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by Ivan Gunawan

Submission date: 29-Mar-2025 09:43AM (UTC+0700)

Submission ID: 2628496227

File name: 9-Subcritical_water_mediated_fenton.pdf (3.1M)

Word count: 6210

Character count: 33328



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Research article

Subcritical water mediated fenton and fenton like degradation of wastewater containing antibiotics

Maria Natasya Inocentia Laban^a, Felycia Edi Soetaredjo^{a,b,*}, Ivan Gunawan^{a,b},
Alfin Kurniawan^c, Jindrayani Nyoo Putro^{a,b}, Shella Permatasari Santoso^{a,b}, Maria Yuliana^{a,b},
I. Dewa Ayu Agung Warmadewanthi^d, Suryadi Ismadji^{a,b,*}

^a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia

^b Collaborative Research Center for Zero Waste and Sustainability, Jl. Kalijudan 37, Surabaya 60114, East Java, Indonesia

^c Research Group for Advanced Materials and Sustainable Catalysis (AMSC), State Key Laboratory Breeding Base of Green Chemistry and Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

^d Department of Environmental Engineering, Faculty of Civil, Planning, and Geo Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia



ARTICLE INFO

Keywords:

Fenton process
Subcritical water
Antibiotic
Heterogeneous catalyst

ABSTRACT

The issue of antibiotic residue causing environmental contamination must be addressed with urgency and seriousness. The present study used a heterogeneous Fenton-subcritical water process to degrade synthetic liquid waste containing a mixture of tetracycline and erythromycin. MIL-88B(Fe) was utilized as a catalyst, produced using the solvothermal method at 150 °C. Utilizing SEM, XRD, and nitrogen sorption, the catalyst was characterized. In addition, the degradation capability of heterogeneous Fenton subcritical water was compared to that of the conventional Fenton process, subcritical water, and homogeneous Fenton-subcritical water processes. The experiment results demonstrated that the heterogeneous Fenton-subcritical water process was preferable to other methods for degrading tetracycline and erythromycin. This study found that tetracycline degraded at a maximum rate of 91.3% and erythromycin at 77.7%. MIL-88B(Fe) experiments were also conducted to determine the catalysts' efficacy.

1. Introduction

Alexander Fleming's discovery of the first antibiotic, penicillin, revolutionized modern medicine, especially for treating various infectious diseases caused by microorganisms. Due to advances in medicinal chemistry, many antibiotics are commercially available today. Most of the available antibiotics are semi-synthetic modifications of various natural compounds. Antibiotics are effective against various bacterial infections, from mild to fatal. Currently, the use of antibiotics is excessive, especially in developing countries; antibiotics can be obtained easily without having to use a doctor's prescription. Because only a tiny part of antibiotics can be assimilated by the human body, and the rest will end up as waste, eventually leading to environmental pollution [1–5]. The presence of antibiotics in the environment for a long time will cause bacteria to adapt to the environment and develop resistance to various types of antimicrobials.

There are three process methods for treating wastewater containing

antibiotics: physical, chemical, and biological. Antibiotic wastewater treatment using physical methods is generally easier and cheaper, but its application is limited to waste containing low concentrations of antibiotics [6]. Biological treatment methods are very effective but take a long time to produce effluent at the desired concentration. [7]. Meanwhile, the effectiveness of waste treatment with chemical methods depends on the oxidizing agent used. Chemical methods are the most effective and efficient among the available processes in treating wastewater containing hazardous pollutants.

The Fenton process is one of the chemical waste treatment procedures for wastewater containing hazardous and toxic chemicals. The Fenton process is one of the advanced oxidation techniques (AOPs) that utilizes the strong oxidizing ability of radicals to convert complex compounds into small compounds and increase their biodegradability [8–15]. However, the effectiveness of the Fenton process for specific organic contaminants, particularly at high concentrations, is unsatisfactory; consequently, modifications to the process are often made to

* Corresponding authors at: Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia.
E-mail addresses: felycia@ukwms.ac.id (F.E. Soetaredjo), suryadi@ukwms.ac.id (S. Ismadji).

<https://doi.org/10.1016/j.nxmate.2024.100129>

Received 31 August 2023; Received in revised form 18 December 2023; Accepted 15 January 2024

Available online 28 March 2024

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increase its efficiency [16–25].

