



Article Efficient Degradation of Printing and Dyeing Wastewater by Lotus Leaf-Based Nitrogen Self-Doped Mesoporous Biochar Activated Persulfate: Synergistic Mechanism of Adsorption and Catalysis

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Abstract: The discharge of printing and dyeing wastewater has been increasing, causing serious environmental pollution with the rapid development of the industry. Based on this, an N self-doped mesoporous lotus leaf biochar (LLC800) was prepared from lotus leaves as raw material for the activation of Persulfate (PS) to degrade wastewater from printing and dyeing. The removal rate of AO7 by PS, LLC800 and LLC800/PS systems were 0.84%, 31.11% and 99.46%, respectively. Electron paramagnetic resonance spectroscopy (EPR) and quench tests showed the presence of free radicals ($^{\circ}OH$, SO₄ $^{\bullet-}$ and O₂ $^{\bullet-}$) and nonradical ($^{1}O_{2}$) in the LLC800/PS system, where nonradicals ($^{1}O_{2}$) play an important role in the degradation of AO7. The "N self-doped" effect formed by the high N content of lotus leaves is the main factor leading to the high adsorption and catalytic performance of lotus leaf biochar. The effect of pyrolysis temperature on the performance of biochar can be attributed to the change of N content and conformation and specific surface area in biochar. Moreover, the LLC800/PS system has a strong resistance to interference. This work can provide technical support for the preparation of high-performance adsorption-catalytic biochar and the development of high-performance activation materials for persulfate.

Keywords: N-self-doped lotus leaf-based biochar; persulfate; AO7; adsorption and catalysis; nonradical and radicals

1. Introduction

The discharge of printing and dyeing wastewater is increasing with the rapid development of industry, among which orange II (AO7) wastewater is particularly prominent [1]. AO7 is a synthetic dye commonly used in industry, and its molecular structure contains one or more azo groups (-N=N-). Printing and dyeing wastewater containing AO7 has the characteristics of high chromaticity, complex composition, mutagenic, carcinogenic and difficulty in degradation [2–4], which will cause serious pollution to the environment and endanger the ecological environment if discharged directly into the environment without treatment [5–7]. There are many common treatment methods for azo dye wastewater, including biological treatments [8], coagulation, adsorption [9,10], membrane filtration [11], photocatalysis [12] and ozone oxidation [13].

In recent years, advanced oxidation technologies (AOPs) based on peroxynitrite have been widely used for the degradation of organic pollutants due to their strong oxidation capacity, no secondary pollution and high mineralization rate [14–16]. Compared to •OH, $SO_4^{\bullet-}$ has a stronger redox potential (2.5–3.1 V), longer half-life ($SO_4^{\bullet-}$: 30–40 µs > •OH: 10^{-3} µs) and better selectivity [17–19]. Biochar has the advantages of a well-developed pore structure, large specific surface area and rich functional groups on the surface, which are widely used to activate persulfate to degrade organic pollutants [20–23]. To further improve the catalytic and adsorption capacity of biochar, many researchers have modified biochar.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). HF and KOH were used for the acid-base modification [24-26]. Common raw materials for metal modification are Fe(NO₃)₃•9H₂O, Co(NO₃)₂•6H₂O and FeSO₄•7H₂O [27–29]. While ammonium nitrate, boric acid and urea were used as heteroatom modification [30-33]. N-doping is one of the heteroatomic modification methods, and previous studies have shown that increasing the proportion of appropriate N elements can significantly improve the catalytic performance of biochar [34-36]. The purpose of the modification is to further improve the performance of biochar materials, but modification not only increases the production cost of catalytic materials but also generates a large amount of secondary waste during the modification process, which is likely to cause secondary pollution to the environment. Therefore, it is a new research idea to find biomass with high N content to prepare biochar and to improve the catalytic performance spontaneously by "N self-doped" instead of N atom modification.

