Natural lead-enriched biochar modifies TiO₂ photocatalytic activation of sodium persulfate to degrade 2,4-dichlorophenol

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Abstract. Due to the rapid development of the modern chemical industry, a large amount of chlorophenol pollutants remain in the environment. It poses a serious threat to the ecological environment and human health. Advanced oxidation technologies (AOPs) have the characteristics of mild reaction conditions and strong oxidation capacity, and are currently recognized as safe and effective pollutant treatment technologies. In this study, natural lead-rich biochar materials were used to activate sodium persulfate to degrade 2,4-dichlorophenol, and natural lead-rich biochar modified TiO₂ photocatalytically degraded 2,4-dichlorophenol. Then, using natural lead-rich metal biochar/TiO₂ material, photocatalysis combined with active sodium persulfate to degrade 2,4-dichlorophenol. The experimental results show that the combination of photocatalysis and activated sodium persulfate reaction can completely degrade 100 mg/L 2,4-dichlorophenol under UV light for 3 h, and the degradation efficiency is much higher than the sum of the two separate reactions. Quenching experiments show that SO₄•⁻ radicals play the most important role in the three free radicals (SO₄•⁻, •OH and •O₂⁻) in the advanced oxidation combination system. Finally, the reaction mechanism of the two advanced oxidation combined systems are speculated.

1 Introduction

Human chemical production and the use of pesticides have lead to a large number of chlorophenol organic pollutants remaining in the environment, causing serious threat to the ecological environment and people's health [1]. Chlorophenolic compounds (CPs) have toxic effects on many microorganisms, and they are difficult to be decomposed by microorganisms and exist in the environment for a long time, which are a kind of hard-to-degrade organic pollutants. CPs are slightly soluble in water and easily soluble in organic solvents. The more chlorine atoms in the CPs benzene ring, the less solubility it has in water [2]. The toxicity of CPs increases with the increase of the number of chlorine atoms on the benzene ring, and the meta-chloro substituent has a significantly higher effect on its toxicity than the ortho-chloro substituent [3]. The biotoxicity, bioenrichment and teratogenic, carcinogenic and mutagenic effects of CPs cause serious harm to the ecosystem [4]. The U.S. Environmental Protection Agency has long listed chlorophenols as a priority pollutant control [5]. China has also listed it in the category of pollutants that need key prevention and control. At present, the main methods for treating chlorophenol pollutants in water are biological method [6], adsorption method [7], advanced oxidation method [8].

The advanced oxidation technology based on sulfate radicals (SO₄•⁻) has the advantages of high efficiency and wide application range, and has great application potential in the field of environmental restoration [9]. Sulfate radicals can be generated by the activation of persulfate. The main methods of activating persulfate include UV light activation [10], thermal activation [11], transition metal activation [12] and activated carbon activation [13], etc. In terms of activating persulfate, variable valence metals have the characteristics of simple reaction system, mild reaction conditions, and low energy consumption, and have received widespread attention. Xia et al. [14] studied the degradation of phenol with persulfate activated by pyrite, and the phenol solution with a concentration of 2 μmol/L can be completely removed by the reaction for 20 min. Photocatalysis has the characteristics of high activity, stable chemical properties, non-toxic to organisms and wide sources of raw materials [15]. The photocatalytic reaction using TiO₂ semiconductor as the photocatalyst has been widely used in the degradation of organic pollutants [16]. Although the TiO₂ photocatalyst has a better application effect, it also has a poor dispersion effect [17], a large forbidden band width has a poor utilization of daylight, and hole-electron pairs are also recombined [18]. Therefore, this study also modified TiO₂ with materials.

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Siberian iris is a wetland plant that has a strong ability to accumulate heavy metals. The plant can be used to repair heavy metal pollution in wetlands. In this experiment, a nutrient solution containing lead metal was used to cultivate Siberian iris seedlings, so that lead metal was naturally absorbed into the plant. Regularly replace the nutrient solution, and obtain lead-rich metal biomass after 2 months of cultivation. The lead-rich metal biomass is dried and calcined to obtain a natural lead-rich metal biochar (Pb@C) material. The material can not only be directly used to activate sodium persulfate (PS) to degrade pollutants, but also can load modified TiO₂ semiconductors to make it have stronger photocatalytic performance.

In this study, natural lead-rich biochar was used to activate sodium persulfate to degrade 2,4-dichlorophenol (2,4-DCP); natural lead-rich biochar modified TiO₂ (Pb@C/TiO₂) was used to photocatalyze degrade 2,4-DCP. There are few studies on the combination of photocatalysis and persulfate activation. In this experiment, the two reactions were combined, using Pb@C/TiO₂ photocatalysis and activation of sodium persulfate to degrade 2,4-DCP. The redox effect of lead metal in the material can promote the transfer of electrons, and the doping of lead oxide with TiO₂ can increase the oxygen vacancy of TiO₂. Biochar can prevent the material from producing agglomeration effect, accelerate the transfer of electrons, and adsorb and degrade a small amount of organic pollutants [19].