This study used a combination of Fenton and subcritical water and a metal-organic framework based on Fe to degrade a mixture of antibiotic-containing wastewater. MIL-88B(Fe) was used as the metal-organic framework catalyst in combination with subcritical and Fenton for the degradation process. MIL-88B(Fe) is one of the most stable metal-organic frameworks in subcritical water conditions [17]. Therefore, the industrial application of MIL-88B(Fe) as a source of Fe for the Fenton-like reaction is conceivable. Tetracycline and erythromycin were model compounds in synthetic waste containing antibiotics. Tetracyclines are drugs used to manage and treat diverse bacterial diseases. Tetracyclines are antibiotics that block protein synthesis and are known for their broad-spectrum activity. Erythromycin is an antibiotic prescribed to treat certain bacterial infections. Both antibiotics are commonly used to treat a wide range of bacterial illnesses. As a result of excessive usage, only a fraction of the substance can be assimilated by the body. At the same time, the remainder is discharged into the environment, posing a significant risk as it can lead to the development of resistance. Due to the significant environmental hazards, the researchers selected the two antibiotics as examples for this investigation.

In this investigation, antibiotic pollutants in multicomponent aqueous mixtures were degraded for the first time using a heterogeneous Fenton-like process with MIL-88B(Fe) microcrystals as a catalyst in subcritical water (SCW). A comparison of the degradation ability of wastewater containing antibiotics by the heterogeneous Fenton-like process with the traditional Fenton and Fenton-subcritical water processes has also been conducted.

2. Materials and methods

2.1. Materials

Tetracycline hydrochloride ($C_{22}H_{24}N_2O_8 \cdot HCl$, $\geq 95\%$), erythromycin ($C_{37}H_{67}NO_{13}$, $\geq 99\%$), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, $\geq 97\%$), Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, $\geq 99\%$), terephthalic acid ($C_8H_6O_4$, $\geq 98\%$), and N, N-dimethylformamide (DMF, $HCON(CH_3)_2$, 99%) were obtained from Sigma-Aldrich. Methanol (CH_3OH , 99%), ethanol (C_2H_5OH , 95%), and hydrogen peroxide (H_2O_2 , 50%) were purchased in local stores in Surabaya, Indonesia. All chemicals purchased are used directly without going through further purification processes. For washing, dissolving, and other purposes, the water used is reverse osmosis water.

2.2. Synthesis of MIL-88B(Fe)

Metal-organic framework MIL-88B(Fe) was prepared using a solvothermal method at 150 °C. The procedure of synthesizing followed Horcajada et al. [26] with slight modification [17]. A brief description of the procedure is as follows: 13.5 g of $FeCl_3 \cdot 6H_2O$ and 8.3 g of terephthalic acid were dissolved in 250 mL of DMF. Subsequently, the mixture was transferred into 500 mL of autoclave (stainless steel lined with Teflon) and heated at 150 °C for 24 h. The resulting solid was washed with ethanol and RO (reverse osmosis) water and dried at 80 °C for 24 h.

2.3. Characterization of MIL-88B(Fe)

The surface morphology of MIL-88B(Fe) was characterized using SEM (scanning electron microscopy) FEI Inspect F50. The pore structure of the MOF was analyzed using the nitrogen sorption method (Micromeritics ASAP 2010 volumetric sorption analyzer), and its pore size distribution was calculated using the DFT (density functional theory) method. The crystallographic structure of the sample was obtained using XRD analysis (Bruker D2 Phaser tabletop diffractometer). Details of the characterization information can be seen elsewhere [17].

