JTE HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNICAL EDUCATION SCIENCE
Ho Chi Minh City University of Technology and Education
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Degradation of Tetracycline by Composite Catalyst Derived from Food Waste and Goethite

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ARTICLE INFO

Received: 07/05/2024
Revised: 04/06/2024
Accepted: 05/06/2024
Published: 28/06/2024

KEYWORDS

Advanced oxidation processes;
Adsorption;
Tetracycline removal;
Soybean curd;
Goethite.

ABSTRACT

Current studies on the removal of emerging contaminants (such as pharmaceuticals, personal care products, and their metabolites) from environmental matrices have received a lot of interest due to their adverse impacts on human health and ecology. Among these emerging contaminants, Tetracycline hydrochloride (TCH) - has become a common antibiotic prominent found in hospital and municipal wastewater. The present research develops soybean curd biochar loading goethite (SBCG) and soybean curd activated carbon loading goethite (SACG), a magnetic material made from soybean curd residue and Fe precursor (α-FeOOH), for advanced oxidation processes (AOPs) of TCH in aqueous solutions. Soybean curd biochar loading goethite and soybean curd activated carbon loading goethite demonstrated decomposition performances of 82.8% and 95.3% for the oxidizing agent H_2O_2 at pH 2, and 87.2% and 94.8% for the oxidizing agent $K_2S_2O_8$ at pH 7, respectively. Furthermore, the oxidant utilized in the reaction was more H_2O_2 than $K_2S_2O_8$. In which the initial concentration was 70 mM H_2O_2 and 20 mM $K_2S_2O_8$, the residual concentration after the reaction was 19 - 22 mM H_2O_2 and 6.5 – 9.35 mM $K_2S_2O_8$ for SACG and SBCG. The consumption of H_2O_2 and $K_2S_2O_8$ per unit treatment agent for SACG material with an initial TCH concentration of 300 mg/L was 75.5 and 20mmol oxidant/mmol TCH, respectively. This demonstrates that combining $K_2S_2O_8$ with SACG produces the most beneficial outcomes, such as saving time, chemicals, and the amount of post-treated water with a neutral pH value.

Doi: https://doi.org/10.54644/jte.2024.1592

1. Introduction

Pharmaceutical residues have been recognized as emerging contaminants (ECs) in water bodies due to the widespread use of medications for human and veterinary health worldwide, causing significant dangers to aquatic habitats [1]. According to the WHO's statistical data, pharmaceutical industry has been grown both domestically and internationally, and Vietnam, which was one of 17 nations that had a thriving pharmaceutical industry [2]. Antibiotics are the most frequently and widely used medicines. Antibiotics are incredibly essential and widely utilized in the treatment of human illnesses, animal husbandry, and agriculture [3]. Tetracycline hydrochloride (TCH), an antibiotic used to treat certain illnesses in humans and animals, is mostly released into wastewater as original chemical compounds [4]. These results indicated that TCH residue might be commonly present in wastewater.

As a result, developing efficient and cost-effective solutions to remove TCH from the aquatic environment is crucial. Several approaches have been used to remove TCH from water, including photodegradation [5], biodegradation [6], catalytic oxidation [7], [8], adsorption [9], [10], and advanced oxidation processes (AOPs) [11], [12]. Fenton treatment, a major technology utilized in AOPs, is the preferred approach for removing TCH. Sulfate radical ($\bullet SO_4^-$) based AOPs are gaining popularity for their effective removal of organic contaminants. Compared to radical ($\bullet OH$), ($\bullet SO_4^-$) radical has a longer lifespan, greater ability to selectively oxidize substances, and a broader range of pH adjustment

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and was mainly produced by Peroxymonosulfate (PMS) and peroxydisulfate (PDS) [13]. PMS with asymmetrical molecular structure makes it faster to activate and produce $\bullet SO_4^-$ than PDS [14].

Goethite (α-FeOOH) is non-toxic, and inexpensive material with a large surface area and many active sites [15]. Goethite is commonly utilized as a catalyst for the removal of organic substances, such as bisphenol A, which was substantially decomposed in the goethite-persulfate composition. However, goethite's catalytic capacity to activate PMS was reduced since it was not stable and Fe(III) was transformed to Fe(II) less effectively [16]. Therefore, to overcome these drawbacks, iron-based biochar being created from sludge and agricultural waste, can be served as catalysts in heterogeneous Fenton [16]. Biochar with high surface area can be used as an adsorbent for organic compounds and the recycle of Fe(III)/Fe(II) may be considerably facilitated to improve the catalytic activity of iron-based catalysts. For instance, the carbonyl group might be integrated with Fe(III), hence increasing •OH yields and facilitating Fe(III)/Fe(II) transformation in the goethite/biochar/ H_2O_2 complex [13].

