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Comparative Study of Organics Removal from Refinery Wastewater by Photocatalytic Fenton Reaction Coupled with Visible Light and Ultraviolet Irradiation

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Abstract

The study investigates photocatalytic advanced oxidation processes using iron-doped zeolite catalysts in heterogeneous Fenton reactions to degrade organic contents as chemical oxygen demand. The research revealed that the heterogenous photocatalytic Fenton process was the most successful treatment method under acidic circumstances and generated a greater rate of chemical oxygen demand degradation in a concise amount of radiation time. Compared to the heterogenous Fenton process with ultraviolet irradiation, it increased oxidation and was affected by catalyst load, power of hydrogen pH, hydrogen peroxide amounts, and temperature. The findings showed that the iron-doped zeolite catalyst, pH, and temperature significantly degraded the chemical oxygen demand. The experiment determined that the optimal conditions were obtained at a catalyst load of 0.07 g, pH of 3, with 20% excess of hydrogen peroxide, 40 °C in 2 hours for the ultraviolet/ iron-doped zeolite/hydrogen peroxide system that gave 99.84 % of the removal of the chemical oxygen demand. The heterogeneous photocatalytic Fenton method accompanied the reactions by hydroxyl radical production, which quickly reached its maximal reduction.

1. Introduction

Numerous organic pollutants found repeatedly in industrial wastewater are resistant to natural decomposition and toxic to animals and humans, posing a significant environmental threat [1, 2]. The effluent from the refinery contained high concentrations of oil and grease, chemical oxygen demand (COD), and biological oxygen demand, which deplete the dissolved oxygen from the receiving water's surface, harming the aquatic life there. It also contains high concentrations of phenols, a mixture of benzene, toluene, and xylene (BTX), and naphthenic acids, which are notoriously toxic and present a formidable challenge for the treatment of significant quantities of petroleum refinery wastewater [3–5]. Conventional wastewater treatment systems for petroleum refinery wastewater vary based on the type of crude oil being processed and the discharge source or unit. The highest level of phenols was found in sewage from the neutralization of discarded caustic [6, 7].

Different technologies, particularly advanced oxidation processes (AOPs), have been improved to treat water and wastewater to ensure the water quality necessary for human existence and industrial production [8–14]. Most AOPs are caused by forming radicals, particularly the hydroxyl radical ($^{\bullet}OH$), which is highly reactive and on-selective [8, 15–17]. The Fenton process, one of the AOPs, involves four steps: oxidation, neutralization, coagulation/flocculation, and precipitation. It is founded on the catalytic degradation of hydrogen peroxide (H_2O_2) with Fe^{2+}/Fe^{3+} ions in highly acidic conditions and is defined as a homogenous Fenton process Eq. (1). This reaction generates the $^{\bullet}OH$, a powerful oxidant. Hydroxyl radical is a nonselective radical with a high oxidation potential (2.8 eV) capable of oxidizing organic and inorganic structures [18–20]. Through these benefits, the Fenton process is an advanced oxidation method that can be readily applied to industrial wastewater treatment and can set wastewater discharge limits. However, the classical homogeneous Fenton method faces three significant obstacles: low pH range, the production of large quantities of iron sludge production, and difficulty in catalyst recovery [18, 21]. Such issues have led to the development of heterogeneous Fenton process applications employing catalysts, mainly iron ions bonded to catalyst support [22–26].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \qquad (1)$$

In the heterogeneous Fenton reaction, the catalyst exhibits high recoverability and may be efficiently reused from the reaction medium [26, 27]. The heterogeneous Fenton reaction includes three major stages: chemisorption of reactants, chemical reaction of H_2O_2 with the surface-active iron catalyst species, and Product desorption [24, 28–31]. The heterogeneous Fenton reaction starts with adsorbing the H_2O_2 molecule onto surface catalysts, and then it forms a surface complex with surface-iron species ($Fe^{2+}_{surface}$ or $Fe^{3+}_{surface}$) as in Eq. (2) and (3). The $(Fe^{2+}\text{-}H_2O_2)_{surface}$ undergoes an intramolecular electron transfer to generate surface-bound hydroxyl radicals ($^{\bullet}OH_{surface}$) with strong oxidation capacity to degrade organic contaminants in water (Eq. (4)). The $Fe^{2+}_{surface}$ produced in this process limits the Fenton reaction by consuming H_2O_2 and generates weakly oxidizing surface-bound hydroxyl peroxide radicals ($^{\bullet}OOH_{surface}$) (Eq. (5)). The $^{\bullet}OOH_{surface}$ can further cause $Fe^{2+}_{surface}$ regeneration (Eq.6) [32].