2.4. Traditional Fenton process

The methods of Fenton oxidation and subcritical water have demonstrated high efficacy in oxidizing organic molecules, including various antibiotic substances. Advanced oxidation tests are typically performed using low to moderate pollutants, but studies involving high concentrations are scarce. Therefore, it is essential to employ elevated quantities of antibiotics to assess the efficacy of the employed procedures. The degradation experiment of synthetic wastewater containing antibiotics as a single component or as a mixture was carried out with the following procedure: 200 mL of synthetic antibiotic wastewater containing 1000 mg/L of tetracycline or erythromycin was added in 500 mL of beaker glass. The pH of the solution was adjusted to 4 by adding 2 N of H_2SO_4 or NaOH. Subsequently, 0.3 g of $FeSO_4$ was added to the solution under constant agitation. After $FeSO_4$ was completely dissolved, 1 mL of 50% H_2O_2 was added to the mixture to initiate the Fenton reaction. After 30 min of reaction, the mixture's pH was adjusted by adding H_2SO_4 or NaOH, and 1 mL of 50% H_2O_2 was added. After the reaction lasted for one hour, the addition of H_2O_2 was repeated. The amount of chemicals used in the Fenton oxidation procedure was based on preliminary experiments. The reaction continued for three hours with constant agitation at 250 rpm. The remaining antibiotic concentration was determined using a UV vis spectrophotometer at wavelength 357 nm for tetracycline and 285 nm for erythromycin.

2.5. Subcritical water degradation

Subcritical water degradation of tetracycline and erythromycin was conducted at 125, 150, 175, and 200 °C. Antibiotic degradation experiments using the oxidation method with aqueous media under subcritical conditions were carried out with the experimental procedure as follows: 200 mL of antibiotics solution with a concentration of 1000 mg/L of each antibiotic was put into the subcritical reactor, then the reactor was tightly closed, after which air flowed into the reactor so that the pressure reached 10 bar. The heater was then turned on until the desired reaction temperature was reached. A PID (proportional integral derivative) controller automatically controls the heater to keep the temperature constant at the desired value. The reaction under subcritical conditions lasted for 2 h. After the reaction occurred according to a predetermined time, the heating stopped. After the reactor temperature reached 40 °C, the pressure control valve was opened so the reactor pressure was 1 atm. The antibiotic concentration after the reaction was determined using a UV-vis spectrophotometer.

2.6. Subcritical water – Fenton process

The research procedure for antibiotic degradation using the subcritical water-Fenton process method is the same as the subcritical water degradation procedure. The slight difference in the subcritical water-Fenton process is that the Fenton reagent was added before introducing the solution into the subcritical reactor. The amount of $FeSO_4$ added to the antibiotics solution was 0.3 g, and the added H_2O_2 was 3 mL (50% H_2O_2).

2.7. Heterogeneous Fenton – subcritical water process

The Fenton heterogeneous-subcritical water process experiment procedure was identical to that of the Fenton subcritical water process, except that MIL-88B(Fe) was used as the Fe source. The addition of MIL-88B(Fe) was 0.3 g.

2.8. Reusability of MIL-88B(Fe)

Reusing MIL-88B(Fe) catalyst for the degradation process is essential as a heterogeneous catalyst. MIL-88B(Fe) catalyst must be used repeatedly without reducing effectiveness. MIL-88B(Fe) catalyst recovery was

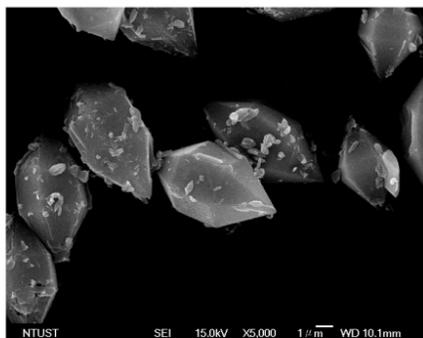


Fig. 1. SEM image of MIL-88B(Fe).

carried out in the following procedure: MIL-88B(Fe) catalyst solids were separated from the reaction mixture by centrifugation, and the solids obtained were then washed with RO water repeatedly until the pH of the washing solution did not change. To remove any remaining organic matter, MIL-88B(Fe) was soaked in ethanol for 2 h and then dried at 105 °C for 12 h. The catalyst was reused using the Fenton heterogeneous-subcritical water process procedure.

3. Results and discussion

3.1. Characterization of MIL-88B(Fe)

The surface topography and crystal form of MIL-88B(Fe) MOF obtained from characterization using SEM can be seen in Fig. 1. The MIL-88B(Fe) synthesized in this study has a truncated octahedral bipyramidal morphology with relatively smooth edges and surfaces, as

depicted in Fig. 1. MIL-88B(Fe) also has a fairly uniform particle size distribution of 6–10 μm, with an average size of 7.8 ± 0.8 μm.