2 Materials and methods

2.1 Experimental materials

Biomass (Siberian iris that is naturally rich in lead metal). All the chemical reagents, including tetra-butyl titanate (TBT), 2,4-dichlorophenol, ethanol, sodium persulfate, methanol, tert-butanol (TBA) and p-benzoquinone (p-BQ) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

2.2 Preparation of natural lead-rich metal biochar

A certain amount of cultivated lead-rich metal biomass is put into a small crucible, and the crucible is put into a tubular muffle furnace for pyrolysis in a nitrogen atmosphere. The heating rate is 10 °C/min, the final pyrolysis temperature is 500 °C, and the final temperature residence time is 120 min. After the pyrolysis is completed, natural cooling is performed. When the temperature drops to room temperature, the sample is taken out and weighed. Wash the sample with ultrapure water, when its pH drops to 7, pass a 0.45 µm filter membrane, and then place it in a drying box for drying at a temperature of 60 °C. After drying for 24 h, take it out and place it in an agate mortar Medium grinding, then passing through a 100-mesh sieve, and finally put it into a sealed bag for storage.

2.3 Synthesis of natural lead-rich biochar modified TiO₂ material

In this experiment, sol-gel method was used to synthesize biochar/TiO₂ photocatalytic material. First measure 40 mL of absolute ethanol and 0.85 mL of tetrabutyl titanate into a 250 mL beaker and stir vigorously for 30 min. Observe whether the liquid in the beaker produces flocculent precipitates. If not, proceed with the experiment. If precipitation occurs, reconfigure the solution. Add 1 g of biochar to the beaker and mix, then slowly add 0.18 mL of deionized water to the beaker (keep stirring during this period). Cover with plastic wrap and stir for 8 h. After the stirring is completed, the beaker is placed in a drying box and dried at 105°C. After drying, it was calcined in a high-temperature tube furnace under nitrogen and anaerobic conditions at 500°C for 2 h to prepare a catalyst (the heating rate was 1 °C/min).

2.4 Degradation experiment

Firstly, 1 L of 100 mg/L of 2,4-dichlorophenol solution and 1 L of 10 g/L of sodium persulfate solution were prepared for use.

Select a 250 mL jacketed beaker and place it on the magnetic stirrer and add the rotor. Select a 250 mL jacketed beaker and place it on the magnetic stirrer, add the rotor, add 0.02 g of lead-rich biochar/TiO₂, add the prepared 200 mL 2,4-dichlorophenol solution, and place it in the dark for constant temperature magnetic stirring. The temperature is 25°C and the rotation frequency is 500 r/min. After the reaction progresses (0 min, 10 min, 30 min, 60 min, 90 min), use a syringe to draw 1 mL of liquid and mix it with methanol 1:1, pass through a 0.22 µm filter membrane, and test the 2,4-dichlorophenol in the solution concentration. After the dark stirring adsorption experiment is completed, put the magnetic stirrer and the beaker directly under the high-pressure mercury lamp or fluorescent lamp, and add 2 mL of sodium persulfate solution. After connecting the cooling water device of the jacketed beaker to cover the reaction system, turn on the power of the lamp. The reaction proceeded (10 min, 20 min, 40 min, 60 min, 90 min, 120 min). 1 mL of liquid was drawn with a syringe and mixed with methanol 1:1, passed through a 0.22 µm filter membrane, and filled into a liquid phase vial for testing.

In this experiment, the concentration of 2,4-dichlorophenol in solution was measured by high performance liquid chromatography-mass spectrometry (HPLC-MS, 1200, Agilent, USA). The detection wavelength is 200 nm. The mobile phase was a mixed solution of methanol and water (70:30, v/v) at a flow rate of 1.0 mL/min.

3 Results and discussion

3.1 Pb@C activates PS to degrade 2,4-DCP

Figure 1 is the comparison of degradation efficiency of Pb@C, C activated sodium persulfate and sodium persulfate alone degraded 2,4-DCP. First add the biochar material and stir for 90 min to make the material reach the state of adsorption equilibrium. Then add sodium persulfate to degrade for 9 h. Through experimental research, it is found that the degradation efficiency of Pb@C, C activated sodium persulfate and sodium persulfate alone on 50 mg/L 2,4-DCP in 10.5 h under the combined action of adsorption and degradation are 76.68%, 20.66% and 6.10%, respectively. Using sodium persulfate alone to degrade 2,4-DCP has almost no effect, indicating that sodium persulfate is not easily activated under natural conditions. Biochar can activate sodium persulfate to a certain extent, which may be due to the functional groups and π electron pairs contained in biochar [20]. Pb@C activates sodium persulfate to degrade 2,4-DCP best, because the variable valence metal undergoes redox reactions during the degradation process to generate electrons, which promotes sodium persulfate to produce more $\text{SO}_4^{\bullet-}$. The adsorption and degradation effect of Pb@C is also very good, indicating that it has a larger specific surface area. In summary, Pb@C has a good effect in activating sodium persulfate to degrade 2,4-DCP.