This study utilizes a high-temperature physical treatment (500 ℃) for converting raw soybean curds residue to biochar (BC). After that, biochar was activated chemically with KOH to produce extremely activated carbon (AC). Operational conditions for generating activated carbon were optimized by changing the ratio of KOH/BC and pyrolysis temperature [17]. The catalytic materials will be synthesized by a combination of BC and Goethite; AC and Goethite. Furthermore, with this background, the current study focused on the efficiency of AOPs that use iron to remove TCH. AOPs formed ($\bullet SO_4^-$) based on the reaction of $S_2O_8^{2-}$ and iron ion is significantly paid more attention than the Fenton process (iron ion combined with H_2O_2 formed •OH). It investigated the efficiency of Fe/H_2O_2 and Fe/$K_2S_2O_8$ oxidation processes for TCH degradation under different operating settings (pH, contact time, and initial H_2O_2 concentration). At the same time, high-level oxidation with a peroxy disulfate radical catalyst ($K_2S_2O_8$) is used to remove TCH during the oxidation process. This study will also aim to compare the catalytic capacity of iron ions combined with H_2O_2 and $K_2S_2O_8$ for AOPs on SBCG and SACG materials produced by soybean curd residue and goethite to break down TCH.

2. Materials and Methods

2.1. Chemicals

All reagents and chemicals in this study (KOH, HCl, $FeCl_3.6H_2O$, ethanol 96^o and Tetracycline hydrochloride (TCH)) were of analytical grade and were prepared with deionized water.

2.2. Preparation of catalyst materials

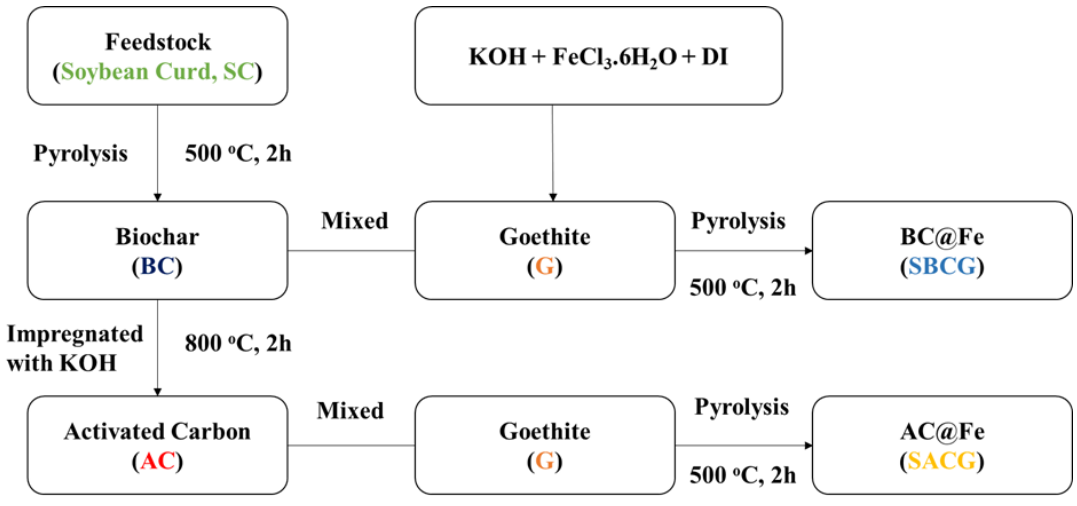

Figure 1. *Materials synthesizing processes*

The synthesizing procedures used in this study with the optimized parameters was done in the previous study [18]. Soybean curd residues from the tofu production process were gathered from marketplaces in Ho Chi Minh City, Vietnam. Firstly, the soybean curd was dried at the temperature of 105 ℃ for 24 hours and sieved to reach a size less than 0.25 mm for storage; it was afterward known as

SC. To create biochar (BC), the sample was then pyrolyzed at 500℃ for 2 hours. The BC material was stored in an airtight container for further activation procedures.

Next, activated carbon (AC) was prepared by mixing BC with KOH (ratio 1:4) for 2 hours using a stirrer in a non-humor steel beaker with the same 25 mL of deionized water and then dried at 150℃ for 4 hours. After that, the solid mixture was crushed and pyrolyzed in an airtight oven at 800 °C for 2 hours. The AC mixture obtained after the pyrolysis process was crushed and stirred with distilled water using a magnetic stirrer at 80 ℃. The excess OH^- ions were eliminated by gradually adding a 1M HCl solution to it. The reaction between HCl and a mixture of K_2CO_3 (formed by the reaction between BC and KOH during pyrolysis) and residual KOH produced CO_2, which stopped when the solution no longer bubbled (the reaction was complete). After treatment, the solid mixture was washed with deionized water to decrease the pH to 7 and eliminate any residue Cl^- ions. Finally, SAC was dried at 105 ℃ for 24 hours before crushing and sieving to a size smaller than 0.075 mm.

Besides that, Goethite, which is also known as α-FeOOH, was produced through the synthesis of $FeCl_3$. Initially, a solution of $FeCl_3.6H_2O$ 1M and a solution of KOH 5M were thoroughly combined using a magnetic stirrer for a duration of 10 minutes. Subsequently, the resulting mixture was subjected to a drying process at a temperature of 70°C for a period of 24 hours, allowing the ferrihydrite to undergo aging and transform into goethite. As a result, the product underwent many washes using ethanol (C_2H_5OH 45%) and deionized water until a pH of 7 was reached. The ultimate outcome was subjected to a drying process at a temperature of 105 ℃ for a duration of 24 hours, followed by sieving process to achieve a particle size of approximately 0.0105 μm [17].

