

Effect of Key Parameters on Heterogeneous Fenton-Like Oxidation of Indigo Carmine Catalyzed by Fe₂V₄O₁₃

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Abstract

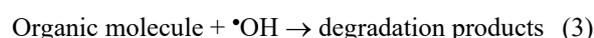
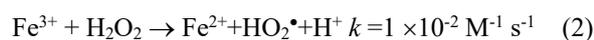
In this study, Fe₂V₄O₁₃ nanoparticle (FeV₂) as a hetero-Fenton catalyst was synthesized using a low-temperature hydrothermal method and characterized by X-ray, SEM, EDX, TEM, and Raman techniques. The effectiveness of the heterogeneous Fenton catalyst of FeV₂ towards the degradation and mineralization of indigo carmine dye (Ind) 0.1 mM was studied by UV-Vis, ICP-MS, and chemical oxygen demand (COD) measurement. The optimal conditions for maximum degradation were pH 4, 66.7 mg/L of Fe₂V₄O₁₃, 0.3 mM of initial H₂O₂ concentration with 0.1 mM of initial Ind concentration, at a reaction temperature of 298K. The effect of temperature on the reaction was also investigated, resulting in the activation energy of the reaction $E_a = 53.5 \text{ kJ mol}^{-1}$. Using the Eyring equation, activated parameters were calculated, indicating the controlling parameter is the activated enthalpy; the step of activated complex formation is an associative and endothermic reaction. It also showed that the FeV₂ catalyst was highly influential in the degradation and mineralization of Ind, with a degradation efficiency of more than 90% and 85% of COD after 10 minutes under optimal operating conditions. Additionally, the FeV₂ catalyst displayed good stability after four cycles, indicating that Fe₂V₄O₁₃ could be a promising catalyst for treating textile dye wastewater containing Ind.

Keywords: Heterogeneous Fenton-like system, hydroxyl radical, indigo carmine, textile dyes, wastewater

1. Introduction

Indigo carmine dye (Ind) is often used to achieve the desirable blue color, especially denim. However, similar to other dyes, the presence of Ind in wastewater is toxic, generates complex sewage color, and has a harmful effect on aquatic ecosystems [1]. There are various treatment methods for the removal of Ind, including chemical degradation, bacterial decomposition, adsorption on different adsorbents, electrochemical decolorization, and employing nanocomposite and activated low-cost charcoal materials [2].

An increasing interest has recently been in developing sustainable and cost-effective methods for treating textile dye wastewater. A promising approach is the use of Fenton's systems, a type of advanced oxidation process (AOPs), to decompose the organic pollutants in the wastewater [3]. In the traditional Fenton's reagent, ferrous ions (Fe²⁺) and hydrogen peroxide (H₂O₂) are used to generate hydroxyl radicals (•OH), which can effectively degrade various organic pollutants due to their high oxidative activity [4]:



However, the homogeneous Fenton system has limitations due to its low pH condition and the impossibility of reusing the catalyst. To address them, heterogeneous Fenton catalysts have been developed by using heterogeneous materials as Fenton catalysts. These catalysts offer several advantages, such as ease of separation, improved stability, and reusability, making it a promising approach for treating wastewater and contaminated water [5].

Fe-based materials have been extensively studied as heterogeneous catalysts for Fenton processes, such as zero-valent iron (ZIV), iron oxides (Fe₂O₃, Fe₃O₄), and oxyhydroxides (α-FeOOH), iron sulfides or oxy oxychloride [6]. These structures contain a closely packed arrangement of O₂⁻ or •OH⁻, which makes them ideal for activating H₂O₂ molecules in the Fenton processes [7]. Moreover, it has been reported that using composite materials that combine iron oxide with other components to form multi-metal compounds can increase the Fenton-like activity of iron oxide in the degradation of organic compounds. This type of catalyst is called a "two-way Fenton-like catalyst" [8]. Among them, vanadium-containing materials exhibit high strength, durability, and minimal leaching when exposed to aqueous solutions, making them ideal Fenton catalysts [9]. Thus, FeV-based materials offer potential as hetero-Fenton-reagent catalysts, in which Fe₂V₄O₁₃ has been of recent interest due to its applications in various fields, such as

a semiconductor for sensing [10] or a catalyst in the photoreduction of hexavalent chromium [11] and in Fenton-like reactions [12] to degrade organic pollutants. However, there is a lack of study on using $\text{Fe}_2\text{V}_4\text{O}_{13}$ as a catalyst in Fenton's processes for the degradation of textile dyes such as Ind.

In this paper, we discuss the efficiency of using a $\text{Fe}_2\text{V}_4\text{O}_{13}$ catalyst in a heterogeneous Fenton-like process for the degradation and mineralization of Ind. We examined various factors that influence the reaction, such as the initial pH of the reaction mixture, the initial concentration of hydrogen peroxide, the amount of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ catalyst, and the reaction temperature was investigated. The results revealed that, under specific reaction conditions, the catalyst efficiently accelerated the degradation of Ind in aqueous solutions. Furthermore, the possibility of regenerating and reusing the catalyst was also investigated, demonstrating its catalytic activity and stability in the heterogeneous Fenton-like catalysis, which overcomes the limitations of homogeneous Fenton systems.