Lotus leaves are highly productive in eutrophic water bodies rich in N and P, and their leaves have high N content and more natural pores, making them a preferred choice for the preparation of "N self-doped" mesoporous biochar. The production of lotus leaves is high, and the resource utilization method is less, which makes it easy to cause resource waste and environmental pollution. Therefore, "N self-doped" lotus leaf-based mesoporous biochar with high-efficiency catalytic properties can be prepared based on lotus leaf without modification, which not only protects the environment, but also expands the utilization of lotus leaf resources. In this work, a novel N self-doped mesoporous lotus leaf-based biochar was prepared using lotus leaves as raw material, which can efficiently catalyze the degradation of AO7 by persulfate. The effects of the amount of biochar added to the activation system, the concentration of PS, pH, temperature, initial concentration of AO7, humic acid (HA) and common anions (Cl^- , HCO_3^- , NO_3^-) in water on the activation reaction system were investigated. The mechanism of AO7 removal by the LLC800/PS activation system and the synergistic effect of adsorption and catalysis were thoroughly analyzed and studied by quenching test, electron paramagnetic resonance spectroscopy (EPR) and other characterization experiments.

2. Results and Discussion

2.1. Characterization of Biochar

The SEM images of lotus leaves at different pyrolysis temperatures are shown in Figure 1. The surfaces of LLC700, LLC800 and LLC900 showed different degrees of porous morphology, and the specific surface area size at different pyrolysis temperatures followed the pattern of LLC800 (676.335 m²/g) > LLC900 (360.488 m²/g) > LLC700 (118.925 m²/g). The increase in pyrolysis temperature from 700 to 800 °C showed a very significant change in specific surface area, presumably due to the volatilization of tar compounds to produce a more abundant porous structure, which indicates that the pyrolysis temperature plays a very important role in the morphology of biochar samples and the development of pores. The development of pore space shows a trend of increasing first and then decreasing with an increase in temperature. Excessive temperature promotes the development of void spaces while also causing collapse and morphological changes in some pore spaces.

To study the effect of different pyrolysis temperatures on the elemental content of LLC, elemental analysis of biochar at different pyrolysis temperatures was conducted (Table 1). The elemental content of C increased with an increase in pyrolysis temperature, while the elemental content of O, N and H decreased, and the ratio of H/C and (N+O)/C decreased with the increase in pyrolysis temperature, indicating the higher carbonization and aromaticity of biochar [37]. Not only that, but the elemental N in biochar also changed the most relative to other elemental N content relative to LLC800 and LLC900 showed the fastest decrease in elemental N content relative to LLC800 and LLC700. Therefore, the increase in temperature, the collapse of pores and morphological changes as well as the weakening of catalytic degradation properties may be related to the loss of N elements leading to changes in the associated N morphology and structure.



Figure 1. SEM images of lotus leaves at different pyrolysis temperatures ((**a**): 700 °C, (**b**): 800 °C, (**c**): 900 °C).

Table 1. Elemental content and pore characteristics of lotus leaf-based biochar at different pyrolysis temperatures.

Biochar	C (%)	O (%)	N (%)	H (%)	H/C (%)	N/C (%)	(N+O)/C (%)	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Size (nm)
LLC700	78.28	16.86	3.43	1.43	1.83	4.38	25.92	118.93	0.04	3.75
LLC800	84.58	11.41	3.10	0.91	1.08	3.67	17.16	676.34	0.25	3.71
LLC900	86.94	10.70	1.58	0.78	0.90	1.82	14.12	360.49	0.15	3.65

The average pore size of the three prepared biochars changed less with the increase in pyrolysis temperature, but the pore volumes all followed the pattern of increasing and then decreasing. Elemental analysis showed that the three elements C, O and N may constitute an important influencing factor for the strong degradation ability of the LLC800 activation system.

The pore structure of LLCs at different pyrolysis temperatures was further evaluated using adsorption-desorption isotherms of nitrogen. The adsorption-desorption isotherm belongs to type IV, and there is a significant hysteresis between the adsorption-desorption isotherms, indicating the presence of a large number of mesopores (Figure 2a). Furthermore, the average pore size of LLC800 is 3.71 nm, and its large specific surface area and high void fraction provide the basis for the efficient adsorption of AO7 by lotus leaf biochar (Figure 2b).

The XRD spectra show a broader diffraction peak of 2θ at 23.3° (002) predicting the presence of the LLC amorphous carbon structure, and a weaker diffraction peak of 2θ at 43.5° attributed to the (100) planar structure of the graphite (Figure 2c) [38,39]. The diffraction peak area of the graphitic structure increased with the increase in pyrolysis temperature, which indicates that the amorphous carbon of biochar transformed into the graphitic structure with an increase in pyrolysis temperature.



