Removal of Rhodamine B dye from aqueous solution by heterogeneous UV-Fenton catalytic process

Hoa-Hung Lam, Tuyet-Mai Tran-Thuy, Trung Dang-Bao*

Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam
Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam

Corresponding author’s email address: dbtrung@hcmut.edu.vn

Abstract. In this study, the removal of Rhodamine B at high concentrations (25–100 ppm) from aqueous solution was carried out via the heterogeneous UV-Fenton catalytic process based on Fe$_3$O$_4$ nanoparticles. The removal efficiency of Rhodamine B ($C_0 = 50$ ppm) reached 100% after 4 hours treatment, corresponding to the mineralization efficiency of 70%. In comparison with the conventional Fenton processes, the assistance of UV irradiation boosted the OH$^\bullet$ radical generation and prevented the formation of ionic complexes between Fe$^{3+}$ and Rhodamine B, permitting the catalyst activity improvement. In addition, Fe$_3$O$_4$ nanoparticles could be easily separated by an external magnet and then re-cycled several times with minimal loss of catalyst activity.

1. Introduction

The development of the textile and dyeing industry has posed an urgent problem regarding the treatment of the industrial wastewater. Textile dyeing wastewater contains organic compounds (azo, anthraquinone, indigo dyes, aromatic nitro derivatives, etc.) that are harmful to humans and the environment. Some substances can be converted into carcinogenic components in anaerobic conditions, in particular aromatic amines derived from azo pigments [1]. The treatment of dyes and pigments in wastewater is based on the following typical methods: physicochemical methods (flocculation, adsorption), chemical oxidation (using strong oxidizing agents such as chlorine or Javen water), advanced oxidation (Fenton, ozonation, photo-catalytic and UV-assisted processes), electrochemical methods (electroflocculation, electrochemical oxidation) [2, 3].

Recently, advanced oxidation processes, likely Fenton techniques, based on highly reactive OH$^\bullet$ radicals have been investigated thanks to their outstanding effectiveness and feasibility in large-scale industrial applications [2, 3]. The basis of such processes focuses on the activation of H$_2$O$_2$ by Fe$^{2+}$ ions to form Fe$^{3+}$ ions and a large amount of OH$^\bullet$ radicals. In addition, Fe$^{3+}$ ions can be reduced by the excess of H$_2$O$_2$ to recreate Fe$^{2+}$ ions as well as to produce more free radicals [4]. Besides the advantages (excellent efficiency and fast reaction time), the Fenton processes using homogeneous catalysts have a significant drawback in high Fe(OH)$_3$ sludge generation. To overcome this problem, heterogeneous catalysts have been applied in Fenton processes involving the iron ores such as goethite ($\alpha$-FeOOH), hematite ($\alpha$-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$) and supported-iron (Fe/SiO$_2$, Fe/TiO$_2$, Fe/activated carbon, Fe/zeolite), etc. [5]. In acidic environment, the interaction between Fe$^{3+}$/Fe$^{2+}$...
takes place on solid catalyst surface. For such technique, Fe₃O₄ nanoparticles are evaluated to be highly active because of the following advantages [6]: (i) the presence of Fe²⁺ ions in structure boosts OH⁺ radicals production in the Fenton cycle; (ii) octahedral sites in reverse spinel structure are mostly on the crystal surface, determining the catalytic activity; (iii) magnetic property favors the catalyst separation from reaction solution by an external magnet; (iv) the physico-chemical properties can be controlled by modification of spinel structure with other transition metals and (v) the dissolution rate of magnetite is higher than that of other iron oxides, resulting the more flexible electrons in the spinel structure. In more effective approach, photo-Fenton processes (UV-Fenton) can improve the catalytic efficiency thanks to the interaction of UV irradiation with the Fenton system; therefore, the decomposition rate of organic pollutants via Fenton reaction can be enhanced [7]. In comparison with conventional Fenton processes, UV-Fenton technique gains faster treatments and post-treated water samples with higher mineralization efficiency. In particular, excess H₂O₂ can be easily decomposed under UV irradiation, producing O₂ and H₂O.