2. Experiment

2.1. Chemicals and Reagents

Ferric nitrate nona-hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.9% w/w) and ammonium metavanadate (NH_4VO_3 , 99.9% w/w), concentrated nitric acid (HNO_3 , 70% w/w) and ammonia solution (NH_3 , 25% w/w) were obtained from Aladdin (China). Indigo carmine (Ind) and hydrogen peroxide solution (H_2O_2 , 30% w/w) were purchased from Merck (Germany). All chemicals were at analytical grade and used as received without further purification. The solutions were prepared from doubly distilled water.

2.2. Catalyst Preparation

The preparation of iron tetrapolyvanadate using a low-temperature hydrothermal process was described in our previous report with modifications [13]. Briefly, 100 mL of a 0.05 M $\text{Fe}(\text{NO}_3)_3$ solution was mixed with 100 mL of a 0.1 M NH_4VO_3 solution at room temperature. Then, 8 mL of 1.0 M HNO_3 was added to the reaction mixture. After that, the reaction temperature was increased to 80 °C in 10 minutes and was stirred at 200 rpm. Next, a 25% NH_3 solution was gradually dropped into the mixture until its pH reached 10. The reaction mixture was kept at 80 °C for 1 hour while continuously stirred. The generated precipitate was separated from the mixture using centrifugation at a rate of 6000 rpm and washed with distilled water to remove residue NH_3 . The solid was filtered and dried at 100 °C for 2 hours, then annealed at 500 °C for 5 hours. The prepared material was denoted as FeV_2 .

2.3. Material Characterization

The synthesized materials were characterized using several techniques: X-ray diffraction (40 kV,

40 mA, $\text{CuK}\alpha$, D8 Advance, Burker, Germany), scanning electron microscopy (SEM) coupled with energy dispersion X-ray spectroscopy (EDX) (JEOL JSM - 7600F, America), Transmission Electron Microscope (TEM) measurements operating at 200 kV was applied using a JEM-2100 (JEOL Japan) instrument and UV-Vis spectrophotometer (DR6000, Hach, Germany).

2.4. Catalytic Activity Determination

The catalytic activity of the materials was evaluated by measuring the decolorization efficiency of Ind via its absorbance at 612 nm using UV-Vis spectrophotometry.

An experiment series was carried out to study the optimal operating conditions, in which only one parameter was changed while the other factors were kept the same. The impact parameters were the initial pH, the catalyst dosage, the H_2O_2 dosage, and the reaction temperature. For optimal conditions, a 30 mL solution of 0.1 mM Ind was added to 2 mg of FeV_2 ; then, the solution pH was adjusted using concentrated HClO_4 and/or NaOH solutions, and the solution was stirred for 10 minutes. Then, the Ind concentration in the mixture was recorded as the initial concentration for the catalytic reaction. Next, 90 μL of 0.10 M hydrogen peroxide was added quickly to the solution. About 1.5 mL of the mixture was extracted every minute to determine the Ind concentration by measuring the solution absorbance at a wavelength of 612 nm. The solution was returned to the reaction solution right after absorbance measurement. Most of the experiments were performed at $T = 298$ K and atmospheric pressure except the series experiments that study the effect of temperature.

To identify the adsorption of Ind by FeV_2 , a test was conducted by recording the absorbance of the mixture every 10 minutes for a total of 30 minutes. The test found that Ind was absorbed by FeV_2 in less than 10 minutes, causing a 7% decrease in quantity. A 10 minute interval was used to ensure adsorption equilibrium.

To detect the leaching of iron and vanadium ions from the FeV_2 catalyst during operation, a kinetic method was employed. The same amount of FeV_2 catalyst was added to 30 mL of the solution with the same initial Ind concentration and pH. After 10 minutes, the catalyst was removed from the mixture, and three μL of 30% H_2O_2 was added. The presence of iron and/or vanadium ions in the Ind solution could promote the Ind oxidation by hydrogen peroxide, leading to the decolorization of Ind. For comparison, the traces of iron and vanadium were determined using the ICP-MS technique (Thermoscientific ICP-MS instrument, model: iCAP RQ) with either the standard mode (for vanadium trace

detection) or the KED (kinetic energy discrimination) mode (for iron trace detection).

An International Standard Method (ISO 6060:1989 standard) was used to determine the chemical oxygen demand (COD) of reaction solutions [14]. For calculating oxygen demand, potassium hydrogen phthalate (PHP) was used as a standard. Before COD measurement, the samples were pre-treated as follows: After the reaction stopped, the catalyst was separated from the solution by centrifugation. To prevent H₂O₂ from interfering with COD recording, extra sodium bisulfite was used to remove unreacted hydrogen peroxide from the solution, whose content was evaluated by iodometric titration [15].