$$Fe^{2+}{}_{Surface} + H_2O_2 \rightarrow \left(Fe^{2+} - H_2O_2\right)_{Surface} \qquad (2)$$

$$Fe^{3+}{}_{Surface} + H_2O_2 \rightarrow \left(Fe^{3+} - H_2O_2\right)_{Surface} \qquad (3)$$

$$\left(Fe^{2+} - H_2O_2\right)_{Surface} \rightarrow Fe^{3+}{}_{Surface} + {}^{\bullet}OH_{Surface} + OH^{-} \qquad (4)$$

$$\left(Fe^{3+} - H_2O_2\right)_{Surface} \rightarrow Fe^{2+}{}_{Surface} + {}^{\bullet}OOH_{Surface} + H^{+} \qquad (5)$$

$$Fe^{3+}{}_{Surface} + {}^{\bullet}OOH_{Surface} \rightarrow Fe^{2+}{}_{Surface} + O_2 + H^{+} \qquad (6)$$

Photocatalytic oxidation processes utilize a catalyst with ultraviolet irradiation (UV) [33]. When ultraviolet rays are used with a catalyst, the catalyst's efficacy increases, and more hydroxyl radicals are produced. In addition, the photolysis of H_2O_2 by UV rays has two molecules of hydroxyl radicals, as shown in Eq.(7-9) [34, 35]. The formed radicals endure an oxidation reaction with the organic compounds in the surrounding environment and degrade the organic matter [36–38]

$$H_2O_2 + h\nu_{(\text{UV energy})} \rightarrow 2{}^{\bullet}OH \qquad (7)$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2^{\bullet} \qquad (8)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (9)$$

The photocatalytic reaction similarly happens in the photo-Fenton process. Reduction of Fe^{3+} to Fe^{2+} caused by photogenerated electrons. H_2O_2 regenerates Fe^{2+} and also effectively prevents e^-/h^+ recombination [39] (Eqs (10)–(16)), promotes the cycle between Fe^{2+}/Fe^{3+} and produces more $^{\bullet}OH$, which improves system oxidation capacity [40]. The investigation of the textural characteristics of the FeX catalyst has also been conducted [27].

$$Catalyst + hv_{\text{ (UV energy)}} \rightarrow h^+ + e \tag{10}$$

$$h^+ + H_2O \rightarrow HO^{\bullet} + H^+ \tag{11}$$

$$h^+ + OH^- \rightarrow HO^{\bullet} \tag{12}$$

$$e^- + O_2 \rightarrow {}^{\bullet}O_2^- \tag{13}$$

$$2H^+ + {}^{\bullet}O_2 + e^- \rightarrow H_2O_2 \tag{14}$$

$$H_2O_2 + e^- \rightarrow HO^{\bullet} + OH^- \tag{15}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{16}$$

The $^{\bullet}OH$ produced via the photo-Fenton reaction and h^+ created by the photocatalytic process oxidizes with organic contaminants present in wastewater, finally mineralizing and decomposing them into CO_2 and H_2O [41–44] (Eq. (17)).

$$^{\bullet}OH/h^+ + \text{organics} \rightarrow H_2O + \text{degradation products} \rightarrow H_2O + CO_2 \tag{17}$$

This study aimed to investigate the performance of heterogenous Fenton oxidation processes using different catalyst loads (CL) of iron-doped zeolite (FeX), pH, H_2O_2 amount, and intensity of light (darkness, natural light, and UV radiation) to remove COD from wastewater. A comparison between heterogeneous Fenton and photo-Fenton investigated the oxidation processes that produced the most significant findings and were examined in deeper detail in this study under different operating conditions.

2. Experimental Work

2.1. Materials

The chemicals used in these experiments were phenol (crystal, Thomas baker, 99%) and hydrogen peroxide (Barcelona, Spain, 50%). Sodium hydroxide (NaOH) (Mumbai, India, 97%), and hydrochloride acid (Sigma Aldrich, USA, 36.5%). Previously prepared and characterized FeX [24, 26] with an average particle size of 75 µm was used as a heterogeneous catalyst.