Fig. 2 displays nitrogen gas adsorption and desorption curves on MIL-88B(Fe). Based on the IUPAC classification, the nitrogen sorption isotherm is a type II isotherm. This type II isotherm is characterized by low nitrogen adsorption at low relative pressure ($p/p_0 < 0.01$). The low adsorption of nitrogen gas at a relative pressure of < 0.01 indicates that MIL-88B(Fe) does not have a microporous structure; this is supported by the pore size distribution curve shown in the same figure. At a higher relative pressure ($0.05 < p/p_0 < 0.8$), there is a gradual increase in the uptake of nitrogen gas; this phenomenon indicates the occurrence of multi-layer adsorption of nitrogen gas, a unique feature of the mesoporous structure. At a relative pressure higher than 0.8, there is a sudden increase in nitrogen gas adsorption until saturation is reached at p/p_0 equal to 1. An inflection on the hysteresis curve indicates a relatively large mesoporous structure on the structure of MIL-88B(Fe).

The pore size distribution of MIL-88B(Fe) was determined by the density functional theory (DFT) method with medium regularization. Fig. 2 shows that the pore size of MIL-88B(Fe) ranges from 3 to 20 nm, with the highest distribution in pore sizes of 3.7 nm and 14.9 nm. The BET surface area of MIL-88B(Fe) (measured at $0.05 < p/p_0 < 0.3$) is $23.1 \text{ m}^2/\text{g}$ with a total pore volume of $0.09 \text{ cm}^3/\text{g}$ (measured at $p/p_0 < 0.997$). The results obtained follow the results in the literature [26,27].

XRD diffractogram of MIL-88B(Fe) can be seen in Fig. 3. The degree of crystallinity of MIL-88B(Fe) is relatively high, as shown in Fig. 3. The characteristic diffraction of MIL-88B(Fe) can be observed at 2θ of 9.70, 12.46, 13.90, 16.18, 16.52, 16.96, 18.68, and 21.92°. This diffraction characteristic is related to the lattice spacing in the hexagonal group.

3.2. Traditional Fenton process

Under acidic conditions, the Fenton reaction uses iron compounds and hydrogen peroxide to produce hydroxyl radicals with high oxidizing abilities. The main drawback to using Fenton for the degradation of organic compounds is that the reaction takes place over a narrow, low pH range around pH 3–4. At a higher pH, the radicals formed are unstable, and the decomposition of H_2O_2 proceeds slowly, creating oxygen

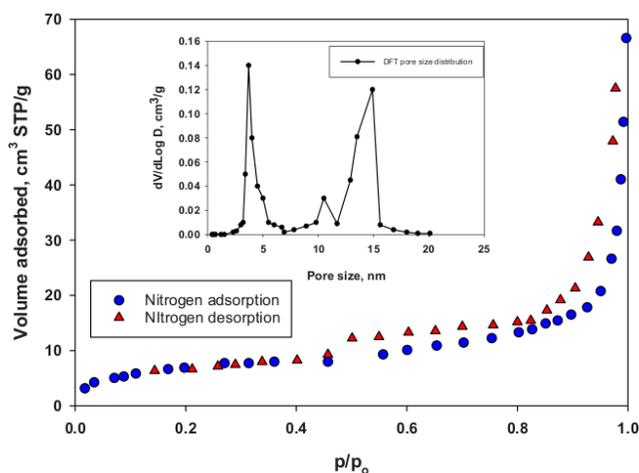


Fig. 2. Nitrogen sorption isotherms of MIL-88B(Fe) and DFT pore size distribution.