The calculation of degradation efficiency for color removal and the COD removal was as follows:

$$\text{Degradation efficiency (\%)} = \left(\frac{C_o - C}{C_o} \right) \times 100\% \quad (4)$$

where C_o (mM) and C (mM) were the initial and the instant concentration of Ind at a reaction time.

$$\text{COD removal yield (\%)} = \left(\frac{COD_o - COD}{COD_o} \right) \times 100\% \quad (5)$$

where COD_o (mg/L) and COD (mg/L) were the chemical oxygen demand of the reaction solution at the beginning of the reaction and a given time interval.

3. Results and Discussion

3.1. Characterization of Obtained Materials

Fig. 1 shows the X-ray pattern of the prepared FeV₂ oxide with characteristic peaks at 12.5°, 18°, 22.5°, 25°, 27°, and a band in the region of 29° - 33°. These peaks correspond to the XRD profile of the Fe₂V₄O₁₃ (reference from the standard JCPDS No. 39-08930, dash line in Fig. 1) monoclinic phase. A small amount of FeVO₄ (reference from the standard JCPDS No. 38-1372) phase was also detected (Fig.1), and its content was estimated via the peak area ratio, resulting in the value being less than one percent. The result is very similar to that of other studies [10,12].

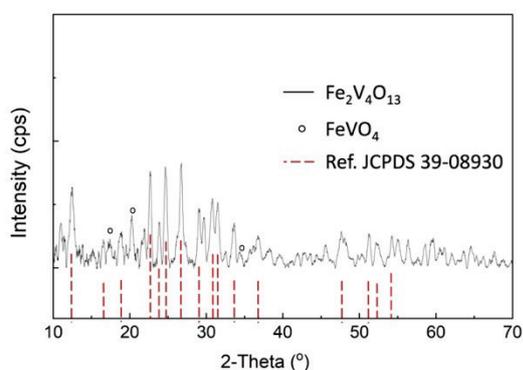


Fig. 1. X-ray pattern diagram of Fe₂V₄O₁₃ with the mark of the three most substantial peaks of the FeVO₄ impurity.

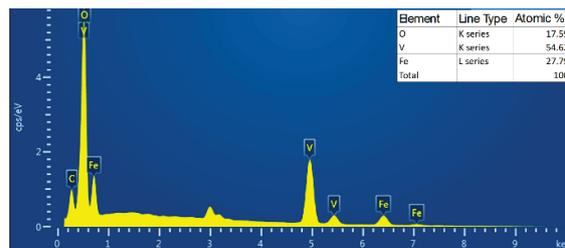


Fig. 2. EDX analysis of a Fe₂V₄O₁₃ bulk sample

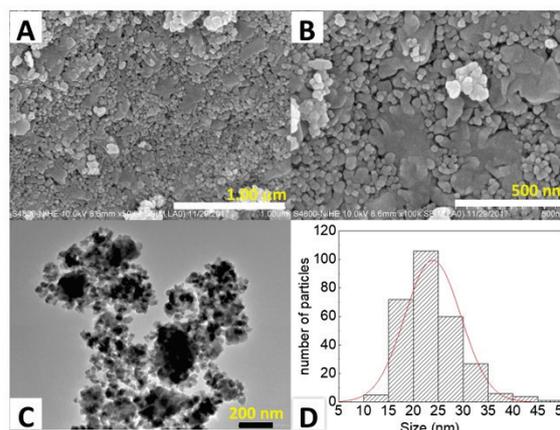


Fig. 3. SEM image of Fe₂V₄O₁₃ at (A) 150k (1 μm) and (B) 50k (300 nm) magnification; (C) TEM image (200 nm) and (D) the particle size distribution

The EDX analysis in Fig. 2 confirmed that the FeV₂ compound obtained had the appropriate stoichiometry. The ratio of Fe to V was approximately 1:2, indicating the existence of Fe₂V₄O₁₃ species.

The morphology of the Fe₂V₄O₁₃ material was characterized using an SEM technique. Its particle size distribution was roughly calculated by ImageJ software (Fig. 3).

The results suggested that the Fe₂V₄O₁₃ material was made of nanoparticles with a spherical shape. There also existed several clusters that distributed interspersed among the nanoparticles on the material surface. These clusters may have formed due to the aggregation of fine particles during the calcination process. It is important to note that the distribution of particle sizes remained consistent throughout our analysis, with an average size of about 25 nm. However, this estimation needed to account for some clusters. These clusters possess a size in the range of 100 - 200 nm.