2.2. Experimental Setup and Procedure

The performance of the Fenton process for treating synthetic wastewater was evaluated in a lab using an artificial aqueous phenol solution to simulate the organic contaminants present in usual wastewater released from refinery units with 500 mg/L of COD. Experiments were carried out utilizing a batch glass reactor at different operating temperatures (25, 40, and 60 °C) under agitation rates (350 rpm, Thermo Fisher Scientific Inc, US) for up to 2 h. In the beginning, the pH of the sample was modified by adding 0.1 N HCl (or 0.1 N NaOH) until the target pH value was attained. At the beginning of each run, various CLs of a FeX were pre-prepared and characterized [24, 26]. The reaction mixture was initiated by adding FeX, which had a particle size smaller than 75 µm and a stoichiometric quantity of H_2O_2. An external jacket was utilized to control the temperature (T) of the reactor. After the end of the experimental procedure, a certain quantity of the reaction mixture was extracted and directly quenched with a few droplets of NaOH to terminate the reaction. The FeX catalyst particles were separated from the treated solution utilizing a membrane filter paper (0.45 µm). The filtered solution was placed in a glass vial, and the COD analyses were directly achieved. All tests have been repeated thrice to increase the reliability of the reported findings. A photoreactor apparatus was utilized in experimental investigations of the photocatalytic oxidation process, as shown in Figure (1). The photoreactor device had UV (365 nm) lamps with 16 W total intensity. The experiments were conducted utilizing a batch glass reactor with three necks, and the lights of the photoreactor device were switched on. The content of COD was recorded by a COD Photometer (Lovibond, MD 200 COD, tube tests, Germany) utilizing COD vials to find the sample COD after treatment and then calculate the maximum removal efficiency. The COD removal was determined by Eq.(18).

$$\text{COD } removal,\% = \frac{COD_o - COD_t}{COD_o} \times 100 \qquad (18)$$

Where COD_o was the initial COD concentration, and COD_t was the concentration of the COD in mg/L at time (t, h).

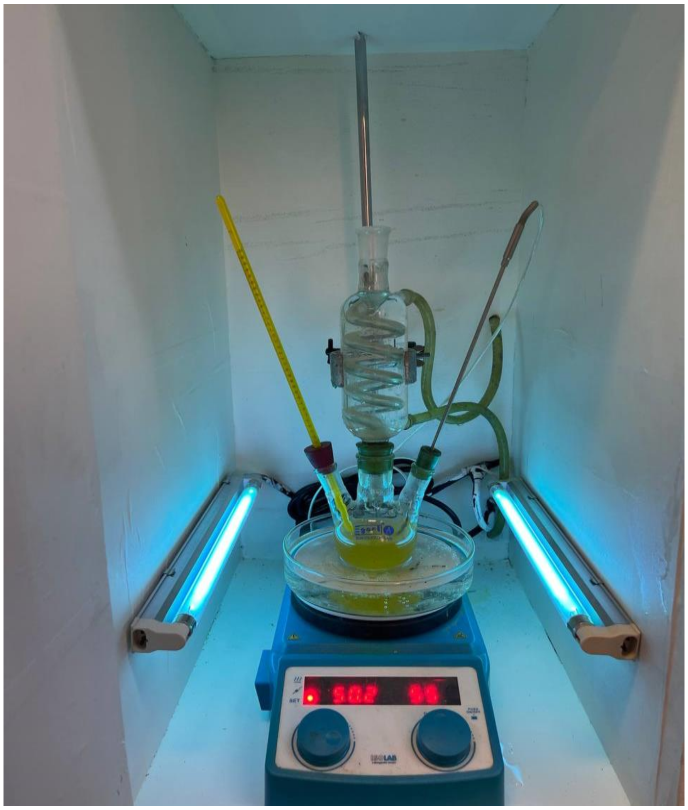

Figure (1). Reactor setup.