In this study, the heterogeneous UV-Fenton process was applied in the removal of Rhodamine B in water, using Fe₃O₄ nanoparticles as catalysts. Rhodamine B (RhB) is a basic dye, mostly used for wool and silk dyeing processes; in addition to cellular staining in biotechnology or food dyeing [8]. RhB is an acute and chronic poison: causes allergy in contact with skin and eyes; causes cough, neck itching, shortness of breath, chest pain through inhalation; induces vomiting from the gastrointestinal tract. If accumulated in human, RhB is harmful to the kidneys, reproductive and nervous systems, even affects the biochemical process of liver cancer cells. In addition, RhB has the risk to disrupt the DNA structure, causing chromosome mutations when introduced into cell culture. Therefore, the removal of RhB in water via a UV-Fenton reaction was studied and then compared with conventional Fenton techniques (homogenous and heterogeneous processes) and oxidation with H₂O₂ in the assistance of UV irradiation.

2. Experimental

2.1. Synthesis and characterization of Fe₃O₄ nanoparticles

FeSO₄·7H₂O (5.56 g) was dissolved in distilled water to obtain the homogeneous solution. NaOH solution (10% w/w) was gradually added to the FeSO₄ solution in 5 minutes; the mixture was then stirred and heated at 100 °C for 1 hour. The solid was obtained using an external magnet and then washed with distilled water until pH 7 and no traces of SO₄²⁻ (checked by BaCl₂). Solid materials were dried at 100 °C for 1 hour and stored in a desiccator.

The crystal composition of Fe₃O₄ nanoparticles was tested by X-ray diffraction method (XRD), measured on D8 BRUCKER ADVANCE diffraction device, with Cu-Kα radiation source (λ = 1.5406 Å), 40 kV voltage and 40 mA power. The iron content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The morphology and size of nanoparticles were observed on JSM 740 scanning electron microscope (SEM).

2.2. Removal of Rhodamine B in aqueous solution by heterogeneous UV-Fenton process

The treatment of RhB in water was carried out in a liquid mixing tank, with a shielding around the tank to ensure a stable irradiation source in the system. The UV lamp was centered in the tank so that the lamp’s radiation was entirely absorbed by the reaction solution. The treatment solution containing RhB in water with various concentrations (25, 50 and 100 mg/L) was adjusted to the appropriate pH. H₂O₂ (73 molar equivalent to RhB) and Fe₃O₄ nanoparticles (0.5 g/L) were added into the mixture and then magnetically stirred during the reaction. The temperature was remained at 28–32 °C with a water-cooled element surrounding the reactor. After each period, a volume of the solution was withdrawn (the catalyst was separated by an external magnet) and diluted. The RhB content in the solution was determined by UV-vis spectroscopy, measured at 553 nm. The concentration of RhB followed the Lambert-Beer’s law with the linearity range of 0.2–6.0 ppm at 553 nm.
The study is the Exo-terra lamp – Reptiglo UVB200, a compact fluorescent lamp with a capacity of 26 W. UV power accounts for about 30–45% of the total radiation of the lamp, of which UVB (290–320 nm) accounts for 10–15% and UVA (320–400 nm) accounts for 25–30%. However, the lampshades are made of ordinary glass; therefore, almost all UVB radiation (λ < 320 nm) was absorbed, only UVA radiation (λ > 320 nm) was applied.

3. Results and Discussion

3.1. Characterization of Fe₃O₄ nanoparticles

The basis of Fe₃O₄ preparation is to perform the precipitation reaction of Fe(OH)₂ from FeSO₄ salt using NaOH solution. After that, the obtained mixture was continuously heated at 100 °C in the presence of O₂ (air) to oxidize Fe(OH)₂ to form Fe₃O₄, described as the reactions below [9].

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \]

\[ 3\text{Fe(OH)}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe(OH)}_3 + 2\text{FeOOH} + \text{H}_2\text{O} \]

\[ \text{Fe(OH)}_3 + 2\text{FeOOH} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \]

The crystal structure of the obtained material was analyzed by X-ray diffraction (XRD), showing the characteristic peaks at 20 positions corresponding to the diffraction on crystal planes of (111), (220), (311), (222), (400), (422), (511) and (440) (Figure 1a). This result was confirmed by the magnetite JCPDS 76-0956 data, evidencing the formation of Fe₃O₄ spinel crystals. The diffraction with broaden peaks proved the presence of small nanoparticles with uniform crystal size. According to the Debye-Scherrer equation, the crystal size was calculated to be 29.1 nm following the diffraction peak (311) at 2θ = 35.86°. Iron content (%Fe = 68.6%, w/w) analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) also exhibited the formation of Fe₃O₄ in the analyzed sample. Besides, the morphology and size of Fe₃O₄ particles were observed by scanning electron microscopy (SEM), confirming the formation of spherical particles with an average diameter of ~50 nm (Figure 1b). However, it should be emphasized that the observation of the nanoparticles surfaces by SEM only allows estimating the size of clusters due to their agglomeration of smaller nanoparticles, in particular magnetic nanoparticles. Therefore, the actual size of the nanoparticles is smaller than that observed on SEM, explaining the size difference estimated from the two methods XRD and SEM.