Figure 1. Pb@C, C activated PS and PS alone in the degradation of 2,4-DCP efficiency.

3.2 Pb@C/TiO₂ photocatalysis and activated PS to degrade 2,4-DCP

Figure 2 is a chart of the degradation efficiency of Pb@C/TiO₂ photocatalytic degradation of 2,4-DCP under UV light and degradation of 2,4-DCP by Pb@C/TiO₂ activate sodium persulfate under UV light. Before the reaction, put Pb@C/TiO₂ into the solution and stir for 90 min to make the material reach the state of adsorption equilibrium. Then transfer the beaker to UV light to degrade for 150 min. In the experiment of photocatalytic activation of sodium persulfate, sodium persulfate was added after stirring and then transferred to

UV light. Through the comparison of the degradation curves in the figure, it can be found that the Pb@C/TiO₂ photocatalyst can degrade 100 mg/L of 2,4-DCP by 95.40% under UV light for 4 h. The degradation rate of 100 mg/L 2,4-DCP by Pb@C/TiO₂ plus sodium persulfate for 3 h under UV light was 100%. Compared with the photocatalytic degradation of 2,4-DCP, the combined system can save 60 min, and it can save more than ten hours of degradation of 2,4-DCP by using metal-activated sodium persulfate alone. Photocatalysis combined with activated sodium persulfate has the highest degradation efficiency, which may be because both metal and UV light can activate sodium persulfate, leading to more active free radicals are generated in the solution.

Figure 2. Pb@C/TiO₂ photocatalysis under UV light and Pb@C/TiO₂ activates PS under UV light to degrade 2,4-DCP efficiency.

3.3 Photocatalytic activation of PS to degrade 2,4-DCP under daylight

Figure 3 is a chart showing the degradation efficiency of using Pb@C/TiO₂ to activate sodium persulfate to degrade 100 mg/L of 2,4-DCP under UV light and daylight. The reaction completely degraded 100mg/L of 2,4-DCP in 3 h under UV light. Although the degradation efficiency under daylight is not as high as under UV light, it also degrades 71.40% of 100 mg/L 2,4-DCP in 4 h. The high degradation efficiency under UV light may not only be good for photocatalysis, but UV light can also activate sodium persulfate and generate more $\text{SO}_4^{\bullet-}$ free radicals. The degradation efficiency under daylight is also higher than that of ordinary photocatalysis. If it is used to treat low concentration organic pollutants, it is believed that it will have better results and can save energy consumption.

Figure 3. Pb@C/TiO₂ photocatalytic activation of PS on the degradation efficiency of 2,4-DCP.

3.4 Free radical quenching experiment

Advanced oxidation technology mineralizes organic pollutants into water and carbon dioxide by generating strong oxidizing free radicals [21]. Figure 4 is a free radical quenching experiment of Pb@C/TiO₂ photocatalytic activation of sodium persulfate to degrade 2,4-DCP. This experiment produced three kinds of active free radicals: SO₄•, hydroxyl radical (•OH) and superoxide radical (•O₂⁻). Three different quenchers were added to explore the free radicals with the strongest effect. Add methanol to quench SO₄• radicals, tert-butanol quenches •OH radicals, p-benzoquinone quenches •O₂⁻ radicals. The degradation efficiencies of 100 mg/L 2,4-DCP were 37.50%, 47.08% and 71.21% respectively after adding three kinds of quenchers. The reaction efficiency is low after the loss of SO₄• free radicals, indicating that SO₄• free radicals have played the greatest role in the reaction. During the reaction, the reduction of SO₄• radicals will also affect the number of •OH radicals.

Figure 4. Degradation efficiency of 2,4-DCP by Pb@C/TiO₂ photocatalytic activation of PS after adding quencher: a, No scavenger; b, Add methanol; c, Add TBA; d, Add p-BQ.

The inferred reaction equation of Pb@C/TiO₂ photocatalytic activation of sodium persulfate:

The irradiation of UV light will separate holes and electrons in TiO₂, and will also excite persulfate ions to produce SO₄•. Holes react with water and hydroxide ions to generate •OH. The reaction of electrons with oxygen produces •O₂⁻. Elemental lead reacts with water to produce divalent lead and hydroxide ions. Lead oxide and the resulting divalent lead react with persulfate ions to generate tetravalent lead and SO₄•. The electrons obtained by tetravalent lead will be reduced to divalent lead. The reaction between SO₄• and hydroxide ions produces •OH. The above reaction equation is only a certain inference of the advanced oxidation reaction process, and more complicated reactions may occur.