To create the potential in the oxidation ability of the material, the BC sample was paired with α-FeOOH to create new materials using a heterogenous oxidation process. The synthesizing process for this material followed the preparing steps to generate goethite but with a minor adjustment [17]. Initially, BC was added into the Goethite mixture with a weight ratio of 2:1. Then, the mixture was calcinated in an air-tight furnace at 500 ℃ for 2 h. After pyrolyzing, the soybean residue biochar loading goethite was referred to as SBCG. Similarly, Soybean crud-activated carbon loading goethite (SACG) was synthesized using the same BC method as AC materials.

2.3. Analytical methods

The heterogeneous oxidation process of TCH onto the catalyst material was investigated by changing the operational parameters (pH, contact time, and initial H_2O_2 or $K_2S_2O_8$ concentration). The solid/liquid (m/V) ratio was kept at 0.5 g/L for all experiments in this research by adding 0.02 g of material to 40 mL of 300 mg/L TCH solution. pH of solutions was adjusted by NaOH 1M and HCl 1M before and during AOP. After that, the solution was mixed at 250 rpm in a shaker for a preset contact time at a determined temperature. After finishing mixing, the mixture was filtered through a 0.45-μm microfiltration. Besides that, the control sample was also done with the same procedure. The solids collected from the filter paper were dried at 105◦C for 24h to examine the characteristics. The TCH concentration before and after experiments was measured at 357 nm absorbance by UV–vis spectrophotometer (U-2910, Hitachi Corp., Japan).

The residuals of H_2O_2 or $K_2S_2O_8$ concentration were determined by the titration method. To titrate the remaining H_2O_2, a 10 mL sample of 0.1N $KMnO_4$ solution was poured into an Erlen flask, followed by 50 mL DI and 0.125 mL 1N H_2SO_4 [18]. The $K_2S_2O_8$ residue was titrated with 0.025N $Na_2S_2O_3$ in a 10 mL sample volume placed in an Erlene flask, followed by 0.025 g $NaHCO_3$ and 8 g Iodine [19].

The surface morphology of materials and main surface elements was presented in the scanning electron microscope (SEM) images and the energy dispersive X-ray spectroscopy (EDS) data (JSM-6510 LV), respectively.

3. Results and Discussion

3.1. Effects *of the solution pH*

Figure 2 shows two TCH treatment processes including adsorption and oxidation. The equilibrium period for the SBCG catalytic material was determined to be 90 minutes after the adsorption process took place (Figure 2a). While the SACG catalyst material reaches equilibrium after 120 minutes of

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adsorption (Figure 2b). These results demonstrate that the activation process of pyrolyzing biochar to create activated carbon with KOH improved adsorption capacity. Furthermore, the results also indicated that the solution pH from 3 to 9 did not affect significantly on the adsorption process in the range of 3 – 9. However, it was one of the most important factors in advanced oxidation processes.