3. Results and Discussion

Effect of Catalyst Load on the COD Removal

The effect of CL optimization experiments was conducted at optimum conditions within the range of 0.02–0.12 g on the reaction rate, depicted in Figure (2). At each CL value, the increase in temperature caused a significant increase in COD removal. The CL findings showed that 0.07 g of FeX impacted the highest COD removal efficiency of 88.87% after 2 h of the reaction at 60 °C, as demonstrated in Figure (2). The significant degradation efficiency is attributed to the fact that increasing FeX created more active sites that promoted the formation of hydroxyl radicals due to Eqs. (2) to (6) [20, 45]. Using a higher CL amount, such as 0.12 g, causes coagulation of catalysts [46], thereby decreasing the number of active sites and contact efficacy between the catalyst and H_2O_2. Consequently, based on the test results, the optimal load of the catalyst was 0.07g.

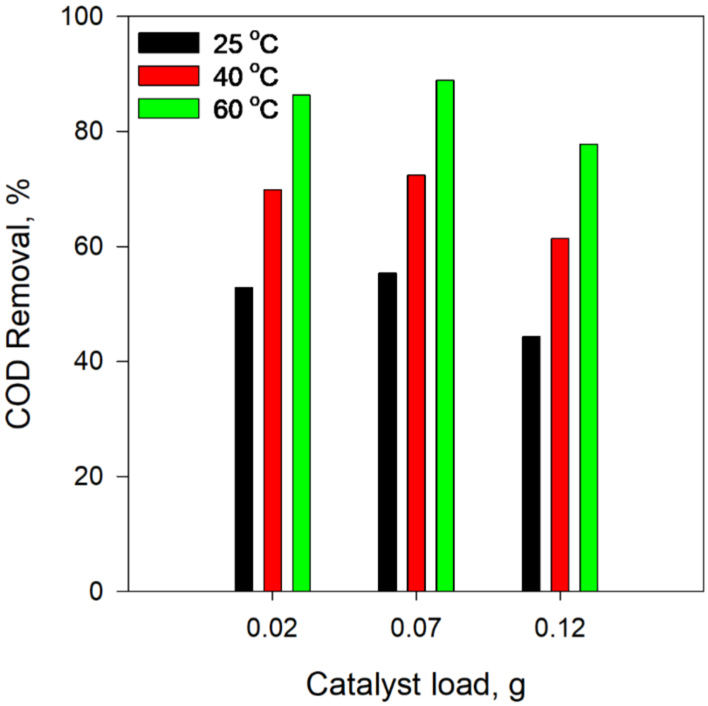

Figure (2). The effect of FeX catalyst load on COD removal after 2 h at 25, 40 and 60 °C.

Effect of pH on the COD removal

The effect of pH on COD removal from wastewater at 0.07g of CL for 2 h was investigated by conducting the COD degradation experiment at three different pH values (3, 5, 7), and the findings were demonstrated in Figure (3). At pH 3 the highest COD removal values were 88.87%, 72.47%, and 55.41% achieved at 60 °C, 40, and 25 °C, respectively. In heterogeneous Fenton processes, the pH has a significant effect on the activity of iron. Iron activity was diminished due to the precipitation of iron ions in conditions of higher pH. In actuality, pH is the principal limitation of the Fenton oxidation process. The creation of the complex species $[Fe(H_2O)_6]^{2+}$, which exhibits a slower reaction rate with H_2O_2 compared to $[Fe(OH)(H_2O)_5]^{+}$, causes a decrease in the production of OH radicals at pH values below 3 [47]. At a higher pH, Fe^{3+} precipitates as $Fe(OH)_3$, resulting in the decomposition of H_2O_2 into O_2 and H_2O [48]