Figure 2. Nitrogen adsorption-desorption isotherms (**a**), pore size distribution (**b**), XRD (**c**) and Raman spectra (**d**) of LLCs at different pyrolysis temperatures.

It can be seen from the Raman spectra that a pair of characteristic peaks appear at 1330 cm⁻¹ (D-peak) and 1570 cm⁻¹ (G-peak) for LLC700, LLC800 and LLC900 (Figure 2d). The D-peak originates from defects and disorder in the carbon layer, while the G-peak is closely related to the graphite structure [40,41]. The intensity ratio (I_D/I_G) of D-peak and G-peak of carbon materials can reveal the degree of defects in carbon materials. The I_D/I_G values of LLC700, LLC800 and LLC900 are 0.97, 1.02 and 1.07 respectively, which indicate that the higher pyrolysis temperatures promoting the transformation of amorphous carbon to graphitized structures caused damage to the graphitized structures, that is, more defective structures were generated with the increase in pyrolysis temperature. The results of Raman analysis are consistent with the results of XRD analysis, and the results indicate that the carbon defects may be important active sites and the abundant carbon defects can significantly improve the catalytic performance of the material [42].

The FTIR spectra of LLC800 before and after use are shown in Figure 3. The stretching vibration at around 3440 cm⁻¹ appears as the vibration peak of–OH, the stretching vibration at around 2920 cm⁻¹ appears as–CH₂, and the stretching vibrations at 1628 cm⁻¹ and 1075 cm⁻¹ are related to the vibration of C=O and C–N, respectively [43,44]. There are abundant reactive groups on the surface of LLC800, and the vibrational peaks of functional groups on the surface of LLC800 did not change significantly before and after the reaction, but the peak area decayed and changed, indicating that the functional groups were involved in the reaction. Therefore, the activation properties of LLC800 are closely related to its surface functional groups.

Exploring the composition and chemical state of N-self-doped lotus leaf biochar LLC samples prepared at different pyrolysis temperatures by XPS (Figure 4), the XPS spectra showed that three characteristic peaks were observed at 284.8 eV, 399.8 eV and 532.5 eV, corresponding to C1s, N1s and O1s, respectively (Figure 4a) [45]. The XPS spectra of C1s of LLC800, which can be decomposed into four regions with binding energies of about 284.6 eV, 285.6 eV, 286.5 eV and 288.76 eV, corresponding to sp2 graphitic carbon, sp2 carbon bound to heteroatoms (C-O or C-N), carbonyl (C=O) and carboxyl (COOH) groups,

respectively (Figure 4b) [46,47]. The O1s XPS spectrum of LLC800 can be decomposed into four regions with binding energies of about 530.65 eV, 531.42 eV, 532.1 eV and 533.12 eV, representing C=O, C–OH, C–C=O and C–O–C, respectively (Figure 4c). Figure 4d–f show the N1s spectra corresponding to the LLC700, LLC800 and LLC900, respectively. The N1s XPS spectra can be decomposed into four regions located at 398.5 eV (pyridine nitrogen), 400 eV (pyrrole nitrogen), 401.2 eV (graphite nitrogen) and 403.5 eV (nitrogen oxide), respectively [48]. The content of 398.5 eV (pyridine nitrogen) and 400 eV (pyrrole nitrogen) was decreased when the pyrolysis temperature was increased from 800 to 900 °C, while the content of 401.2 eV (graphite nitrogen) was increased. The results showed that the high temperature induced the conversion of pyridine and pyrrole nitrogen to graphite nitrogen, which resulted in a much lower catalytic performance of LLC900 than that of LLC800 [49]. That is, the reaction sites of biochar in activated persulfate are pyridine and pyrrole nitrogen. In all, active sites including pyridine nitrogen, pyrrole nitrogen, defects, heterocarbon and C=O were successfully obtained in the prepared LLC800.





Figure 4. XPS spectra of LLCs at different pyrolysis temperatures (**a**); C1s (**b**) and O1s (**c**) XPS spectra of LLC800; N1s XPS spectra of LLC700 (**d**); N1s XPS spectra of LLC800 (**e**); N1s XPS spectra of LLC900 (**f**).