![Figure 1](image1.png)

Figure 1. (a) XRD pattern and (b) SEM image of Fe₃O₄ nanoparticles.

3.2. Removal of Rhodamine B in aqueous solution by UV-Fenton process using Fe₃O₄ nanoparticles

Before studying the catalytic UV-Fenton process based on Fe₃O₄ nanoparticles, the RhB adsorption of Fe₃O₄ nanoparticles (in the absence of H₂O₂ and UV, Figure 2a) and the RhB oxidation by H₂O₂ (in the absence of Fe₃O₄ and UV, Figure 2b) were examined as the blank tests. Both the results showed that after 120 minutes, the RhB concentrations remained unchanged; in other words, the RhB treatment efficiency of heterogeneous UV-Fenton process (see next section) was not governed by these two processes. In water, RhB exists in three forms and metabolizes following the increase of pH: lactone → RhBH⁺ → RhB⁻ [10]. In the solution with a high pH (pH ≥ 4), RhB mainly exists in the neutral form RhB⁺, interacting with Fe³⁺ to form an ion complex [–Fe(OH)(RhB²⁺)]⁺ [10, 11]. This
causes an increase in the absorbance of the solution, resulting in RhB concentration determined by UV-vis spectroscopy that may be larger than the original concentration. Moreover, the concentration of RhB greater than 100 ppm favors the dimerization to form RH\textsubscript{2} and RH\textsubscript{2}, making the RhB analysis more complicated. In this study, the RhB treatment was performed in the range below 100 ppm and at the low pH.

**Figure 2.** RhB concentration changes (C\textsubscript{0} = 100 ppm) over time under different pH conditions: (a) Fe\textsubscript{2}O\textsubscript{3} 0.5 g/L and (b) H\textsubscript{2}O\textsubscript{2} (73 molar equivalent to RhB).

A comparative study of RhB treatment efficiency in water was performed in three different processes: heterogeneous Fenton, advanced oxidation using H\textsubscript{2}O\textsubscript{2} with the assistance of UV (UV-H\textsubscript{2}O\textsubscript{2}) and heterogeneous Fenton with the assistance of UV irradiation (UV-Fenton) (Figure 3a). In the absence of UV irradiation, the heterogeneous Fenton reaction (using Fe\textsubscript{2}O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}) could not process within the RhB concentration range of the survey. The principle of the Fenton reaction is the mutual-to-stock conversions of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ions under the assistance of H\textsubscript{2}O\textsubscript{2}, to produce OH\textsuperscript{*} radicals. These free radicals can vigorously oxidize organic compounds, a precondition for the decoloring process in water. However, the amount of OH\textsuperscript{*} generated depends on RhB concentration and catalyst nature. With high RhB concentration, the interaction between RhB and Fe\textsuperscript{3+} allows the formation of insoluble complexes, preventing the catalysis of Fe\textsuperscript{3+} species [10, 11]. In fact, the previous studies showed RhB treatment efficiency in water at an initial concentration of 5–10 ppm applying the homogenous Fenton processes [12]. In this study, homogenous Fenton technique (using FeSO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} as a catalytic system) was tested for RhB treatment in water at high concentration (C\textsubscript{0} = 50 ppm): after the first 30 minutes, the treatment efficiency reached 40% and the RhB concentration was almost unchanged over a 30–120 minute period. This result once again confirmed the limitation of Fenton technique (homogenous or heterogeneous reactions) for the treatment of RhB in water at high concentration, due to the formation of ionic complexes between Fe\textsuperscript{3+} and RhB.