Fig. 4 exhibits the Raman spectrum of the Fe₂V₄O₁₃ crystals, which shows the vibrational bands of their structure. The band with characteristic peaks at 999, 970, 937, and 907 cm⁻¹ are attributed to the stretching of terminal V-O bonds, whereas the band in the range of 600 - 800 cm⁻¹ is connected with the mixed bridging V-O-V and V-O-Fe stretching vibrations.

Deformation and stretching vibration modes of V-O-V, and Fe-O are related to the 400 -600 cm^{-1} wavenumber range, and the stretching vibration of the Fe-O-Fe bonds is responsible for peaks in the range of 200 - 400 cm^{-1} [16]. Raman spectrum exhibits the insight of bonding types of the material, providing more information on $\text{Fe}_2\text{V}_4\text{O}_{13}$ structure.

3.2. The Fenton Catalytic Activity of $\text{Fe}_2\text{V}_4\text{O}_{13}$

The catalytic activity of FeV_2 material for a Fenton-like process was first tested by its operation in the hydrogen peroxide decomposition (Fig. 5).

The kinetic curves expressed via generated oxygen volumes show that the decomposition occurred much faster in the presence of the FeV_2 oxide. The oxygen volume was 1.1 mL after 12 minutes in the catalyzed reaction, whereas in the non-catalyzed reaction, that value was only 0.13 mL. The results imply that FeV_2 can effectively catalyze the

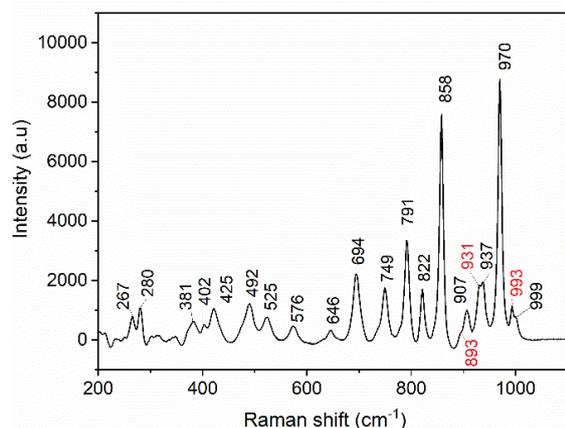


Fig. 4. Raman spectrum of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ material thermally treated at 500 °C in 2 hours.

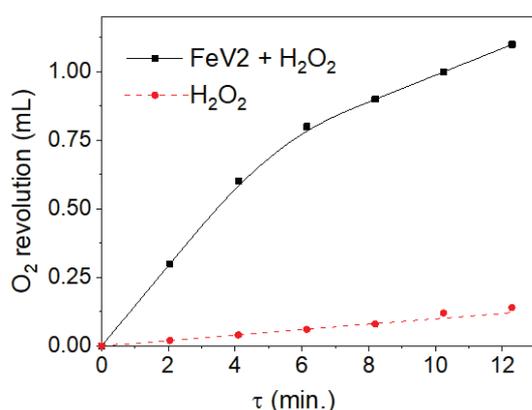


Fig. 5. The curves of oxygen revolution vs. time in catalyzed (solid line) and non-catalyzed (dash-line) reactions of hydrogen peroxide decomposition, $[\text{H}_2\text{O}_2] = 0.2 \text{ mM}$, $m_{\text{FeV}_2} = 0.9 \text{ mg}$, the reaction volume $V_{\text{rxn}} = 30 \text{ mL}$.

decomposition of hydrogen peroxide, a required step for a Fenton process.

The FeV_2 material was also tested for the oxidation of Ind using H_2O_2 (Fig 6). The results showed that no reaction occurred without H_2O_2 (dot line), whereas the reaction was very slow without FeV_2 (dash line) (degradation efficiency < 10 %). However, when FeV_2 was present, the reaction rate was significantly enhanced, resulting in an Ind degradation yield of about 85% within 6 minutes and 95% within 10 minutes. Besides, both the non-catalyzed and catalyzed reactions of hydrogen peroxide with Ind follow the first-order law for Ind concentration.

For further study, the full-range absorbance spectra of the reaction mixture during Ind degradation using a FeV_2 -based Fenton process were recorded at different time intervals, as shown in Fig. 7.

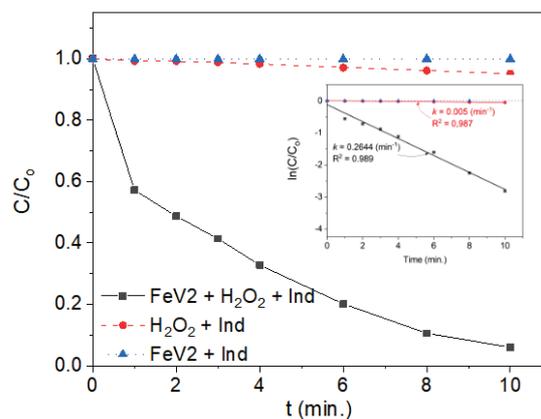


Fig. 6. Kinetic curves of Ind degradation for three mixtures: $\text{FeV}_2 + \text{H}_2\text{O}_2 + \text{Ind}$ (solid line); $\text{H}_2\text{O}_2 + \text{Ind}$ (dash line); and $\text{FeV}_2 + \text{H}_2\text{O}_2$; $[\text{Ind}] = 0.1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 0.2 \text{ mM}$ and $C_{\text{FeV}_2} = 30.0 \text{ mg/L}$.