2.2. Effect of Different Systems on the Removal of AO7

To investigate the removal effect of AO7 under different systems, different activation reaction systems were constructed (the reaction temperature was 25 °C, the concentration of AO7 was 200 mg/L, the dosage of LLC was 0.25 g/L, the dosage of PS was 4 g/L). The system containing only PS had almost no effect on the removal of AO7 at a reaction time of 30 min, which was only 0.84% (Figure 5). The removal of AO7 by LLC700, LLC800 and LLC900 at 30 min was 7.09%, 31.11% and 20.61% in the system containing only LLC, which was consistent with the LLC surface area size pattern. The removal of AO7 by LLC700/PS, LLC800/PS and LLC900/PS at 30 min was 9.88%, 99.46% and 51.30%, respectively, when LLC and PS were present simultaneously. The higher removal rate of AO7 by the LLC800/PS system compared to LLC800 and PS alone may be attributed to the larger specific surface area of LLC800. That is, the removal rate of AO7 by different LLC/PS systems is positively correlated with the specific surface area of LLC. Obviously, LLC800 has excellent adsorption performance and efficient catalytic performance.



Figure 5. Removal effect of AO7 by different systems. Reaction conditions: LLC = 0.25 g/L, PS = 4 g/L, AO7 = 200 mg/L, temperature = 25 °C and pH = 6.4 ± 0.1 .

2.3. Effect of Multiple Factors on the Removal of AO7

The AO7 removal efficiency is governed by various factors. Here, the effects of PS and LLC dosing, pH, initial concentration of AO7 and reaction temperature on the AO7 removal efficiency were investigated (Figure 6). The removal rate of AO7 increased with the increase of LLC800 dosage, and the removal rate of AO7 increased from 91.83% to 99.46% when the dosage of LLC800 increased from 0.2 g/L to 0.25 g/L. Interestingly, the removal rate of AO7 was 99.58% when LLC800 was dosed at 0.3 g/L, which was not a significant increase compared to the 0.25 g/L dose, but only accelerated the reaction process (Figure 6a). The above results are attributed to the fact that the addition of LLC800 provides more adsorption sites and activation sites, but also results in a certain degree of wastage of adsorption sites and activation sites.



Figure 6. Effects of LLC (**a**) and PS (**b**) dosing, pH (**c**) and initial concentration of AO7 (**d**) on the degradation efficiency of AO7.

Similarly, the dosage of PS also affects the removal rate of AO7. The removal rate of AO7 increased as the PS dosage increased from 2 g/L to 4 g/L, which may be attributed to the increased contact between PS and the activation sites on the surface of LLC800 (Figure 6b). The AO7 removal rate only increased from 99.46% to 99.51% with the content of PS increasing from 4 g/L to 5 g/L, and the removal effect had a little incremental effect. Therefore, 0.25 g/L of LLC800 was the optimal dosing amount and was used for subsequent experiments. In brief, 0.25 g/L of LLC800 and 4 g/L of PS were considered to be the optimum dosing amounts and were used in the subsequent experiments.

The initial pH of the reaction solution is one of the most important factors affecting the degradation efficiency. Figure 6c shows the effect of different initial pH values on the degradation of AO7 by the LLC800/PS system. The removal rate decreases from 99.14 % to 92.88 % when the initial pH of the reaction solution rises from 7 to 9, probably because under alkaline conditions, a small amount of the generated $SO_4^{\bullet-}$ is converted to \bullet OH (Equation (1)).

$$\mathrm{SO}_4^{\bullet-} + \mathrm{OH}^- \to \mathrm{SO}_4^{2^-} + \bullet \mathrm{OH} \tag{1}$$

The redox potential of •OH is lower than that of $SO_4^{\bullet-}$, which leads to a decrease in the redox capacity of the system and ultimately to a decrease in the removal rate of AO7 [50]. The fact that the decrease in removal rate is small demonstrates that the initial pH of the reaction solution has a limited effect on the removal rate of AO7 and indirectly indicates that the LLC800/PS system is a nonradical dominated reaction.