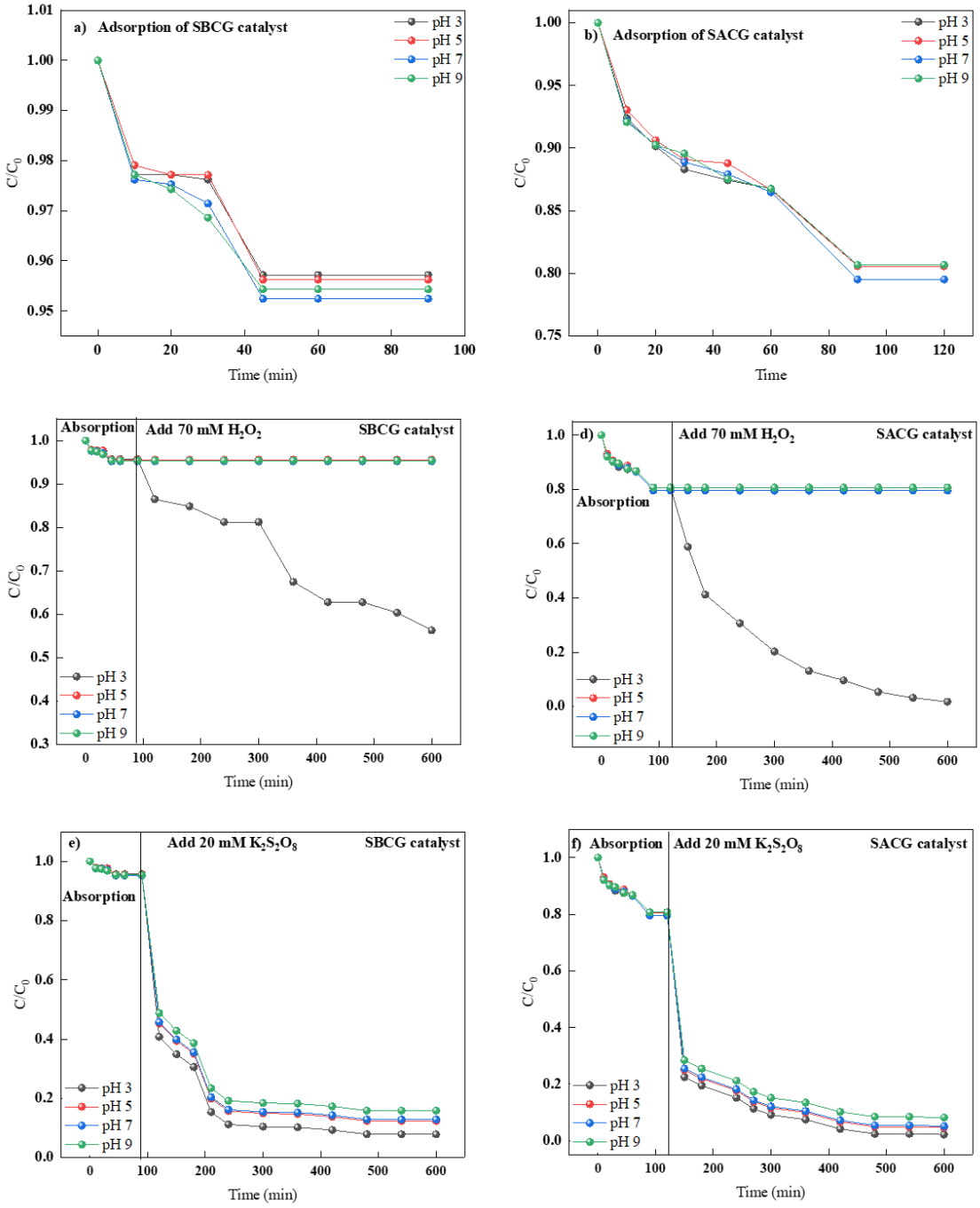

Figure 2. *Effect of pH (a) adsorption of SBCG, (b) adsorption of SACG, (c) H_2O_2 oxidation and (e) $K_2S_2O_8$ oxidation for SBCG catalyst; (d) H_2O_2 oxidation and (e) $K_2S_2O_8$ oxidation for SACG catalyst*

Figure 2.c, d shows that pH affected on TCH elimination efficiency in the Fe/H_2O_2 system with 70 mM H_2O_2 for both materials. Under acidic environment, the degradation of organic matters for Fe/H_2O_2 was enhanced with 86.3% and 95.3% of TCH removal at pH 3.0 after 600 min for SBCG and SACG, respectively. This results from the high oxidation ability of •OH in an acidic condition. When pH increase, the oxidation ability of •OH is reduced [20] due to the dominant form of HO_2^- . The which had

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the molar extinction coefficient of H_2O_2 was higher than that of HO_2^- in the Fe/H_2O_2 system [21]. Moreover, more $Fe(OH)^{2+}$ radicals occur at pH 2 – 4, [22]. Compared to Fe^{2+}, $Fe(OH)^{2+}$ are more active and readily react with H_2O_2 to generate •OH radicals. At pH > 6, mostly $Fe(OH)_3$ and mostly $Fe(OH)_2$ from pH 5 to 7. While Fe^{3+} precipitates quickly to $Fe(OH)_3$ at high pH values, the reaction's treatment efficiency declines as pH rises because $Fe(OH)_3$ interaction with H_2O_2 does not produce •OH radicals. Iron is primarily found as ferrous iron at pH 2 – 3, which promotes the creation of •OH radicals with high oxygen activity. Additionally, a study conducted by Buxton revealed that the oxidation potential of hydroxyl radical •OH is 2.8 eV at pH 2 – 3 and 1.9 eV at pH 7 [23]. The ability of this radical to oxidize organic compounds decreases as the oxidation potential decreases.

Figure 2.e.f presents that pH did not significantly affect TCH removal using Fe/ $K_2S_2O_8$ with 20 mM $K_2S_2O_8$. TCH removal effectiveness at various pH ranges was approximately 88.1% and 95.2% for SBCG and SACG, respectively. This is slightly different in removal efficiency when pH was from 3 to 9. As a result, pH 3 was regarded as having the best efficiency, whereas pH 7 also performed the same as the former. Additionally, to avoid the chemical waste of pH adjustment, the recommended optimal pH was 7. This behavior corresponds to the production of •OH when $•SO_4^-$ combines with OH^- ion, as shown in Equation (1) [21]. Therefore, •OH radical can contribute to the breakdown of organic molecules in the Fe/$K_2S_2O_8$ system.