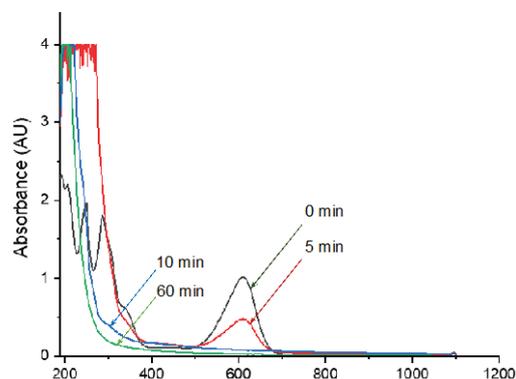


Fig. 7. The absorption spectra of the solution mixture during Ind degradation at 0, 5, 10, and 60 minutes; the reaction conditions: $\text{pH} = 4$; $[\text{H}_2\text{O}_2] = 0.3 \text{ mM}$; $[\text{Ind}] = 0.1 \text{ mM}$; $C_{\text{FeV}_2} = 66.7 \text{ mg/L}$; $T = 298\text{K}$.

It can be observed that after 5 minutes, the typical peak of Ind at 612 nm decreased while the absorption at the band of 200-300 nm sharply increased. It may be interpreted that the deconstruction of Ind generates small molecules that absorb light at around 300 nm. The reduction in the absorbance at the region of 250-300 nm decreased significantly in 10 minutes, showing further oxidation steps during the reaction.

Thus, the Ind molecule may undergo not only degradation but also the mineralization process. This statement was also confirmed by the COD removal measurements (see Fig. 13 bellow).

3.3. Performance Optimal Parameters

To get more details on the catalytic activity of $\text{Fe}_2\text{V}_4\text{O}_{13}$, the catalyst-operating conditions of the Ind degradation were also investigated, including initial pH, initial concentration of hydrogen peroxide, catalyst dosage, initial Ind concentration, and the reaction temperature.

3.3.1. Effect of initial pH of the reaction solution

Among the key parameters, pH is the most important. The influence of initial pH on the oxidation of Ind using H_2O_2 catalyzed by FeV_2 is demonstrated in Fig. 8.

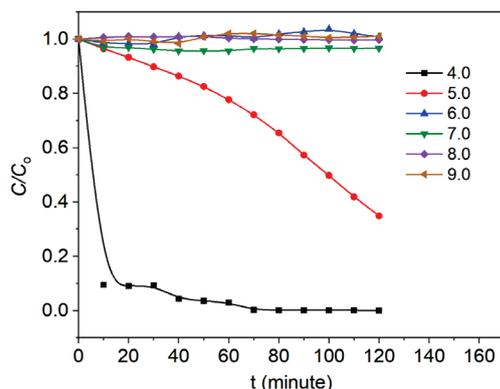


Fig. 8. Effect of pH on the reaction: $[\text{Ind}] = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2] = 0.3 \text{ mM}$; $C_{\text{FeV}_2} = 66.7 \text{ mg/L}$; $T = 298\text{K}$.

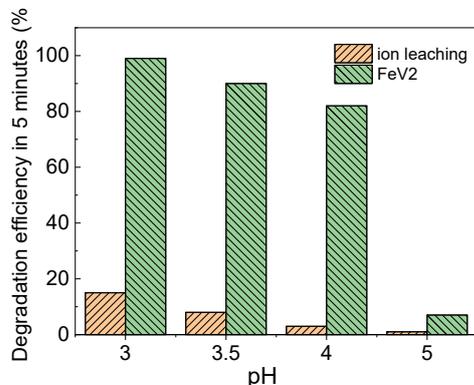


Fig. 9. Detection of ion leachability in comparison to the degradation efficiency of Ind in the presence of FeV_2 ; $[\text{Ind}] = 0.1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 0.3 \text{ mM}$, and $C_{\text{FeV}_2} = 66.7 \text{ mg/L}$.

The results indicated that the pH of the solution highly influenced the efficiency of the Fenton-like process. When the pH was 4, the removal of Ind reached 95% within 10 minutes and up to 99% within 80 minutes. However, the reaction rate dropped significantly as the pH was 5. In the pH range of 6 to 9, the degradation of Ind occurred so slowly that changes in Ind concentration were hardly observed. The influence of pH can be explained by the generation of hydroxyl radical, which is a strong oxidant and is more favorable in acidic conditions. Nonetheless, if the solution pH drops below 4, Fe^{3+} and V^{5+} ions may leach out, which can destroy the catalyst.