The removal effect of the LLC800/PS system was further investigated for different initial concentrations of AO7 (100, 200, 300, and 400 mg/L). The removal rate of AO7 by the LLC800/PS system could reach 99.67% in 10 min when the initial concentration of AO7 was 100 mg/L (Figure 6d). Differently, when the initial concentrations of AO7 were 200 mg/L,

300 mg/L and 400 mg/L, the removal rates of AO7 by the LLC800/PS system were 99.46%, 71.06% and 49.32% within 30 min, respectively. This may be attributed to the excessive adsorption of AO7 by LLC800, which covered part of the activation site and eventually led to a decrease in the removal rate.

To further illustrate that LLC800 has both excellent adsorption performance and efficient catalytic performance, a comparison with other modified and unmodified biochars is presented here (Table 2). Compared to other biochars, LLC800 has an excellent performance in terms of the amount of biochar applied, the concentration of degraded AO7 and the degradation rate.

Samples	Biochar Raw Materials	Modification Method	Specific Surface Area (m²/g)	Dosing Amount (g/L)	AO7 Concentration (mg/L)	Degradation Rate %	Ref.
LSB-800	luffa sponge	/	304.49	0.20	20	96.00	[51]
B-nZVI	bush branch	FeSO ₄ ·7H ₂ O	52.21	2.00	20	98.30	[52]
Fe-N-BC	straw	FeSO ₄ ·7H ₂ O/ur	ea 362.5	0.20	20	98.20	[53]
NRSBC800	rice straw	urea	471.10	0.10	50	100.00	[54]
SBC-700	sawdust	/	208.59	1.5	50	90.00	[55]
LLC800	Lotus leaf	/	676.34	0.25	200	99.81	This work

Table 2. Comparison of AO7 removal effect with other biochar.

The effect of different temperatures on the removal rate of AO7 was investigated under the condition that the initial concentration of AO7 was 200 mg/L (Figure 7). The removal rate of AO7 by the LLC800/PS system could reach 97.36% within 10 min when the reaction temperature was increased from 25 °C to 45 °C, which suggested that increasing the reaction temperature could effectively improve the degradation efficiency of AO7.



Figure 7. Effect of temperature on degradation efficiency.

To further explore the mechanism of temperature enhancement of degradation efficiency, the removal effect of AO7 by different systems at different temperatures was investigated separately. The system where only PS exists has almost no effect on the removal of AO7, and the removal rate increased from 0.84% to 1.42% as the temperature increased from 25 °C to 45 °C. The increase in the removal rate was due to the activation of $S_2O_8^{2-}$ by heat, which caused the PS to generate $SO_4^{\bullet-}$ adicals and the decomposition of a small amount of AO7 [56]. The removal rates of AO7 by the LLC800 system were 31.11%, 34.56% and 35.86%, which indicates that the adsorption of AO7 by LLC800 is a heat absorption process and the temperature can effectively accelerate the adsorption rate of AO7 by LLC800. Interestingly, the removal rates of AO7 by the LLC800/PS system were as high as 99.46%, 99.47% and 99.49%, respectively. The above results indicated that temperature could significantly accelerate the degradation efficiency of AO7. In summary, the temperature has a limited effect on the degradation of AO7 by the PS system but can effectively accelerate the adsorption rate of LLC800. The greatest effect on the efficiency of the LLC800/PS system to degrade AO7 was found to be attributed to the enhancement of the adsorption efficiency of LLC800, which effectively exerted the synergistic mechanism of adsorption and catalysis.

2.4. Identification of Reactive Oxygen Species

To elucidate the mechanism of AO7 degradation by the LLC800/PS system, radicals (\circ OH, SO₄ $^{\bullet-}$ and O₂ $^{\bullet-}$) and singlet oxygen (¹O₂) in the system were identified by quenching experiments using ethanol (EtOH), tert-butyl alcohol (TBA) and p-benzoquinone (p-BQ), respectively [47]. Ethanol is used as a scavenger of the free radicals SO₄ $^{\bullet-}$ and \bullet OH, which can rapidly react with the SO₄ $^{\bullet-}$ and \bullet OH generated during the activation process [57]. The removal rate of AO7 by the LLC800/PS system decreased from 96.07% to 76.81% with the continuous addition of ethanol (0–5000 mM) (Figure 8a). Furthermore, the removal efficiency decreased from 99.46% to 43.05% with an increasing concentration of TBA (0–5000 mM), and there was a significant decrease in removal compared to the quenching results of EtOH, which was attributed to the blocked adsorption of AO7, indicating that \bullet OH on the surface of biochar played an important role in the degradation of AO7 [58] (Figure 8b). P-benzoquinone (p-BQ) was used as a scavenger of O₂ $^{\bullet-}$ [59]. The removal efficiencies decreased from 99.46% to 90.07% when p-BQ (0–10 mM) was added to the removal system, indicating the presence of a small amount of O₂ $^{\bullet-}$ playing a role in the removal of AO7 (Figure 8c).