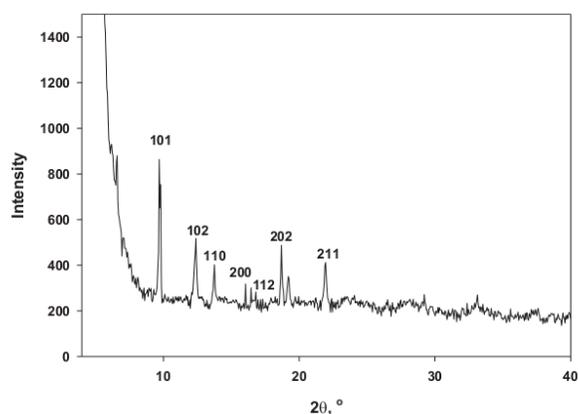
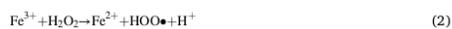


Fig. 3. XRD diffractogram of MIL-88B(Fe).

and hydrogen rather than radicals. Meanwhile, at a pH above 5, insoluble $\text{Fe}(\text{OH})_2$ will be formed. At too acidic pH ($< \text{pH } 3$), reduction of radical formation takes place strongly. For this reason, during the reaction process, the pH of the solution is controlled at pH 4 by adding H_2SO_4 or NaOH solution.

Tetracyclines and erythromycin were rapidly degraded within the first 30 min. The concentration of the remaining tetracycline in the solution was 562 mg/L, while the concentration of erythromycin was 658 mg/L (at 30°C). In the following 30 min, the concentrations of tetracycline and erythromycin decreased by a lower amount than in the previous 30 min. The concentration of tetracycline in the solution drops from 562 mg/L to 519 mg/L, while for erythromycin, the remaining concentration drops from 658 mg/L to 623 mg/L. The final concentration of tetracycline and erythromycin after 3 h of the process was 421 mg/L and 558 mg/L, respectively.

In general, the chemical reaction equation between iron ions and hydrogen peroxide in the Fenton reaction is as follows:



In the presence of catalytic Fe^{2+} ions, it immediately decomposes hydrogen peroxide into the hydroxyl radical $\text{HO}\bullet$. Highly reactive hydroxyl radicals will directly attack and decompose antibiotic compounds in the solution. The formation of Fe^{3+} ions simultaneously degrades H_2O_2 to produce $\text{HOO}\bullet$, a hydroxyl radical that is less reactive than $\text{HO}\bullet$. These phenomena caused rapid degradation of tetracycline and erythromycin in the first 30 min, and the decrease in both antibiotics was quite sharp. In the next 30 min, despite adding H_2O_2 , some of the Fe^{2+} that turned into Fe^{3+} may have precipitated as hydroxide during the reaction, even though there was a pH adjustment at 30 min. This phenomenon causes a decrease in the concentration of antibiotics that is not as significant as the initial thirty minutes.

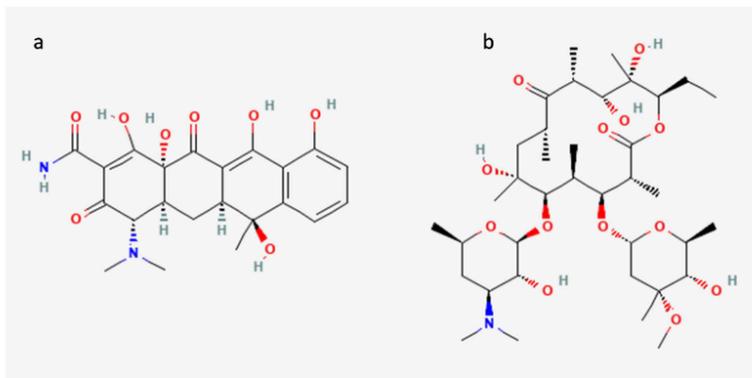


Fig. 4. The molecular structure of (a) tetracycline and (b) erythromycin.

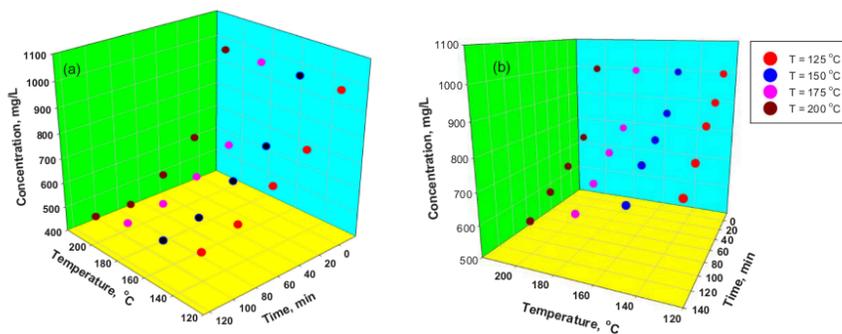


Fig. 5. Sub-critical water degradation of a mixture of antibiotics at various temperatures and times: (a). Tetracycline, and (b) Erythromycin.