To investigate the leaching of ions, both the kinetic method and the ICP-MS technique were applied. In the kinetic method, a series of experiments were carried out under similar conditions to Ind degradation but using solutions that may contain leaching ions as the catalyst in various acidic media (as depicted in Fig. 9). The results indicated that at the solution pH of 4.0 or higher, the concentration of leached ions from the FeV_2 materials was small (in the ion leaching study, the concentration of hydrogen peroxide is 1 mM). Using the ICP-MS technique, we determined the presence of iron and vanadium in the filtrate (at pH of 4.0), in which the concentrations of iron and vanadium ions were 0.062 mg/L (0.45%) and 2.656 mg/L (10%), respectively. The leaching was less than 1% iron and 10% vanadium. These results explained about 5% of the solution's Ind degradation yield at pH = 4. When the initial solution pH was lowered (e.g., 3.5 or 3.0), the amount of leached ions showed a significant increase, which could negatively affect the stability of the catalyst during long-term operation. Therefore, a pH of 4.0 was selected for further experiments to avoid the ions and to get the Ind conversion yield over 90% within 10 minutes.

3.3.2. Effect of the initial H_2O_2 concentration

The initial concentration of hydrogen peroxide plays a crucial role in determining the rate of the oxidation of Ind during the heterogeneous Fenton process with FeV_2 as the catalyst. Increasing the initial H_2O_2 concentration is supposed to result in a higher reaction rate. In this study, the removal of Ind using FeV_2 as a heterogeneous Fenton's catalyst at pH of 4 with different initial concentrations of H_2O_2 was carried out, and the results were demonstrated in Fig.10.

From Fig. 10, the pseudo-first-order rate constants (k_{Ind}) of the Ind decomposition were estimated using the equation (6):

$$\ln \frac{c}{c_0} = -k_{\text{Ind}} \times t \quad (6)$$

in which, t (min) is the time of the reaction. In most of the estimations, the reaction time was 5 minutes. The obtained results are collected in Table 1.

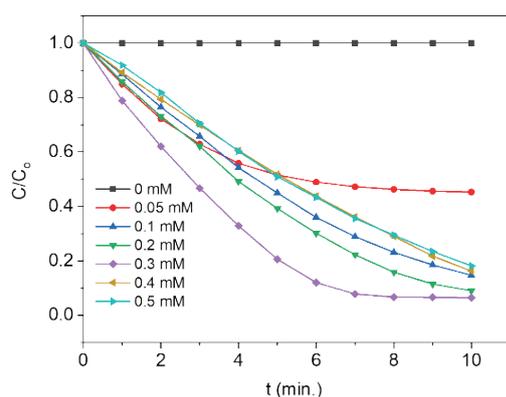


Fig. 10. Effect of the initial concentration of hydrogen peroxide on the reaction: pH = 4; [Ind] = 0.1 mM; $C_{\text{FeV}_2} = 66.7$ mg/L; $T = 298\text{K}$.

Table 1. The pseudo-first-order rate constants at different initial concentrations of hydrogen peroxide and the relevant correlation coefficients

[H ₂ O ₂] (mM)	k_{Ind} (min ⁻¹) in 5 mins	R^2
0.05	0.2018 (in 2 mins.)	0.9946
0.10	0.1656	0.9941
0.20	0.1968	0.9955
0.30	0.2749	0.9964
0.40	0.1397	0.9935
0.50	0.1418	0.9926

When the initial concentration of hydrogen peroxide equals 0.05 mM, the reaction occurred quickly, within 2 minutes, and then almost stopped due to the lack of the oxidation agent compared to the dye compound. Adding hydrogen peroxide (0.1 - 0.3 mM) enhanced the pseudo-first-order rate constant (k_{Ind}) of the Ind destruction from 0.143 to 0.264 min⁻¹, as indicated in Table 1. This is because hydrogen peroxide acts as an effective oxidizing agent in the Fenton process, generating highly reactive hydroxyl radicals ($\bullet\text{OH}$) in the presence of the FeV₂ catalyst. These hydroxyl radicals then react with the Ind molecules, initiating oxidation. As the concentration of hydrogen peroxide increases, the availability of hydroxyl radicals also increases, accelerating the oxidation rate.

However, the reaction rate decreased as the amount of H₂O₂ exceeded. This decrease can be attributed to the interaction between hydroxyl radicals and H₂O₂ molecules, see (4), to be the domain when the concentration of hydrogen peroxide is excessively high. In this step, hydroperoxyl radicals (HO₂ \bullet) were produced, which have lower oxidation activity compared to hydroxyl radicals ($\bullet\text{OH}$) [5]. As a result, the rate of Ind degradation by hydroxyl radicals decreased.