To characterize the role of nonradicals in the removal of AO7 from the LLC800/PS system, L-histidine was used as a scavenger of ${}^{1}O_{2}$ [60]. The removal efficiency of AO7 by the LLC800/PS system decreased from 99.46% to 33.05% when L-histidine was added from 0 to 10 mM, indicating that the LLC800/PS system-generated nonradical ${}^{1}O_{2}$, which plays an important role in the degradation of AO7 (Figure 8d).

Possible radicals •OH, SO₄•⁻ and O₂•⁻ in the LLC800/PS system were further confirmed by EPR, and the trapping agent was DMPO (5,5-dimethyl-1-pyrroline-N-oxide) [61]. The EPR signals of DMPO–•OH and weak DMPO–SO₄•⁻ adducts were observed, indicating that both •OH and a small amount of S SO₄•⁻ are involved in the degradation of AO7 in the LLC800/PS system (Figure 9). Moreover, a weak signal peak appeared in the detection of free radical O₂•⁻, indicating that a small amount of O₂•⁻ was also present in the LLC800/PS system, which was all consistent with the quenching experimental results. Previous reports indicated that the nonradical pathway in the advanced oxidation process is mainly the singlet oxygen (¹O₂). It is speculated that the presence of nonradical singlet oxygen ¹O₂ in the LLC800/PS system plays an important role in the degradation of AO7 based on the results of the quenching experiments [62]. Thus, the presence of these radicals (•OH, SO₄•⁻ and O₂•⁻) and nonradical (¹O₂) in the degradation of AO7 in the LLC800/PS system was confirmed by electron paramagnetic resonance spectroscopy (EPR) and quenching tests, where the nonradical ¹O₂ plays an important role in the degradation of AO7.



Figure 8. Effect of quenching agents on the degradation efficiency of AO7 ((**a**): EtOH, (**b**): TBA, (**c**): p-BQ, (**d**): L-Histidine). Reaction conditions: LLC800 = 0.25 g/L, PS = 4 g/L, AO7 = 200 mg/L, temperature = $25 \degree$ C and pH = 6.4 ± 0.1 .



Figure 9. EPR spectra for •OH, SO₄ • $^-$, O₂ • $^-$ and 1 O₂ in the LLC800/PS system.

The mechanism of degradation of AO7 by the LLC800/PS system is shown in Figure 10, where the adsorption sites and activation sites on the surface of LLC800 are limited. Pollutants are enriched on the surface of biochar by adsorption, and the catalytic generation of free radicals and nonradicals rapidly degrades the adsorbed pollutants, regenerates the adsorption sites, and then accelerates the adsorption of residual pollutants. The reaction is carried out simultaneously with adsorption and degradation, effectively exerting the synergistic effect of adsorption and catalysis. Most reactions are likely to take place on the surface of the biochar in a restricted area, effectively avoiding losses caused by the transfer of reactive oxygen species in aqueous solutions. The limited adsorption capacity of biochar results in the transfer of activated oxygen species from the biochar surface to the aqueous solution to degrade the target pollutant. Unfortunately, the short half-life of reactive oxygen species inevitably results in the loss of some reactive oxygen species in the delivery process. The adsorption capacity plays a crucial role in the degradation of AO7 by biochar, and how to regulate the adsorption and catalytic capacity of biochar to avoid the loss of reactive oxygen species is also a key point to improving the degradation efficiency.



Figure 10. Degradation mechanism of AO7 by LLC800/PS system.