$$•SO_4^- + OH^- \Rightarrow SO_4^{2-} + •OH \quad (1)$$

3.2. Effects of the initial H_2O_2 or $K_2S_2O_8$ concentration

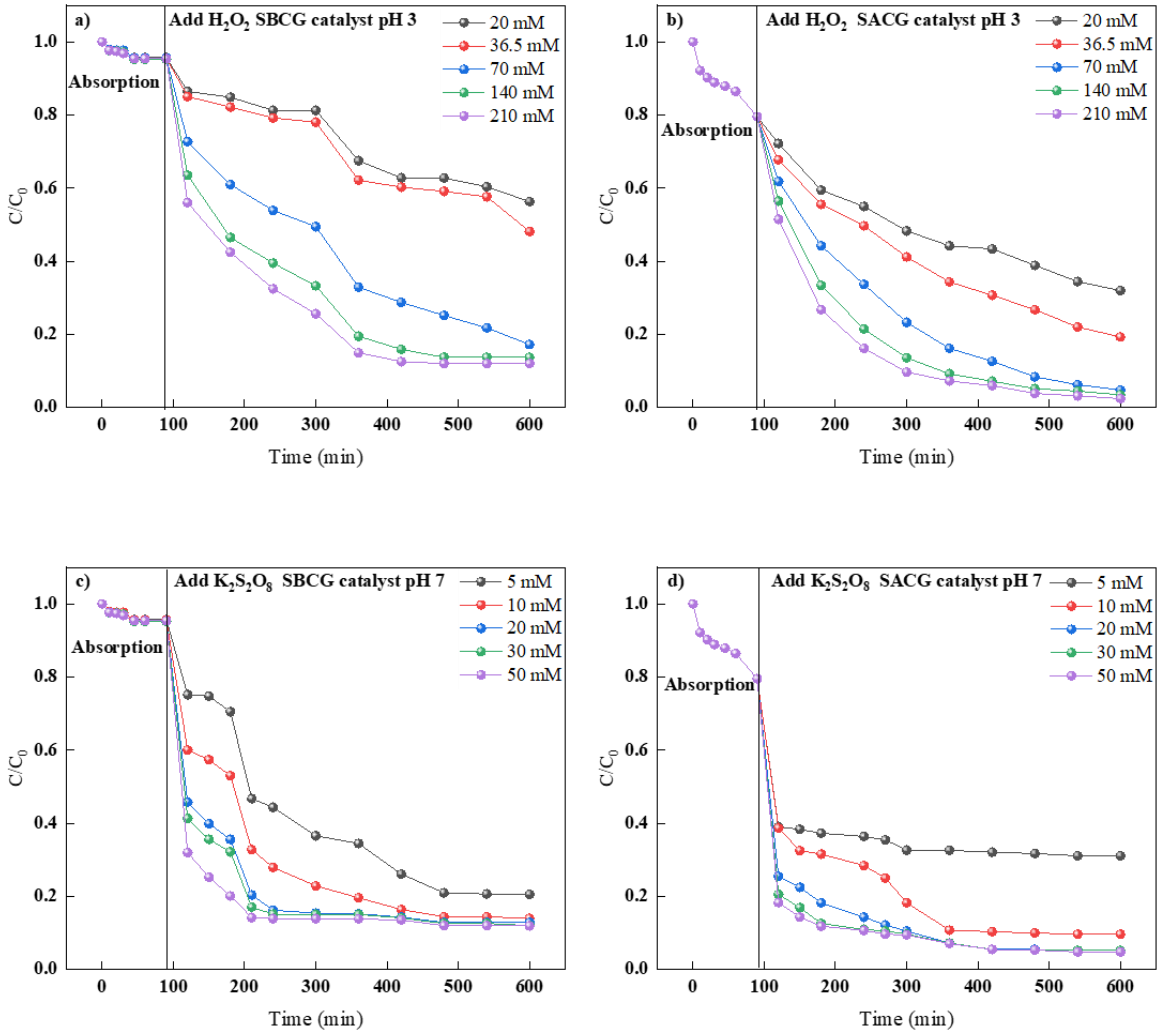

Figure 3. *Effect of the initial (a) H_2O_2 oxidation and (c) $K_2S_2O_8$ oxidation for SBCG catalyst; (b) H_2O_2 oxidation and (d) $K_2S_2O_8$ oxidation for SACG catalyst)*

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The initial concentration of oxidant H_2O_2 and $K_2S_2O_8$ was changed from 20 to 210 mM at the optimum pH of 3 and from 5 to 50 mM at pH 7, respectively to see its effect on the TCH removal. Figure 3.a, b shows the effect of oxidant level on TCH removal in the Fe/H_2O_2 system for SBCG and SACG catalysts. As can be seen, increasing the H_2O_2 value resulted in much higher TCH removal rates, which maximum at 210 mM H_2O_2 for both materials. For the SBCG catalyst, the TCH removals at 120 min were 13.3%, 15%, 27.3%, 36.5%, and 44% for 20 mM, 36.5 mM, 70 mM, 140 mM, and 210 mM, respectively. When H_2O_2 concentration was 70 mM, TCH elimination efficiency was 86.3%. Otherwise, the TCH removal efficiencies at 120 min were 27.8%, 32.3%, 38.2%, 43.6, and 48.6% for 20 mM, 36.5 mM, 70 mM, 140 mM, and 210 mM, respectively for SACG. With 70 mM H_2O_2, the TCH removal efficiency of was 95.3%. This is a result of an increase in H_2O_2 level concentration, more H_2O_2 functions as a scavenger for •OH radicals. H2O2 exhibits a greater inhibitory impact at higher concentrations compared to the optimal concentration. This study displayed similar results to previous research: when too many H_2O_2 residues formed $•HO_2$, it reduced the removal efficiency of pollutants, as shown in Equation (2). Optimizing oxidant value is critical because it not only affects the effectiveness of removal but also has the potential to raise the cost of the procedure [24].

$$H_2O_2 + •OH \Rightarrow •HO_2 + H_2O \quad (2)$$

Figure 3.2.c, d illustrates the impact of the concentration of oxidant on the elimination of TCH in a system consisting of Fe and $K_2S_2O_8$ at an optimal pH of 7. As indicated, increasing the $K_2S_2O_8$ concentration improves TCH removal efficiency since the dosage of $•SO_4^-$ radicals may increase as well. For the SBCG catalyst, the TCH removals at 120 min were 25.2%, 42.6%, 60.1%, 64.4%, and 74.8% for 5 mM, 10 mM, 20 mM, 30 mM, and 50 mM, respectively. At 20 mM $K_2S_2O_8$ concentration, TCH removal was 88.1%. Otherwise, the TCH removals at 120 min were 61.4%, 74.5%, 79.5%, and 81.7% for 5 mM, 10 mM, 20 mM, 30 mM, and 50 mM, respectively. At 20 mM $K_2S_2O_8$ dosage, TCH removal was 95.2% for the SBCG catalyst. This behavior corresponds to the formation of free radicals including $•SO_4^-$ and •OH radicals when using $K_2S_2O_8$. Abundant amount of $K_2S_2O_8$ can act as a scavenger for the principal oxidizing agents, in which $K_2S_2O_8$ vies with free radicals for the decomposition of organic molecules. Furthermore, sulfate and hydroxyl radicals have higher redox potential than that of the peroxy-disulfate radical [21], [25].