In experiments involving mixed degradation of tetracycline and erythromycin and in experiments involving degradation of a single component, tetracycline was significantly more easily degraded than erythromycin. After 3 h of reaction, the concentration of tetracycline in solution was 578 mg/L, and the concentration of erythromycin was 732 mg/L. The experimental results showed that Fenton more easily degraded tetracycline than erythromycin. The tetracycline structure consists of an inflexible skeleton of four rings containing different functional groups, such as amine, alkyl, and hydroxyl [28]. These functional groups are attached to upper or lower peripheral zones. The chemical structure of erythromycin consists of erythronolide A, a cyclic ketone with a complex structure. The molecular structure of both antibiotics is depicted in Fig. 4. This figure shows that erythromycin has a more complex molecular structure than tetracycline. With a more complex molecular structure, erythromycin will be more difficult to degrade by hydroxyl radicals.

3.3. Subcritical water degradation

Subcritical water has unique properties that can be used to degrade organic compounds. In this study, the subcritical water was utilized as an oxidizing agent for antibiotics removal. Antibiotic degradation in a mixture as a function of temperature and time in subcritical water

conditions can be seen in Fig. 5. As shown in Fig. 5, temperature significantly affects the degradation of tetracycline and erythromycin under subcritical water conditions. Temperature positively affects the degradation of tetracycline and erythromycin; with increasing temperature, the degradation of both antibiotics also increases. Within 2 h at 125 °C, the concentration of tetracycline decreased by 38.8% (from 1000 mg/L to 612 mg/L), while the concentration of erythromycin decreased by 25.5% (from 1000 mg/L to 745 mg/L). At 200 °C with a degradation time of 2 h, 48.9% tetracycline and 39.7% erythromycin were degraded.

Compared to the traditional Fenton process, the degradation of antibiotics using water under sub-critical conditions is faster and more efficient. The physical properties of subcritical water differ from those of water at ambient conditions, such as the dielectric constant, which is usually used to measure polarity and can be easily modified by adjusting temperature and pressure. The ionization constant of water (k_w) is another essential property under subcritical conditions. Temperature increases k_w value in subcritical conditions. The concentration of hydronium ions (H_3O^+) will increase as the k_w value rises. This hydronium ion is highly reactive at high temperatures and an excellent reagent for several organic compounds, including some antibiotics. Therefore, by increasing the concentration of this hydronium ion, the degradation of tetracycline and erythromycin will be accelerated, and the amount of

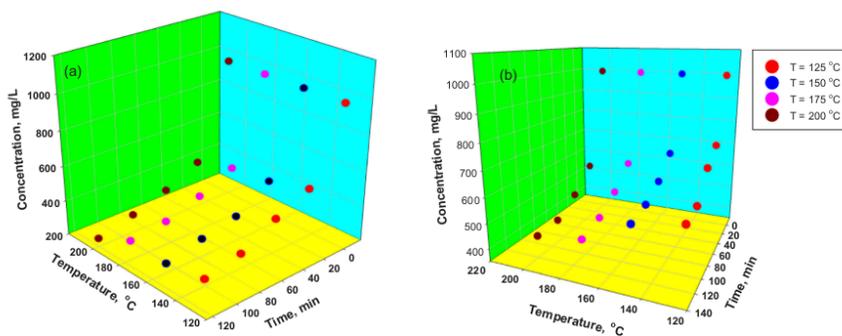


Fig. 6. Fenton - sub-critical water degradation of a mixture of antibiotics at various temperatures and times: (a). Tetracycline, and (b) Erythromycin.