Therefore, controlling and optimizing the initial concentration of hydrogen peroxide is crucial for achieving highly efficient and rapid oxidation of Ind using the heterogeneous Fenton process with Fe₂V₄O₁₃ as the catalyst. The value of 0.3 mM was chosen as the optimal initial H₂O₂ concentration of H₂O₂ for further study.

3.3.3. Effect of catalyst dosage

The impact of the FeV₂ catalyst in removing Ind was analyzed by varying its dosage from 16.7 mg/L to 133.3 mg/L. A control experiment was also performed without the FeV₂ catalyst to verify its role, as depicted in Fig. 11. In the absence of the catalyst, the reaction rate was notably slow. At the same time, the presence of FeV₂ material accelerated the rate of Ind degradation significantly.

The first noticeable observation is that the kinetic curves exhibited the induction periods at the beginning of the reaction in most cases. It is because of the slow reduction rate of the high oxidation state of surface metal species (such as $\equiv\text{Fe}^{3+}$ or $\equiv\text{V}^{5+}$) by hydrogen peroxide. The reduction reaction creates catalytic species that continuously interact with H₂O₂ molecules to form hydroxyl radicals, which accelerates the rate of the degradation reaction.

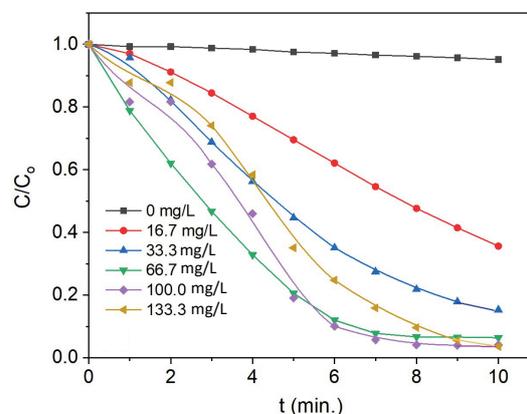
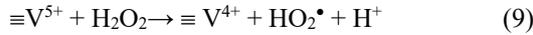
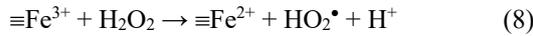


Fig. 11. Effect of the FeV₂ dosage on the reaction: pH = 4; [H₂O₂] = 0.3 mM; [Ind] = 0.1 mM; $T = 298\text{K}$ with different catalyst dosages (16.7, 33.3, 66.7, 100.0 and 133.3 mg/L)

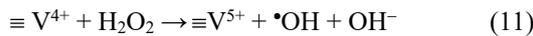
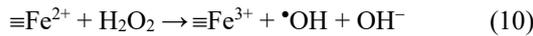
Furthermore, it could be revealed that the reaction rate increased when the catalyst dosage was raised from 16.7 to 66.7 mg/L. This can be attributed to the higher number of active sites available for H₂O₂ decomposition, leading to an increased generation of hydroxyl radicals. However, when the catalyst dosage was further increased to 133.3 mg/L, the reaction rate initially decreased for 5 minutes. This decrease can be explained by an induction period resulting from the slow reduction of Fe³⁺ (or V⁵⁺) by hydrogen peroxide, see (5) and (6). During this period, there is insufficient

catalyst dosage to rapidly reduce Fe³⁺ to Fe²⁺ or (V⁵⁺), limiting the availability of Fe²⁺ and hydroxyl radicals [9, 12].



where \equiv indicates species on the catalyst surface.

After that, the catalyst species (i.e., $\equiv\text{Fe}^{2+}$ or $\equiv\text{V}^{4+}$) became dominant, leading to an acceleration in the reaction rate and reaching a high efficiency of Ind degradation by the 10th minute (10), (11), and (7) [9]:



The induction period is a characteristic feature of the reduction of high oxidative state species by hydrogen peroxide, and further studies are needed to optimize reaction conditions and understand its specifics. Once the induction period is overcome, the reaction proceeds faster due to the enhanced availability of Fe²⁺ (and/or V⁴⁺) and hydroxyl radicals, resulting in improved degradation efficiency.

3.3.4. Effect of temperature

The effect of temperature on Ind degradation using Fe₂V₄O₁₃ as a catalyst in a heterogeneous Fenton process is a crucial aspect to consider in optimizing the reaction conditions. Fig. 12 exhibits the dependence of the Ind degradation rate on temperature.

Increasing the temperature can generally enhance the reaction rate and efficiency of Ind degradation. After calculating using the Arrhenius equation, the apparent activation energy for the reaction was estimated to be 53.5 kJ/mol. This finding indicated that the reaction was moderately sensitive to temperature changes; therefore, it was not controlled by a diffusion process. Furthermore, the presence of induction periods at the beginning of the reaction implies that the decomposition of hydrogen peroxide on the active sites of the FeV₂ surface may be the rate-determined step of the overall reaction.