$$S_2O_8^{2-} + •SO_4^- \Rightarrow •S_2O_8^- + SO_4^{2-} \quad (3)$$

3.3. Residual of H_2O_2 and $K_2S_2O_8$ concentration

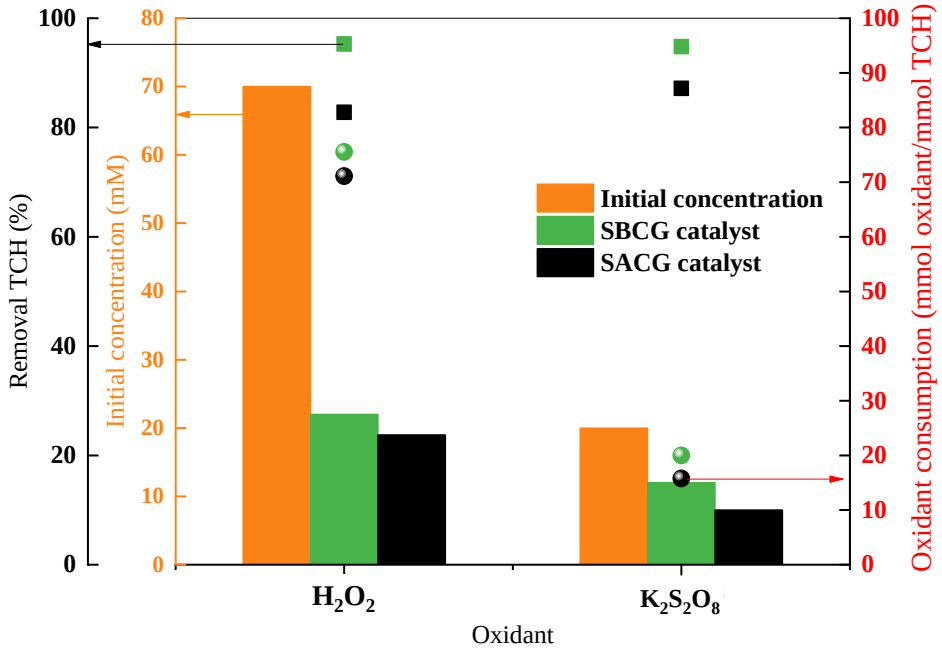

Figure 4. *Residual of H_2O_2 and $K_2S_2O_8$ concentration for SBCG and SACG catalyst at equilibrium*

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Figure 4 shows the residual number of oxidants after the equilibrium time of the two catalytic materials SBCG and SACG with an initial TCH concentration was 300 mg/L. The amount of oxidant used by SACG is slightly higher than that of SBCG. This can be explained by the fact that goethite content can be synthesized better on AC than on BC. At the same time, this was the same for the oxidant $K_2S_2O_8$ and with that the amount of $K_2S_2O_8$ used is less than the amount of H_2O_2. As can be shown, for both varieties of catalyst materials, the consumption of H_2O_2 was extremely high at 71.1 – 75.5 mmol oxidant/mmol TCH, while the consumption of $K_2S_2O_8$ was very low at only 15.6 – 20.0 mmol oxidant/mmol TCH, indicating the $K_2S_2O_8$ dose need to provided is much less than H_2O_2 dose. This result suggests the use of $K_2S_2O_8$ might be more economical than H_2O_2.

3.4. Catalyst characterization

According to the EDS analyses (Table 1), the iron content of the SBCG and SACG catalysts was1.48% and 3.49%, respectively. Due to the high degree of solid hydration experienced throughout the preparation process, which made it challenging to achieve the desired iron contents, there were minor differences between the samples' determined and predicted iron contents. After the reaction, the iron concentration of the SACG/H_2O_2 system was 3.06% and 3.00% for the SACG/$K_2S_2O_8$. However, only a minor quantity of iron concentration was lost. Additionally, a small amount of iron from the material was released into the reaction solution while the reaction was taking place at a pH 3.0 and pH 7 for SACG/H_2O_2 and SACG/$K_2S_2O_8$, respectively.

SEM morphological (Figure 5) observations demonstrate the surface morphology of three different types of materials (SACG, laden SACG/H_2O_2, and laden SACG/$K_2S_2O_8$). The surface of AC activated carbon (3306 m^2/g) benefits the iron particles of iron-containing sludge on the surface of activated carbon, generating a large contact area to increase the catalytic process' efficiency. After the synthesis of SACG material, the surface of activated carbon was bonded to the sludge, these particles of small size coated the surface of activated carbon.