2.5. Effect of Humic Acid and Anion in Water

Wastewater from printing and dyeing is a complex water body, and usually, a large number of anions and humic acids (HA) are present. The effect of humic acid (HA) and three common anions (Cl⁻, HCO₃⁻, NO₃⁻) on the degradation of AO7 by the LLC800/PS system were simulated (Figure 11). Inorganic anions can usually react with radicals, leading to the formation of secondary radicals in the course of the reaction [63,64]. The experimental results showed a slight inhibition of degradation when Cl⁻ (20 mM) was added, and the removal rate decreased from 99.46% to 96.24%. Previous studies have shown that Cl⁻ is an effective radical trapping agent that reacts with to generate chlorine radicals (Cl₂ •, $E_0 = 1.6$ V), leading to a slight decrease in degradation efficiency (Equations (2)–(5)) [65].

$$\mathrm{SO}_4^{\bullet-} + \mathrm{Cl}^- \to \mathrm{SO}_4^{2-} + \mathrm{Cl} \bullet$$
 (2)

$$Cl \bullet + Cl^- \to Cl_2^- \bullet$$
 (3)

$$\operatorname{Cl}_{2}^{-} \bullet + \operatorname{Cl}_{2}^{-} \bullet \to \operatorname{Cl}_{2} + 2\operatorname{Cl}^{-} \tag{4}$$

$$\operatorname{Cl}_{2}^{-} \bullet + \operatorname{Cl} \bullet \to \operatorname{Cl}_{2} + \operatorname{Cl}^{-}$$
 (5)



Figure 11. Effect of Cl⁻, HCO₃⁻, NO₃⁻ and HA on the degradation efficiency of AO7. Reaction conditions: LLC800 = 0.25 g/L, PS = 4 g/L, AO7 = 200 mg/L and temperature = 25 °C.

Similarly, the addition of HCO_3^- (20 mM) also had a slight inhibitory effect on degradation, reducing the removal rate from 99.46% to 95.77%. It may be attributed to two reasons, one of which is that HCO_3^- may react with •OH or $SO_4^{\bullet-}$ to form HCO_3^{\bullet} with a lower redox potential [66] (Equations (6) and (7)).

$$HCO_3^- + SO_4^{\bullet -} \to SO_4^{2-} + HCO_3^{\bullet}$$
(6)

$$\text{HCO}_3^- + \bullet \text{OH} \to \text{H}_2\text{O} + \text{HCO}_3^{\bullet}$$
 (7)

Moreover, both NO₃⁻ (20 mM) and HA (10 mg/L) hardly affected the degradation of AO7 by the LLC800/PS system. Generally, the inhibition of HA is attributed to the quenching of free radicals, which further indicates that the LLC800/PS system is dominated by the nonradical $^{1}O_{2}$ in the degradation of AO7. Overall, the LLC800/PS system has a strong antiinterference ability. Therefore, the constructed LLC800/PS system has potential application in treating actual printing and dyeing wastewater or complex industrial wastewater.

2.6. Exploration of the Storage Time for LLC800/PS System

The expiration date of LLC800 is also a key indicator for its practical application. Here, the sealed storage and air exposure experiments of LLC800 were conducted for 30 and 60 days, respectively. The removal rate was 97.14% for 30-day sealed storage and 97.06% for air exposure, while the removal rate was 95.26% for 60-day sealed storage and 93.43% for air exposure (Figure 12). Although the removal rate decreased slightly with the extension of the preservation days, the removal rate could still reach 93.43%. This may be due to the fact that LLC800 is unmodified, and the material is very stable and minimally influenced by air, reducing the cost in actual applications.



Figure 12. Exploration of storage time for LLC800.

3. Experimental

3.1. Materials and Reagents

Lotus leaves were collected from the pond on the campus of Anhui Polytechnic University. Orange II (AO7), HCl, H₂SO₄, tert-butanol (TBA), ethanol (EtOH), p-benzoquinone (*p*-BQ), L-histidine, sodium bicarbonate and sodium nitrate purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). NaCl and sodium persulfate(ps) were obtained from Shanghai Aladdin Biochemical Technology Co. (Shanghai, China). Humic acid (HA) was purchased from Jiangsu Green Leaf Biotechnology Co. (Yancheng, China). The needle filtration membrane used is manufactured by Tianjin Jinteng Experimental Equipment Co. (Tianjin, China). All reagents were analytically pure, and all solutions were prepared with ultrapure water (resistivity 18.2 M Ω ·cm⁻¹).