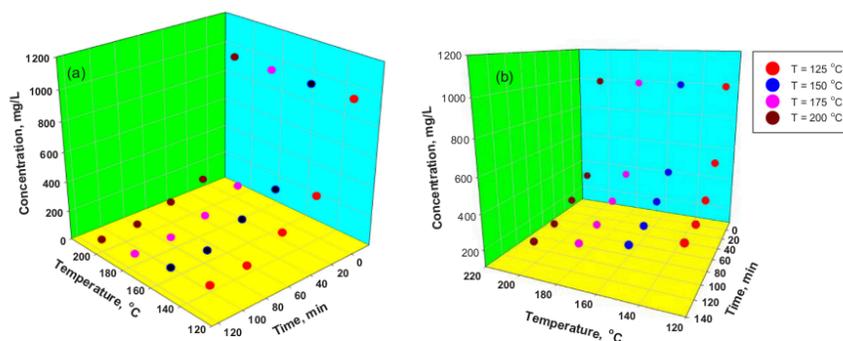


Fig. 7. Heterogeneous Fenton – subcritical water degradation of a mixture of antibiotics at various temperatures and times: (a). Tetracycline, and (b) Erythromycin.

antibiotics degraded will increase.

3.4. Subcritical water – homogeneous Fenton process

The degradation of antibiotic compounds using the Fenton combination in sub-critical water conditions is rarely studied, especially for the degradation of tetracycline and erythromycin. Fig. 6 displays the concentrations of tetracycline and erythromycin as a function of temperature and time during the Fenton degradation process under subcritical water conditions. Fig. 6 demonstrates that the Fenton-subcritical water process degrades tetracycline and erythromycin more effectively than traditional Fenton and subcritical water processes.

In the first 30 min, tetracycline and erythromycin degraded rapidly; at 125 °C, approximately 39% of tetracycline and 25% of erythromycin were degraded, and the degradation efficiency increased with increasing temperature. The degradation efficiency of tetracycline increased to 53% at 200 °C, while that of erythromycin increased to approximately 41%. The degradation of both antibiotics was nearly constant after 60 min. At the end of the degradation process at 200 °C, the remaining tetracycline in solution was 249 mg/L (removal efficiency 75.1%), while erythromycin concentration was 438 mg/L (removal efficiency 56.2%).

At the beginning of the degradation process, the Fenton oxidation process plays a more dominant role than oxidation by hydronium ions. The formation of hydroxyl radicals takes place quickly, according to Eq. 1. Gradually, with the consumption of H_2O_2 and the presence of OH^- ions from subcritical water, which further reacted with Fe^{2+} or Fe^{3+} to form hydroxides, the reaction will run more slowly; at that time, hydronium ions play an essential role in antibiotic degradation. Some water will dissociate under subcritical conditions into OH^- and H_3O^+ . The weakening of the hydrogen bonds in water causes this dissociation.

Consequently, several physical properties of subcritical water, including density, dielectric constant, and k_w , will be lower than those of water at ambient temperature [29]. The hydroxide anion can react with the aromatic ring in the antibiotic structure via heterolytic hydroxylation [30], destabilizing the ring structure and resulting in a ring-opening reaction. Through the carbonium mechanism, the hydronium ion is responsible for dealkylation and substitution reactions in the aromatic ring of antibiotic compounds [30]. Dealkylation and substitution reactions degrade the aromatic rings present in the structure of antibiotics into simpler compounds.

3.5. Heterogeneous Fenton – subcritical water process

MIL-88B(Fe) is one of the most stable metal-organic frameworks in

subcritical water conditions [17]. Therefore, the industrial application of MIL-88B(Fe) as a source of Fe for the Fenton-like reaction is conceivable. Fig. 7 depicts the performance of the Fenton-like process with MIL-88B(Fe) as a catalyst in the degradation of tetracycline and erythromycin. The significance of MIL-88B(Fe) in the degradation of tetracycline and erythromycin is evident in Fig. 7. The decrease in the concentration of the two antibiotics in the solution after undergoing degradation using the heterogeneous Fenton-subcritical water process in the first 30 min appeared to be very significant. Temperature and time are essential in degrading tetracycline and erythromycin, as in the previous processes. Temperature and time have a positive effect on the degradation of both antibiotics.