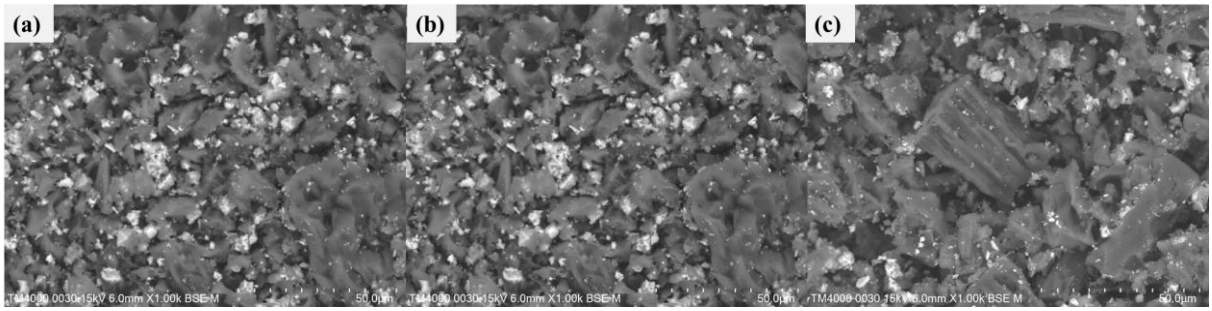

Figure 5. *SEM images of (a) SACG, (b) laden SACG/H_2O_2, and laden SACG/ $K_2S_2O_8$ catalyst*

Table 1. *Elemental composition of SACG, laden SACG/H_2O_2, and laden SACG/$K_2S_2O_8$ (in wt%)*

Materials	C	N	O	Si	Fe
SBCG	76.11%	2.57%	18.06%	1.78%	1.48%
SACG	76.56%	2.93%	17.02%	3.98%	3.49%
laden SACG/H_2O_2	75.29%	-	21.65%	10.88%	3.06%
laden SACG/$K_2S_2O_8$	76.94%	-	19.47%	0.27%	3.00%

4. Conclusions

This study assessed the efficacy of Fe/H_2O_2 and Fe/$K_2S_2O_8$ systems in removing TCH. The Fe/H_2O_2 system exhibited higher effectiveness at a pH of 3.0, whereas a pH of 7.0 was found to be suitable for the Fe/$K_2S_2O_8$ system. The catalytic material made from activated carbon (AC) and goethite had the highest treatment efficiency for TCH degradation at 500 ^oC for 2 hours. When comparing the catalytic materials, it is clear that both produce effective outcomes for the TCH removal process using the oxidants H_2O_2 and $K_2S_2O_8$. SBCG and SACG materials demonstrated the best TC decomposition

performance at 70 mM H_2O_2 in 10 hours and 20 mM $K_2S_2O_8$ in 7 hours under conditions including pH 3 (H_2O_2), pH 7 ($K_2S_2O_8$), temperature 30 ^oC, and catalyst concentration 0.5 g/L. The decomposition efficiency of SBCG and SACG was 82.8% and 95.3% for the oxidizing agent H_2O_2 and 87.2% and 94.8% for the oxidizing agent $K_2S_2O_8$, respectively. Moreover, the comparison results of SBCG and SACG in the TCH process efficiency displayed the well-being performance of both materials. However, SACG should be applied because its catalytic processing rate is higher than that of SBCG. Additionally, the SACG result also illustrated that the absorption capability was outstanding compared to the remaining one. On the other hand, the consumption of $K_2S_2O_8$ for TCH degradation was less than H_2O_2; therefore, the oxidant $K_2S_2O_8$ should be used for the treatment of TCH. This research should evaluate the mineralization of TCH by analyzing total organic carbon (TOC) as well as intermediate compounds through decomposition from free radicals •OH and $•SO_4^-$ in to clarify the ability to decompose TCH with oxidants H_2O_2 and $K_2S_2O_8$. It is also required to find out whether the material is recyclable and calculate the total amount of iron lost after each reaction to assess the economic feasibility and application.

