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ACTIVATION OF PEROXYMONOSULFATE BY COBALT-IMPREGNATED BIOCHAR (CO-SCG) FOR EFFICIENT DEGRADATION OF TETRACYCLINE IN WATER

Nguyen Van Truc[1*], Nguyen Thanh Binh[2], Vo Thi Dieu Hien[3], Cheng-Di Dong[2]

[1]Department of Environmental Sciences, Saigon University, Ho Chi Minh City, Vietnam.
Email: truc1021006@gmail.com
[2]Department of Marine Environmental Engineering, National Kaohsiung University of Science and Technology, Kaohsiung, Taiwan; ntbinh179@nkust.edu.tw; cddong@nkust.edu.tw
[3]Faculty of Environmental and Food Engineering, Nguyen Tat Thanh University, HCM City, Vietnam.
Email: hien.ic.tracodi@gmail.com
Corresponding authors: E-mail address: truc1021006@gmail.com

ABSTRACT

Cobalt-impregnated spent coffee ground biochar (Co-SCG) was synthesized and applied for tetracycline (TC) removal from water. The results showed that TC was almost completely degraded in 25 min with a rate constant of 17.78 x 10^{-2} min^{-1} under the following optimal condition: TC concentration of 0.2 mM, PMS concentration of 0.6 mM, Co-SCG dosage of 100 mg L^{-1}, and pH of 7.0. Co-SCG was characterized for surface properties by SEM, TEM, HRTEM, and BET. The concentration of 16 PAHs in Co-SCG biochar was studied also. Results demonstrated that Co-SCG was an effective eco-friendly material for the removal of tetracycline from water.

Keywords: Tetracycline; biochar; peroxymonosulfate; PAHs; degradation.

1. INTRODUCTION

Advanced oxidation processes (AOPs) are known to be effective for degrading a wide list of organic compounds through reaction with hydroxyl radical ($OH^{\bullet}$) and sulfate radical ($SO_4^{\bullet-}$). Sulfate radical-based AOPs (SR-AOPs), using persulfate or peroxymonosulfate (PMS) oxidant, have received much attention in environmental applications (Guo et al., 2013). Recently, there are intensive interests on Oxone, the commercial name of PMS (2 $KHSO_5$. $KHSO_4$. K_2SO_4), an eco-friendly oxidant and a source of $SO_4^{\bullet-}$ (Sun et al., 2009). More importantly, sulfate radicals can be generated from PMS through catalytic activation by transition metal ions. For the activation of Oxone, Co^{2+} is believed to be the best candidate compared with Ag^{+}, Ce^{3+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+} (Sun et al., 2009). Co^{2+} coupled with PMS can lead to superior sulfate production and highly effective removal of organic contaminants (Anipsitakis and Dionysiou, 2004).

Coffee is one of the most abundant agricultural product and second in the list of most traded commodity worldwide; consequently, it contributes to large amount of coffee wastes as spent coffee ground (SCG) to landfill every year. Biochar derived from spent coffee ground has received much attention recently for its economy and promising applications in environmental treatment technology (Nguyen et al., 2019). In addition, biochar exhibits intriguing properties such as abundant surface functionality, porosity and large surface areas; which are highly desirable for biochar destined to be used for the rational design of functional materials as catalysts or adsorbents. Typically, biochar can be utilized as promising support to disperse and stabilize nanoparticles (NPs) to enhance their reactivity for catalytic reactions (Pastor Navarro et al., 2009). Therefore, the unique architecture of biochar and the outstanding catalytic performance of Co NPs provide a great impetus use of biochar as promising support to judiciously decorate Co NPs for the formation of highly active and green heterogeneous catalyst. Tetracycline (TC), an emerging organic pollutant, is frequently detected in the water environment. TC can exhibit severe environmental problems including ecological risks and human health, and develop antibiotic-resistant pathogens (Pastor

Navarro et al., 2009). In this work, cobalt-impregnated spent coffee ground biochar (Co-SCG) has been synthesized and used it as a catalyst for PMS activation and the degradation of TC as the model compound. The TC degradation efficiency of Co-SCG in the presence of PMS activator was evaluated. Co-SCG was characterized for surface properties by SEM, TEM, HRTEM, and BET. Parameters such as initial TC concentration, biochar dosage, PMS loading, the initial pH of solution were studied.