4 Conclusions

This experimental study shows that the efficiency of using natural lead-rich metal biochar to activate sodium persulfate to degrade 2,4-dichlorophenol is not high. The photocatalytic efficiency of natural lead-rich metal biochar/TiO₂ is relatively high. Since UV light can also activate sodium persulfate, the combination of two advanced oxidation technologies is considered. The experimental results found that the combination of these two advanced oxidation technologies indeed show better degradation performance. The degradation of 100 mg/L 2,4-dichlorophenol under the natural lead-rich biochar/TiO₂ photocatalytic conditions in 4 h degraded 95.40%. By contrast, it only takes 3 h to degrade 100 mg/L 2,4-dichlorophenol in a photocatalytic system with sodium persulfate added. In addition, the combination of two advanced oxidation technologies under daylight also produced good results, degrading 71.40% of 100 mg/L 2,4-dichlorophenol in 4 h. Through the quenching experiment to explore the free radicals of the reaction system, it can be seen that SO₄• radicals play an important role in this reaction system. Finally, the reaction mechanism of the combined system of natural lead-rich biochar/TiO₂ photocatalysis and activated sodium persulfate is speculated. Electrons and holes are the most important carriers in the reaction system, and they affect the speed of the reaction. This study provides a good research idea for subsequent research on the degradation of refractory organic pollutants.

References

1. M. Alawi, M. Masaad, M. Al-Hussaini. *Environ. Monit. Assess.*, **190**, 470 (2018)
2. M. Czaplicka. *Sci. Total Environ.*, **322**, 21-39 (2004)
3. J. Huff. *Chemosphere*, **89**, 521-525 (2012)
4. M. Alshabib, S. A. Onaizi. *Sep. Purif. Technol.*, **219**, 186-207 (2019)
5. A. O. Olaniran, E. O. Igbinosa. *Chemosphere*, **83**, 1297-1306 (2011)
6. A. J. Khoei, N. J. G. Joogh, P. Darvishi, K. Rezaei. *Turk J Fish Aquat Sc*, **19**, 21-28 (2019)
7. Z. Noorimotlagh, S. Shahriyar, R. D. C. Soltani, R. Tajik. *Desalin Water Treat*, **57**, 14213-14226 (2016)
8. M. Hannah, V. E. Kwinten, D. Raf. *Water*, **10**, 247 (2018)
9. J. Ma, Y. Ding, L. Chi, X. Yang, Q. Shi. *Environ Technol*, 1-37 (2019)
10. S. A. Hakim, S. Jaber, N. Z. Eddine, A. Baalbaki, A. Ghauch. *Data in Brief*, **27**, 104614 (2019)
11. K. T. Xu, G. F. Lin, Q. Lv, Y. Zhen-Nan, Z. Jin-Mei. *Environ Eng*, **36**, 188-194 (2018)
12. J. Wang, L. Hu, Y. Yang, M. Yu, Y. Liu. *J Environ Eng*, **8**, 3767-3772 (2014)
13. X. W. Huo, P. Zhou, J. Zhang, Y. Liu, Y. Zhang. *J Hazard Mater*, **391**, 122055 (2020)
14. D. Xia, Y. Li, G. Huang, R. Yin, P. K. Wong. *Water Res*, **112**, 236-247 (2017)
15. Y. Huang, S. Ho, Y. Lu, R. Niu, L. Xu, J. Cao, S. Lee. *Molecules*, **21**, 56 (2016)
16. S. Wu, J. Lv, F. Wang, N. Duan, Q. Li, Z. Wang. *Sci Rep*, **7**, 14435 (2017)
17. S. P. Yadav, R. Manohar, S. Singh. *Liq Cryst*, **42**, 1-7 (2015)
18. E. Liu, L. Kang, F. Wu, T. Sun, X. Hu, Y. Yang, H. Liu. *Plasmonics*, **9**, 61-70 (2014)
19. H. Tong, M. Hu, F. B. Li, C. S. Liu, M. J. Chen. *Soil Biol. Biochem.*, **70**, 142-150 (2014)
20. A. Singh, A. P. Singh, T. J. Purakayastha. *Arch Agron Soil Sci*, **65**, 1302-1315 (2019)
21. M. Muruganandham, R. P. S. Suri, S. Jafari, M. Sillanp, G. J. Lee, J. J. Wu, M. Swaminathan. *Int J Photoenergy*, **2014**, 164-167 (2014)