Acknowledgments

The authors would like to gratefully support from Ho Chi Minh City University for the apparatus and instrument for doing experiments.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] K. Samal, S. Mahapatra, and M. H. Ali, "Pharmaceutical wastewater as emerging contaminants (EC): Treatment technologies, impact on environment and human health," *Energy Nexus*, vol. 6, p. 100076, 2022.
[2] M. Tannoury and Z. Attieh, "The influence of emerging markets on the pharmaceutical industry," *Current Therapeutic Research*, vol. 86, pp. 19-22, 2017.
[3] T. Cherian, C. Ragavendran, S. Vijayan, S. Kurien, and W. J. G. M. Peijnenburg, "A review on the fate, human health and environmental impacts, as well as regulation of antibiotics used in aquaculture," *Environmental Advances*, p. 100411, 2023.
[4] Y. Dai *et al.*, "A review on pollution situation and treatment methods of tetracycline in groundwater," *Separation Science and Technology*, vol. 55, no. 5, pp. 1005-1021, 2020.
[5] L. Wang *et al.*, "Degradation of tetracycline hydrochloride (TCH) by active photocatalyst rich in oxygen vacancies: Performance, transformation product and mechanism," *Applied Surface Science*, vol. 589, p. 152902, 2022.
[6] X. Peng, J. Cao, B. Xie, M. Duan, and J. Zhao, "Evaluation of degradation behavior over tetracycline hydrochloride by microbial electrochemical technology: Performance, kinetics, and microbial communities," *Ecotoxicology and Environmental Safety*, vol. 188, p. 109869, 2020.
[7] Q. Li *et al.*, "Catalytic degradation of antibiotic by Co nanoparticles encapsulated in nitrogen-doped nanocarbon derived from Co-MOF for promoted peroxymonosulfate activation," *Chemical Engineering Journal*, vol. 429, p. 132269, 2022.
[8] J. Ye, M. Zhou, Y. Le, B. Cheng, and J. Yu, "Three-dimensional carbon foam supported MnO2/Pt for rapid capture and catalytic oxidation of formaldehyde at room temperature," *Applied Catalysis B: Environmental*, vol. 267, p. 118689, 2020.
[9] Z. Zhang *et al.*, "Effective and structure-controlled adsorption of tetracycline hydrochloride from aqueous solution by using Fe-based metal-organic frameworks," *Applied Surface Science*, vol. 542, p. 148662, 2021.
[10] A. J. Sayyed, D. V. Pinjari, S. H. Sonawane, B. A. Bhanvase, J. Sheikh, and M. Sillanpää, "Cellulose-based nanomaterials for water and wastewater treatments: A review," *Journal of Environmental Chemical Engineering*, vol. 9, no. 6, p. 106626, 2021.
[11] S. O. Ganiyu, S. Sable, and M. G. El-Din, "Advanced oxidation processes for the degradation of dissolved organics in produced water: A review of process performance, degradation kinetics and pathway," *Chemical Engineering Journal*, vol. 429, p. 132492, 2022.
[12] T. Yu, H. Chen, T. Hu, J. Feng, W. Xing, L. Tang, and W. Tang, "Recent advances in the applications of encapsulated transition-metal nanoparticles in advanced oxidation processes for degradation of organic pollutants: A critical review," *Applied Catalysis B: Environmental*, vol. 342, p. 123401, 2024.
[13] Y. Guo *et al.*, "Goethite/biochar-activated peroxymonosulfate enhances tetracycline degradation: Inherent roles of radical and non-radical processes," *Science of The Total Environment*, vol. 783, p. 147102, 2021.
[14] J. Liu, C. Peng, and X. Shi, "Preparation, characterization, and applications of Fe-based catalysts in advanced oxidation processes for organics removal: A review," *Environmental Pollution*, vol. 293, p. 118565, 2022.
[15] M. O. Akharame *et al.*, "Beta-FeOOH nanoparticles: A promising nano-based material for water treatment and remediation," *Journal of Nanoparticle Research*, vol. 23, pp. 1-33, 2021.
[16] T. T. Loc, N. D. Dat, and H. N. Tran, "Nano-sized hematite-assembled carbon spheres for effectively adsorbing paracetamol in water: Important role of iron," *Korean Journal of Chemical Engineering*, vol. 40, no. 12, pp. 3029-3038, 2023.
[17] P. T. T. Ninh, N. D. Dat, M. L. Nguyen, N. T. Dong, H. P. Chao, and H. N. Tran, "Two-stage preparation of highly mesoporous carbon for super-adsorption of paracetamol and tetracycline in water: Important contribution of pore filling and π-π interaction," *Environmental Research*, vol. 218, p. 114927, 2023.

[18] R. T. Rasheed, H. S. Mansoor, and R. R. Al-Shaikhly, "Preparation and a new method to determinate catalase mimics activity of MnO2, Fe2O3 and MnO2: Fe2O3," in *AIP Conference Proceedings*, AIP Publishing, 2020.
[19] Y. Liu *et al.*, "Current analytical methods for the determination of persulfate in aqueous solutions: A historical review," *Chemical Engineering Journal*, vol. 416, p. 129143, 2021.
[20] M. R. C. Díaz, E. C. López, A. C. Naranjo, and M. L. R. Cervantes, "On the textural and crystalline properties of Fe-carbon xerogels. Application as Fenton-like catalysts in the oxidation of paracetamol by H2O2," *Microporous and Mesoporous Materials*, vol. 237, pp. 282-293, 2017.
[21] A. A. Babaei and F. Ghanbari, "COD removal from petrochemical wastewater by UV/hydrogen peroxide, UV/persulfate and UV/percarbonate: Biodegradability improvement and cost evaluation," *Journal of Water Reuse and Desalination*, vol. 6, no. 4, pp. 484-494, 2016.
[22] Y. Yang, P. Wang, S. Shi, and Y. Liu, "Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater," *Journal of Hazardous Materials*, vol. 168, no. 1, pp. 238-245, 2009.
[23] G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, "Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O⁻ in aqueous solution," *Journal of Physical and Chemical Reference Data*, vol. 17, no. 2, pp. 513-886, 1988.
[24] N. B. Bermúdez, M. G. Avendaño, I. L. Touriño, A. C. Naranjo, and M. L. R. Cervantes, "Fe-Cu doped multiwalled carbon nanotubes for Fenton-like degradation of paracetamol under mild conditions," *Nanomaterials*, vol. 10, no. 4, p. 749, 2020.
[25] S. Zong, X. Xu, G. Ran, and J. Liu, "Comparative study of atrazine degradation by magnetic clay activated persulfate and H2O2," *RSC Advances*, vol. 10, no. 19, pp. 11410-11417, 2020.

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