In order to improve the RhB treatment in water, in particular at high concentrations, the UV irradiation was applied for the further investigation. Obviously, in the UV-H\textsubscript{2}O\textsubscript{2} process (without Fe\textsubscript{2}O\textsubscript{3}), the formation of OH\textsuperscript{*} radicals from H\textsubscript{2}O\textsubscript{2} under the energy effect of Reptiglo UVB200 lamp (320–700 nm, 26 W power) is a key factor for the decomposition of RhB in water. Unlike conventional Fenton reactions (OH\textsuperscript{*} generation depends on Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ion pairs), the oxidizing agents of organic compounds (OH\textsuperscript{*} radicals) are continuously generated under UV irradiation; therefore, RhB treatment efficiency (∼30% after 180 minutes) was better than that on heterogeneous Fenton process (∼0% after 180 minutes). This result promoted the study of heterogeneous photo-Fenton process (UV-Fenton) to remove RhB in water at high concentrations: the RhB treatment efficiency (C\textsubscript{0} = 50 ppm) reached over 85% after 180 minutes (Figure 3a). The RhB treatment efficiency in water was arranged in the following order: UV-Fenton > UV-H\textsubscript{2}O\textsubscript{2} > heterogeneous Fenton. Besides, UV-Fenton technique was also applied to decompose RhB at different concentrations (C\textsubscript{0} = 20 ppm, 50 ppm and 100 ppm) (Figure 3b), promising an effective protocol in the treatment of organic dyes in water, even at high concentrations. The high efficiency of photo-Fenton process (UV-Fenton) can be explained by
the two factors: (i) continuous UV irradiation provokes the formation of OH$^\cdot$ free radicals and (ii) the decomposition of Fe(III)-RhB complexes under UV [7, 11]. Obviously, in such processes, the OH$^\cdot$ formation rate determines the reaction rate, which is governed by the mutual-to-stock conversions of Fe$^{3+}$/Fe$^{2+}$ ions under the assistance of H$_2$O$_2$ and UV irradiation. Besides, the formation of stable complexes between Fe$^{3+}$ and RhB inhibiting the catalysis of Fe$^{3+}$/Fe$^{2+}$ species (mainly observed in conventional Fenton processes) can be ruled out by applying UV irradiation.

Figure 3. (a) RhB treatment efficiency ($C_0 = 50$ ppm) in water at pH 2, RhB:H$_2$O$_2$ = 1:73, Fe$_3$O$_4$ 0.5 g/L (Fenton and UV-Fenton) and using Reptiglo UVB200 lamp (UV-H$_2$O$_2$ and UV-Fenton); (b) Applying UV-Fenton process in the treatment of RhB in water at different concentrations (100 ppm, 50 ppm and 20 ppm) at pH 2, RhB:H$_2$O$_2$ = 1:73, Fe$_3$O$_4$ 0.5 g/L using Reptiglo UVB200 lamp.

In order to better understand the effect of pH, a comparative study in the removal of RhB in water ($C_0 = 50$ ppm) was conducted at different pH conditions (Figure 4a): at pH 2, the treatment efficiency was much better than those of pH 3 and pH 4, related to the better formation of OH$^\cdot$ radicals. Meanwhile, at pH < 2, UV-Fenton process is unfavorable because that Fe$^{3+}$ mainly exists as Fe(H$_2$O)$_6^{3+}$, very weak absorption of UV irradiation greater than 300 nm. Moreover, a high H$^+$ concentration is favorable for the formation of oxonium ions [H$_3$O$_2$]$^+$, stabilizing peroxide in the system and thus reducing the activity of H$_2$O$_2$ with Fe$^{2+}$. Conversely, if the pH increases (pH $\geq$ 3), the formation of Fe(OH)$_3$ precipitates impedes the radicals formation, resulting in a significant decrease of catalytic activity. Therefore, UV-Fenton treatment of RhB in water should be carried out at pH 2–3.

Taking into account of magnetic property, Fe$_3$O$_4$ nanoparticles could be easily separated from aqueous solution by applying an external magnet. The catalyst after reaction was reused for the subsequent RhB treatments without adding fresh catalysts. In fact, the treatment efficiency of RhB in water ($C_0 = 50$ ppm) was insignificantly changed after 3 runs (Figure 4b).