Heterogeneous Fenton – subcritical water process is superior to the subcritical water – Fenton process; at 200 °C, heterogeneous Fenton provides a tetracycline decomposition efficiency of 92%, while homogeneous Fenton subcritical water provides a decomposition efficiency of 75.1%. The removal efficiency for erythromycin was 77.4% for the heterogeneous Fenton-subcritical water process, while the separation efficiency was 56.2% for the subcritical water-homogeneous Fenton process. Generally, both processes operate under identical conditions, with the primary distinction being that Fe exists in solid form in heterogeneous Fenton-subcritical water. In contrast, Fe exists in the ionized form in the homogeneous Fenton-subcritical water as Fe^{2+} or Fe^{3+} . Under subcritical conditions, water will partially ionize into OH^- or H_3O^+ , as previously explained. In this condition, a portion of the Fe ions will precipitate as hydroxide, reducing the efficiency of catalysis to convert H_2O_2 into hydroxy radicals and, consequently, decreasing antibiotic degradation.

The degradation process of tetracycline and erythromycin occurred according to the following mechanism: the two antibiotics are first adsorbed on the MIL-88B(Fe) connecting bridge via phi-phi and carbonyl interactions with aromatic groups present in the antibiotics [17]. In the meantime, the H_2O_2 molecule, a strong Lewis base, reacts with Fe at the MIL-88B(Fe) center to produce the $Fe(II/III)-H_2O_2$ complexes [31] and the hydroxyl radical OH^\bullet . This hydroxy radical will react efficiently with the adsorbed antibiotic compounds on the MIL-88B(Fe) surface. The reactions that occur can be expressed by the following reaction equations [17]:



Where L is the bridging ligand.



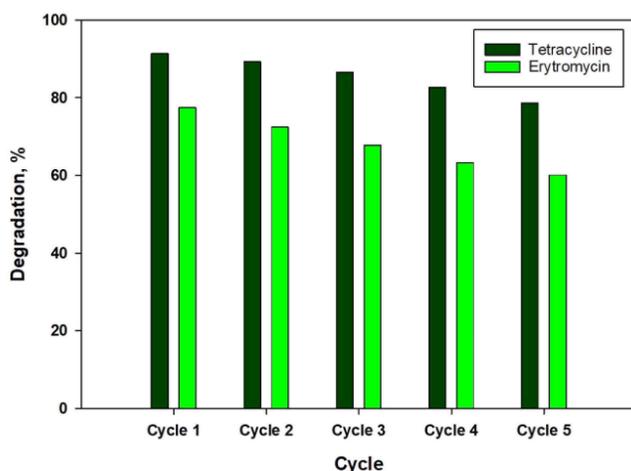
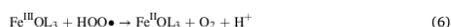


Fig. 8. Reusability of MIL-88B(Fe).



3.6. Reusability of MIL-88B(Fe)

The experiment of reusing MIL-88B(Fe) catalyst was conducted five times at 200 °C for two hours. Fig. 8 depicts the results of the degradation of tetracycline and erythromycin in the catalyst reuse experiment. Fig. 8 demonstrates that the degradation ability of the catalyst diminishes with each cycle; after five cycles, the degradation ability of the catalyst falls from 91.3% to 78% for tetracycline and from 77.4% to 60.1% for erythromycin. After five cycles, the degradation ability of the two antibiotic compounds decreased by approximately 20%. This ability to degrade is because some of the Fe metal contained in MIL-88B (Fe) has been released during the degradation process or lost during laundering. The effectiveness of degradation decreases by 20% after five repetitions of the process, so it will be necessary in the future to discover a way to maintain the catalyst's capacity for degradation.

4. Conclusions

Utilizing a modification of the Fenton process, the solid catalyst MIL-88B (Fe) as a source of Fe, and subcritical water, organic waste containing a combination of tetracycline and erythromycin antibiotics was effectively degraded. The heterogeneous Fenton-subcritical water process provides greater antibiotic degradation efficiency than the traditional Fenton process, the subcritical water process, and the homogeneous Fenton-subcritical water process. Tetracycline's degradation efficiency was 91.3%, while erythromycin's was 77.4%. In the experiment on the reusability of the MIL-88B(Fe) catalyst for five cycles, the catalyst degradation efficiency decreased by approximately 20%, so in the future, it will be necessary to devise a method for preserving the MIL-88B(Fe) catalyst's efficacy in degrading antibiotics waste.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the Directorate of Research and Community Service, Deputy for Research and Development Strengthening, Ministry of Research and Technology/National Agency for Research and Innovation, Republic of Indonesia, through contract number 268F/WM01.5/N/2023.

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