2. MATERIALS AND METHODS

Chemicals

All chemicals used, namely, tetracycline hydrochloride (99.9% purity), methanol (HPLC grade, ≥ 99.9% purity), acetonitrile (HPLC grade, ≥ 99.9% purity), oxalic acid dehydrate (98% purity), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) (98% purity), and Oxone ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$ (98% purity) were provided by Merck & Co., Inc. (Kenilworth, N.J. USA).

3. RESULTS AND DISCUSSION

Influence of operating parameters on TC degradation

Effect of catalyst dose

The TC removal efficiency increased significantly from 35 to 85% when the Co-SCG biochar concentration was increased from 10 to 100 mg L^{-1}, in 25 min. Increasing biochar dosage may enhance the interaction between adsorbents and adsorbates, resulting in increasing TC adsorption. Additionally, increasing Co-SCG dosage favored the generation of sulfate radicals, which led to increasing TC degradation (Khataee et al., 2015). However, when the Co-SCG loading was increased from 100 to 300 mg L^{-1}, TC degradation was decreased from 85 to 67%. Further increase in biochar dose might overproduce oxidizing radicals, which promoted interaction among the free radicals (Eq. 2 - 4) and led to decrease in the decomposition of pollutants. Therefore, TC decomposition efficiency decreased with increasing biochar doses (Fan et al., 2017).

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (2)$$

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \quad (3)$$

$$SO_4^{\bullet -} + OH^{\bullet} \rightarrow HSO_5^{-} \quad (4)$$

Effect of PMS dose

The activation of PMS by metal ions and metal oxide was based on Eq. (5) (Wang and Wang, 2018), which shows the production of sulfate radicals ($SO_4^{\bullet -}$). It is known that sulfate radical has a higher redox potential (2.5 - 3.1 V) than that of hydroxyl radical (1.8 - 2.7 V). Therefore, sulfate radical plays an important role in TC degradation.

$$HSO_5^{-} + M^n \rightarrow M^{n+1} + OH^{-} + SO_4^{\bullet -} \quad (5)$$

The TC degradation significantly was increased from 46 to 97% with PMS concentration being increased from 0.1 to 0.6 mM. The presence of PMS produced reactive radicals, which resulted in higher TC removal. Based on the above results, 0.6 mM of PMS was used in all further TC degradation experiments.

Effect of initial TC concentration

TC was removed completely in less than 10 min at an initial concentration of 0.1 mM; whereas complete TC removal occurred after 25 min with the initial concentration being increased from 0.2 to 0.6 mM. At the same Co-SCG catalytic dosage and PMS concentration, the amount of sulfate radical formed was unchanged. As the TC concentration increased, the production of free radicals was not sufficient for TC decomposition, leading to a reduction in TC removal efficiency (Luo et al., 2019). Our result clearly demonstrated that TC degradation over Co-SCG/PMS could reach 97% in 25 min at the initial TC concentration of 0.2 mM.

Effect of initial pH

The influence of initial pH on the TC removal efficiency was conducted in the pH range from 3 to 11. The highest TC degradation was achieved at pH of 9 when TC seemed to be removed completely in less than 15 min. At pH 7, TC removal reached 99% after 25 min. It is observed that the extent of TC degradation increased sharply as the initial pH value was increased from 3 to 9. However, the extent of TC degradation significantly was decreased when the pH value was further increased to 11. At acidic condition, there was formation of strong hydrogen bonds between H^+ and O-O in PMS, which led to inhibit the interaction between PMS and Co-SCG, and subsequent decrease in TC degradation (Du et al., 2016). In addition, the formation of Co-OH complexes on the Co-SCG surface may impede the activation capacity of PMS. Increase in pH could weaken the hydrogen bonds. As a result, the interaction of PMS and Co-SCG became stronger, meaning more sulfate and hydroxyl radicals production and increase in TC degradation (Fan et al., 2017). However, it is known that more divalent PMS anions were formed at strongly alkaline condition (e.g. pH 11) (Tan et al., 2014). The negative PMS anions could repel the negatively charged Co-SCG catalyst and subsequent decrease in TC degradation. Similarly, Su et al. (2013) reported that the degradation of organic pollutants over $Co_xFe_{3-x}O_4$/PMS was low under strongly acidic and alkaline conditions.