3.2. Preparation of Biochar

The lotus leaves are first washed with ultrapure water and dried. Next, the dried lotus leaves are crushed by a pulverizer and then passed through a 100-mesh sieve for use. The tube furnace was purged with nitrogen for 10 min before calcination. The quartz boat loaded with 10 g of lotus leaf powder was placed in a tube furnace, heated to the set temperature at a rate of 5 °C/min under a nitrogen atmosphere and pyrolyzed for 2 h. Next, the LLC produced at different pyrolysis temperatures (700 °C, 800 °C, 900 °C) was acid-washed with 1 mol/L hydrochloric acid after cooling to room temperature, and then washed with deionized water several times until the pH value was neutral; the samples were vacuum dried overnight. The lotus leaf-based biochar prepared according to different pyrolysis temperatures were named LLC700, LLC800 and LLC900.

3.3. Characterization of Biochar

The morphological and structural analysis of the samples was carried out using scanning electron microscopy (SEM). The specific surface area of samples and analysis of the pore size are obtained from a fully-automated specific surface and porosity analyzer (BET/BJH). An elemental analyzer is used for the quantitative analysis of the elemental content of biochar. Information on the surface functional groups of biochar was obtained by

X-ray photoelectron spectroscopy (XPS) and Fourier infrared spectroscopy (FTIR). Raman spectroscopy (Raman) is used to analyze the degree of graphitization of materials. X-ray powder diffractometry (XRD) is used to characterize materials for physical properties.

3.4. Degradation Experiment of AO7

The reaction was carried out in a conical flask containing 100 mL AO7 (200 mg/L). The initial pH of the solution was adjusted with NaOH (0.1 mol/L) and H_2SO_4 (0.1 mol/L). Sodium persulfate (0.4 g) was added to the conical flask and shaken well until completely dissolved, and then lotus leaf-based biochar (0.025 g) was added to it. The conical flask was placed in a thermostatic water bath shaker, and the shaker was set to run at 170 rpm at 25 °C. Samples were taken at 5 min intervals after the start of the experiment and measured after filtration using a 0.22 μ m needle filter membrane. No special emphasis was placed on the initial pH of the reaction being the pH (6.4 \pm 0.1) of the original solution and the reaction temperature being 25 °C.

3.5. Analysis of Nonradical and Radicals

The absorbance of the filtrate was measured at its maximum absorption wavelength of 484 nm using a TU-1901 UV-Vis spectrophotometer (Beijing, China). The concentration of AO7 was obtained by setting the standard curve. Quenching experiments were performed using ethanol, tert-butanol, L-histidine and p-benzoquinone as chemical quenching agents, and the types of radicals and nonradicals generated in the reaction system were determined using electron paramagnetic resonance Poppermeter (EPR) and related trapping agents.

4. Conclusions

In this work, an N self-doped lotus leaf biochar was successfully prepared by simple, slow thermal cracking using lotus leaf as raw material, in which LLC800 exhibited excellent adsorption and catalytic properties. This is attributed to the high pyridine and pyrrole nitrogen content, the abundance of defects and functional groups, and the large specific surface area of LLC800. The activation system LLC800/PS constructed based on LLC800 has free radicals ($\bullet OH$, $SO_4 \bullet^-$ and $O_2 \bullet^-$) and a nonradical (1O_2), where the nonradical oxidation pathway plays an important role in the degradation of AO7. LLC800/PS system has a strong anti-interference ability in the process of AO7 removal, and also shows significantly high performance over a wide pH range (3.0–11.0). The temperature increased the adsorption rate of AO7 by biochar, which intensified the catalytic degradation reaction on the surface of biochar. The synergistic effect of adsorption and catalysis is an important reaction mechanism for efficient degradation. Hence, the strength of adsorption capacity and catalytic capacity and the degree of matching of their synergistic effects are the focus of developing activation systems with synergistic adsorption-catalysis effects. This study reveals the efficient mechanism of activated persulfate reaction of the prepared lotus leafbased biochar LLC800 and its synergistic mechanism of AO7 adsorption and catalysis, which can provide new research ideas for the preparation of biochar with both adsorption and catalytic abilities.

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