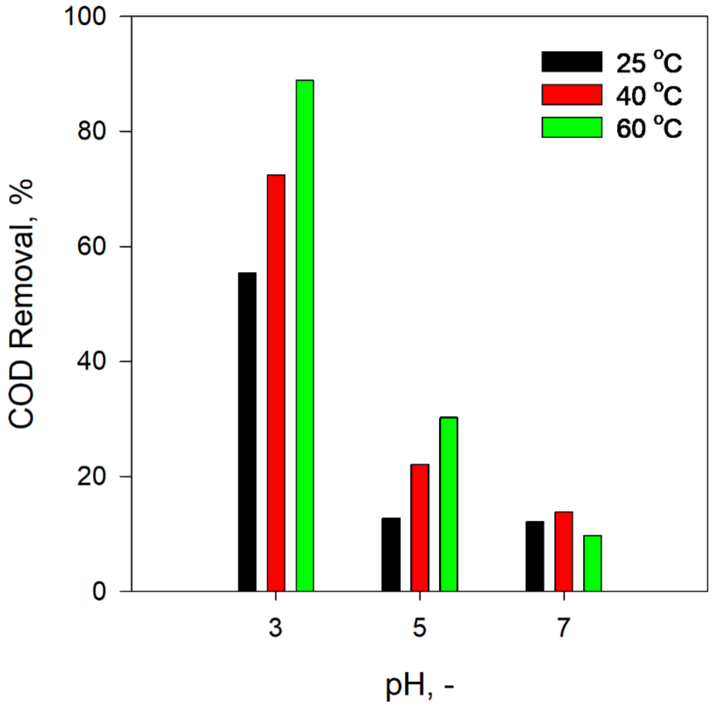

Figure (3). The effect of pH on the COD removal process after 2h with 0.07 g FeX catalyst load at 25, 40, and 60 °C.

Effect of H_2O_2 Amount and Light Type on the COD Removal

The principal oxidative active molecules in Fenton reactions, $^{\bullet}OH^{\cdot}$ are produced by interacting H_2O_2 with the catalyst's surface. Theoretically, 14 mol of H_2O_2 was needed to completely degrade 1 mol of phenol, as shown in Eq. (19).

$$C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \qquad (19)$$

As a result, the doses employed utilized values above the stoichiometric amount for complete mineralization. Hence, 0.17 cm^3 (50 wt.%) of H_2O_2 was required to completely degrade 100 cm^3 of aqueous phenol solution equivalent to 200 mg/L of phenol.

Experiments were conducted to determine the effect of H_2O_2 amounts on removing COD from wastewater by the heterogenous Fenton process when the H_2O_2 amount was varied between 1-2. Table (1) summarized the impact of the H_2O_2/phenol ratios on COD removal at different light intensities (darkness, visible light, and UV light). According to Eqs. (2) to (6), increasing the concentration of H_2O_2 should increase the rate of COD oxidation as $^{\bullet}OH^{\cdot}$ production increases. An additional enhancement in COD removal was observed by employing UV irradiation as opposed to darkness and natural light. The utilization of UV light demonstrated a beneficial impact on the rate of decomposition of H_2O_2 and the reduction of Fe^{3+} to Fe^{2+}, thereby significantly expediting the generation of $^{\bullet}OH$ as illustrated in Eqs. (10) to (16). The addition of a 20% excess of H_2O_2 combined with the FeX catalyst and UV irradiation for 2 h led to the total removal of COD in synthetic wastewater.

However, according to reaction Eq. (20), adding too much H_2O_2 negatively influences the oxidation rate. In other words, a competitive reaction between H_2O_2 and phenol for the $^{\bullet}OH$ has a negative impact on the mineralization process [49, 50].

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad (20)$$

Therefore, an H_2O_2 concentration 1.2 times that of the stoichiometric relationship appears to be the optimal amount of oxidizing agent in UV presence and led approximately to total COD removal compared with darkness and visible light.

Table (1). The effect of mass ratio H_2O_2/phenol on the COD removal after 2 h at pH = 3, CL = 0.07 g, and 60°C.

H_2O_2/phenol	**COD removal, %**		
	Darkness	**Visible light**	**UV light**
1	81.60±0.46	89.37±1.34	94.91±1.28
1.2	86.24±1.16	95.69±0.51	99.84±0.87
1.5	86.65±0.96	99.96±0.03	Total removal
2	96.70±0.25	Total removal	Total removal

The effect of the light type (natural or UV) on COD removal in synthetic wastewater has been investigated by employing a heterogenous Fenton oxidation reaction utilizing stoichiometric quantities of H_2O_2 at pH= 3, and CL of FeX =0.07g for 2 h. The experiment was conducted at three different temperatures (25, 40, and 60 °C), and the results were shown in Figure (4).