4. CONCLUSIONS

The feasibility of tetracycline oxidation by Cobalt-impregnated biochar (Co-SCG) via heterogeneous activation of peroxymonosulfate (PMS) was studied. The highest percentage of TC degradation was obtained at the TC concentration of 0.2 mM, PMS concentration of 0.6 mM, Co-SCG dosage of 100 mg L^{-1}, and pH 7.0. The findings demonstrated that Co-SCG developed in this study could be an efficient catalyst for PMS activation in advanced oxidation processes for the removal of TC from water.

REFERENCES

[1]. Anipsitakis, G.P., Dionysiou, D.D. (2004). Radical generation by the interaction of transition metals with common oxidants. Environ. Sci. Technol., 38(13), 3705-3712. https://doi.org/10.1021/es035121o.

[2]. Du, Y., Ma, W., Liu, P., Zou, B., Ma, J. (2016). Magnetic $CoFe_2O_4$ nanoparticles supported on titanate nanotubes ($CoFe_2O_4$/TNTs) as a novel heterogeneous catalyst for peroxymonosulfate activation and degradation of organic pollutants. J. Hazard. Mater., 308, 58-66. https://doi.org/10.1016/j.jhazmat.2016.01.035.

[3]. Fan, Y., Ma, W., He, J., Du, Y. (2017). $CoMoO_4$ as a novel heterogeneous catalyst of peroxymonosulfate activation for the degradation of organic dyes. RSC. Adv., 7(57), 36193-36200. 10.1039/C7RA04761D.

[4]. Guo, W., Su, S., Yi, C., Ma, Z. (2013). Degradation of antibiotics amoxicillin by Co_3O_4 ‐ catalyzed peroxymonosulfate system. Environ. Prog. Sustain. Energy, 32(2), 193-197. https://doi.org/10.1002/ep.10633.

[5]. Khataee, A., Salahpour, F., Fathinia, M., Seyyedi, B., Vahid, B. (2015). Iron rich laterite soil with mesoporous structure for heterogeneous Fenton-like degradation of an azo dye under visible light. J. Ind. Eng. Chem., 26, 129-135. https://doi.org/10.1016/j.jiec.2014.11.024.

[6]. Luo, H., Xie, Y., Niu, J., Xiao, Y., Li, Y., Wang, Y., Zhang, Y., Xie, T. (2019). Cobalt ‐ doped biogenic manganese oxides for enhanced tetracycline degradation by activation of peroxymonosulfate. J. Chem. Technol. Biotechnol., 94(3), 752-760. https://doi.org/10.1002/jctb.5820.

[7]. Nguyen, V.T., Nguyen, T.B., Chen, C.W., Hung, C.M., Vo, T.D.H., Chang, J.H., Dong, C.D. (2019). Influence of pyrolysis temperature on polycyclic aromatic hydrocarbons production and tetracycline adsorption behavior of biochar derived from spent coffee ground. Bioresour. Technol., 284, 197-203. https://doi.org/10.1016/j.biortech.2019.03.096.

[8]. Pastor Navarro, N., Maquieira, Á., Puchades, R. (2009). Review on immunoanalytical determination of tetracycline and sulfonamide residues in edible products. Anal. Bioanal. Chem., 395(4), 907-920. 10.1007/s00216-009-2901-y.

[9]. Su, S., Guo, W., Leng, Y., Yi, C., Ma, Z. (2013). Heterogeneous activation of Oxone by CoxFe3−xO4 nanocatalysts for degradation of rhodamine B. J. Hazard. Mater., 244-245, 736-742. https://doi.org/10.1016/j.jhazmat.2012.11.005.

[10]. Sun, J., Li, X., Feng, J., Tian, X. (2009). Oxone/Co^{2+} oxidation as an advanced oxidation process: Comparison with traditional Fenton oxidation for treatment of landfill leachate. Water Res., 43(17), 4363-4369. https://doi.org/10.1016/j.watres.2009.06.043.

[11]. Tan, C., Gao, N., Deng, Y., Deng, J., Zhou, S., Li, J., Xin, X. (2014). Radical induced degradation of acetaminophen with Fe_3O_4 magnetic nanoparticles as heterogeneous activator of peroxymonosulfate. J. Hazard. Mater., 276, 452-460. https://doi.org/10.1016/j.jhazmat.2014.05.068.

[12]. Wang, J., Wang, S. (2018). Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. Chem. Eng. J., 334, 1502-1517. https://doi.org/10.1016/j.cej.2017.11.059.