Figure 4. (a) RhB treatment efficiency ($C_0 = 50$ ppm) in water at different pH conditions, RhB:H$_2$O$_2$ = 1:73, Fe$_3$O$_4$ 0.5 g/L using Reptiglo UVB200 lamp; (b) Recycling Fe$_3$O$_4$ nanoparticles for RhB treatment ($C_0 = 50$ ppm) in water at pH 2, RhB:H$_2$O$_2$ = 1:73, Fe$_3$O$_4$ 0.5 g/L using Reptiglo UVB200 lamp.
In order to evaluate the quality of post-treated wastewater, chemical oxygen demand (COD) and mineralization coefficient (produces simple non-toxic inorganic products such as CO$_2$, H$_2$O) are the most important factors. The different RhB concentrations (25–100 ppm) exhibited the mineralization coefficients above 70% (Table 1). Normally, for the treatment of pigments in wastewater, the decoloring is still a priority; meanwhile mineralization index may need to reach only 50–70% for the subsequent treatment processes such as adsorption, filtration, biological treatment, etc.

**Table 1. COD and mineralization index for RhB treatment by heterogeneous UV-Fenton process.**

| Entry | C$_{(\text{RhB})}$ (ppm) | Time (h) | COD (mg O$_2$/L) | Mineralization index (%) |
|-------|-----------------|---------|-----------------|--------------------------|
|       |                 |         | Before treatment | After treatment          |
| 1     | 25              | 2       | 48.2            | 13.9                     | 71.2                     |
| 2     | 50              | 4       | 94.6            | 27.6                     | 70.8                     |
| 3     | 100             | 6       | 191.2           | 50.6                     | 73.5                     |

4. Conclusions
The high efficiency of RhB treatment in water by Fe$_3$O$_4$-based UV-Fenton process was achieved. In comparison with conventional Fenton methods, heterogeneous UV-Fenton technique not only provided a better organic pigments treatment, but also worked well at high concentrations (RhB initial concentration up to 100 ppm). This result demonstrated the positive impact of UV irradiation in the formation of OH$^+$ radicals (based on the effect of UV and/or in combination with the mutual-to-stock conversions of Fe$^{3+}$/Fe$^{2+}$ ions). Furthermore, UV irradiation assisted to decompose the complexes between Fe$^{3+}$ and RhB (this complex formation inhibits the free radicals generation due to a significant decrease of Fe$^{3+}$ ions, observed in conventional Fenton processes). After treatment, the results of COD and mineralization efficiency (> 70%) of wastewater showed the high conversions of toxic organic compounds into simple minerals such as CO$_2$, H$_2$O. In particular, the catalyst could be reused several times with minimal loss of activity, promising an effective protocol in wastewater treatment.

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References
[1] Puvaneswari N, Muthukrishnan J, Gunasekaran P 2006 Indian J. Exp. Biol. 44 618–626.
[2] Garrido-Cardenas J A, Esteban-Garcia B, Agüera A, Sánchez-Pérez J A, Manzano-Agugliaro F 2020 Int. J. Environ. Res. Public Health 17 170.
[3] Tran-Thuy T M, Lam H H, Dang Q T, Phan T S, Truong-Pham D N, Nguyen V D, Dang-Bao T 2020 Chem. Eng. Trans. 78 385–390.
[4] Liu X, Sang Y, Yin H, Lin A, Guo Z, Liu Z 2018 MOJ Ecol. Environ. Sci. 3 10–15.
[5] Navalon S, Alvaro M, Garcia H 2010 Appl. Catal. B. 99 1–26.
[6] Pouran S R, Raman A A A, Daud W M A W 2014 J. Clean. Prod. 64 24–35.
[7] Bahnemann D W, Robertson P K J 2013 The Handbook of Environmental Chemistry – Environmental Photochemistry Part III vol 35 (Springer).
[8] Nestmann E R, Douglas G R, Matula T I, Grant C E, Kowbel D J 1979 Cancer Res. 39 4412–4417.
[9] Hui C, Shen C, Yang T, Bao L, Tian J, Ding H, Li C, Gao H J 2008 J. Phys. Chem. C. 112 11348–11356.
[10] Arbeloa I L, Ojeda P R 1981 Chem. Phys. Lett. 79 347–350.
[11] Dekkiche B A, Seraghi N, Debbache N, Ghoul I, Sehili T 2018 Int. J. Chem. React. Eng. 17.
[12] Cao Z, Sun L, Cao X, He Y 2011 Adv. Mat. Res. 233–235 737–740.