solution as Fenton-like heterogeneous catalyst”; *Chemosphere*, 168(2017), 254–263.
- [12] Lejin Xu, Jianlong Wang; “Magnetic Nanoscaled $\text{Fe}_3\text{O}_4/\text{CeO}_2$ Composite as an Efficient Fenton-Like Heterogeneous Catalyst for Degradation of 4-Chlorophenol”; *Environ. Sci. Technol.* 2012, 46, 18, 10145–10153.
- [13] Lejin Xu, Jianlong Wang, “Degradation of 2,4,6-trichlorophenol using magnetic nanoscaled $\text{Fe}_3\text{O}_4/\text{CeO}_2$ composite as a heterogeneous Fenton-like catalyst”, *Separation and Purification Technology* Volume 149, 27 July 2015, Pages 255-264.