Activated parameters, including activated enthalpy (ΔH^\ddagger), activated entropy (ΔS^\ddagger), and activated Gibbs free energy (ΔG^\ddagger), could be calculated using Eyring equation as following:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln\left(\frac{k_B}{h}\right) \quad (12)$$

where R is the ideal gas constant, h is the Planck constant, and k_B is the Boltzmann constant, and:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (13)$$

The obtained values of ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger are listed in Table 2.

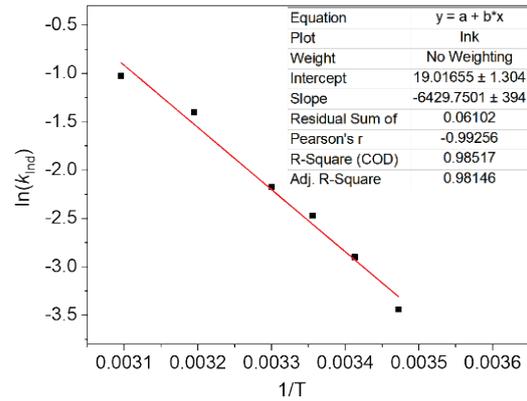


Fig. 12. The pseudo-first-order rate constants of Ind degradation versus $1/T$ and its fitting line; pH = 4; [H₂O₂] = 0.3 mM; [Ind] = 0.1 mM; T = 298K; C_{FeV₂} = 33.3 mg/L

Table 2. Activated parameters calculated from Eyring equation:

T (K)	288	293	298	303	313	323
ΔG^\ddagger (kJ mol ⁻¹)	78.2	78.7	79.2	79.6	80.5	81.5
R^2	0.9835					
ΔH^\ddagger (kJ mol ⁻¹)	50.9					
ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	-95					

The high value of ΔH^\ddagger suggests that activated enthalpy is the controlling factor of the reaction. The negative value of activated entropy indicates that the formation of activated complex is associative, in which hydrogen peroxide molecules interact with the active sites on the surface of the FeV₂ materials. The increase of ΔG^\ddagger value with temperature shows that more energy is required for the reaction, implying its endothermic nature.

3.4. The Catalytic Stability of Fe₂V₄O₁₃

During actual application, the long-term stability of a catalyst is crucial. Four more runs of catalyst samples were performed at the optimal performance condition to evaluate the repeatable use of the catalyst. The decolorization effectiveness of Ind and COD removal of the reaction mixture was measured after 10 minutes. It was noticed that in the fifth run, the catalyst was calcinated at 500 °C before reusing. The results are reported in Fig. 13.

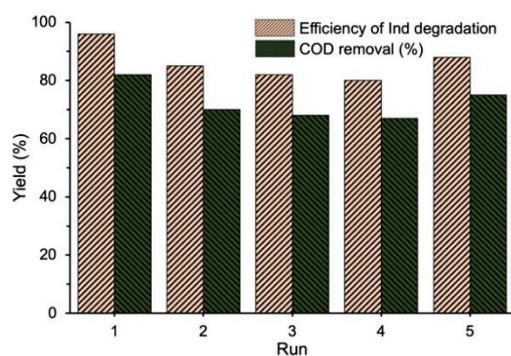


Fig. 13. The efficiency of Ind degradation by H_2O_2 catalyzed by $\text{Fe}_2\text{V}_4\text{O}_{13}$ in five runs. Reaction conditions: $C_{\text{FeV}_2} = 66.7$ mg/L; $[\text{Ind}] = 0.1$ mM; $[\text{H}_2\text{O}_2] = 0.3$ mM; pH 4; $T = 298$ K, $t = 10$ minutes.

In the first run, the efficiency of the Ind color removal was more than 95%, and the COD removal yield was about 80%. After the first run, the activity of the heterogeneous Fenton-like catalyst decreased but still maintained its effectiveness by about 80% for color removal of Ind and about 70% for COD removal in the subsequent three runs. After the first run, the reduction in catalytic activity could be due to the aging process of $\text{Fe}_2\text{V}_4\text{O}_{13}$ to a more stable state that could remove some active sites at defect positions of the catalyst surface [17]. However, the following three runs indicated the reasonable stability of the catalyst. The heating treatment of the catalyst at high temperature (in the 5th run, the catalyst was calcinated at 500 °C before reusing) may recover some active sites, increasing the Ind degradation and COD removal efficiency to 90% and 75%, respectively.

4. Conclusion

Our research focused on the optimal key parameters for the catalytic performance of the $\text{Fe}_2\text{V}_4\text{O}_{13}$ material that was synthesized by the low-temperature hydrothermal method. The most effective catalytic activity was achieved with $C_{\text{FeV}_2} = 66.7$ mg/L, $[\text{Ind}] = 0.1$ mM, $[\text{H}_2\text{O}_2] = 0.3$ mM, and pH = 4 at 298K. Even after four runs, the catalyst maintained its efficiency in decolorizing Ind by up to 80% and removing COD by up to 70%. This material shows great potential in treating wastewater containing persistent dyes like Ind with heterogeneous Fenton-like systems.

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