The highest COD removal of 88.87% was achieved at 60 °C, 72.47, and 55.41 % of COD were removed at 40 and 25 °C, respectively, without UV light. The oxidation reaction increases when the temperature increases, which was predicted based on the exponential relationship between the kinetic constants (for forming radicals or their interaction with organic molecules) and temperature (as described by the Arrhenius equation). Nevertheless, the results match other previously reported studies [51, 52]. Longer reaction times have diminished the efficacy of the catalyst as the temperature rose. At higher temperatures, the accelerated decomposition of H_2O_2 reduces efficiency [53].

Experiments involving the photocatalytic oxidation process were conducted at the optimum operating conditions to compare with the heterogeneous Fenton oxidation. The obtained COD removal efficiency was significantly higher in UV irradiation presence. The maximum COD removal reached 94.91% at 60 °C, and about 91.87% and 69.54% COD was removed at 40 and 25 °C, respectively. The results are in agreement with previously reported [35, 54, 55]. Utilizing UV emissions improves the efficacy of the oxidation process.

Moreover, due to the UV oxidation activity, UV emissions increase the catalyst's effectiveness and lower the temperature range, increasing radical formation. Thus, the decomposition rate of organic contaminants in the reaction with $^{\bullet}OH^{\cdot}$ was faster than in the visible light, and the reaction time was short [36, 56, 57]. Furthermore, UV emissions increase the catalyst's efficacy and conversion rate due to the UV oxidation activity, increasing radical formation. Consequently, the rate of organic matter decomposition has accelerated [37]. Therefore, based on the test results, the optimal temperature in the presence of UV is 40 °C, considered the most suitable application in the petroleum refinery.

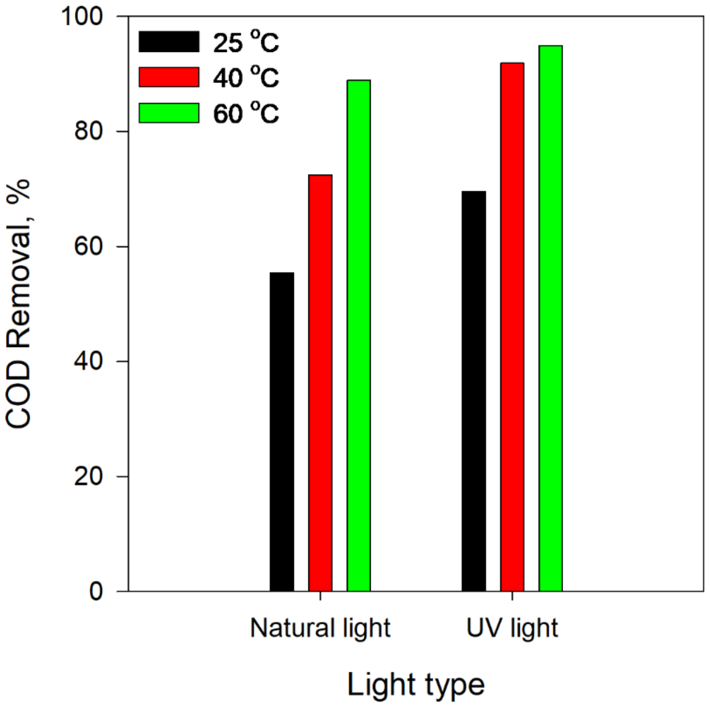

Figure (4). The effect of light type on the COD removal after 2 h at pH = 3, with 0.07 g FeX catalyst load at 25, 40 and 60 °C.

4. Conclusions

The findings of this study demonstrated that heterogeneous photocatalytic oxidation processes substantially accelerated the rate of COD degradation. Combining UV/FeX compounds, the photo-Fenton process generated the highest elimination rate for COD compared with the Fenton process. The oxidation rate was affected by numerous variables, including the CL, pH, H_2O_2 amount, temperature, and UV irradiation. Optimal conditions for COD degradation of the UV/FeX/H_2O_2 system were pH of 3, a FeX load of about 0.07 g, and a 20% excess of H_2O_2, temperature 40 °C in 2 h while the temperature was 60 °C in 2 h for the FeX/ H_2O_2 system. The reaction speed was also improved with the increase in light intensity. The benefits of the heterogeneous photo-Fenton process as an oxidative pre-treatment step over other photocatalytic oxidation processes are economics, productivity, mainly when aromatic compounds are to be damaged, ease of management since no specialized technical apparatus was required, low initial investment, less energy request, and inoffensive process products.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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