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Degradation of Acid Orange 7 at neutral pH by heterogeneous activation of peroxydisulfate using Co-GAC catalyst under UV irradiation

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ABSTRACT

Granular activated carbon (GAC) supported cobalt catalyst (Co-GAC) was prepared and used as heterogeneous catalyst for the activation of peroxydisulfate (PS, $S_2O_8^{2-}$) under UV irradiation. The effects of some important reaction parameters such as PS concentration, catalyst addition, reaction temperature, and initial pH on the degradation of Acid Orange 7 (AO7) at neutral pH were investigated. Results showed that the decolorization efficiency by Co-GAC/PS process is enhanced in the presence of UV irradiation. The decolorization efficiency increased with the increase of PS concentration, catalyst addition, and reaction temperature, but decreased with the increase of initial pH. The decolorization efficiency was 96.2% and the chemical oxygen demand removal efficiency was 38.5% when initial pH value was 7, PS concentration was 1.0 g/L and catalyst dosage was 0.8 g/L.

Keywords: Co-GAC; UV irradiation; Heterogeneous catalysis; Peroxydisulfate; Acid Orange 7

1. Introduction

In recent years, the textile industry causes considerable water pollution by discharging effluents into various water bodies [1]. The effluents from textile industry contain large amounts of organic dyes, representing a major threat to the environment due to their impacts on photosynthesis of aquatic plants and the carcinogenic nature of many of these dyes and their break-down products [2,3]. Decolorization of dye wastewaters is one of the significant problems as the dyes will be visible and undesirable even at low concentration. Azo dyes represent more than 15% of the world production of dyes used in the textile manufacturing industry [4,5]. Acid Orange 7 (AO7) is generally used as a model substrate for the aromatic azo dyes [6], not only because of its complicated constitution and high-chemical stability, but also due to its hazardous nature, high toxicity, and harmful effects on public health [4,7]. Conventional treatment processes like adsorption and flocculation are not efficient methods as they would lead to solid waste and thus create other environmental problems requiring further treatment [8]. In view of this, advanced oxidation processes (AOPs) were used to control these contaminants.

Recently, sulfate radical ($SO_4^{-\bullet}$)-induced AOPs have gained more and more attention for the degradation of organic contaminants [9,10]. $SO_4^{-\bullet}$ has a remarkably high standard redox potential (2.5–3.1 V) at neutral

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pH [11]. Moreover, $SO_4^{-\bullet}$ exhibits a longer half life than hydroxyl radicals mainly because of their preference for electron transfer reactions [12]. There are many studies related to the activation of peroxydisulfate (PS) by UV [9,13–15], heat [8,16], ultrasound [17], and transition metals [18–20] to generate $SO_4^{-\bullet}$ for the degradation of organic pollutants. Increasing attention has been paid to the transition metals, and it was found that Co(II) can activate PS to generate $SO_4^{-\bullet}$ via Eq. (1) [21]:

$$S_2O_8^{2-} + Co^{2+} \rightarrow SO_4^{-\bullet} + SO_4^{2-} + Co^{3+} \tag{1}$$

However, few studies have reported the use of granular activated carbon (GAC) supported Co oxide as a heterogeneous activator of PS for the removal of AO7 in aqueous solution. In addition, UV can also activate PS to generate sulfate radicals [22]:

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\bullet} \tag{2}$$

Therefore, in this study, Co-GAC catalyst was prepared and AO7 was decolorized by the combined UV/Co-GAC/PS process was investigated. The effects of initial pH, Co-GAC dosage, and PS concentration on the decolorization efficiency were investigated. Furthermore, the chemical oxygen demand (COD) removal was performed to evaluate the mineralization efficiency in this process.

2. Experimental

2.1. Materials

Acid Orange 7 (4-(2-hydroxynaphthylazo) benzenesulfonic acid sodium salt) was purchased from Shanghai No. 3 Reagent Factory (China) and used without further purification. The GAC was purchased from Tianjin Bodi Chemical Co., Ltd. (China). The specific surface area of GAC was performed by the N_2 Brunauer–Emmett–Teller (BET) method on an ASAP2020 analyzer (USA). The BET surface area, pore volume, and pore size of the GAC were 165.4 m^2/g, 0.1 cm^3/g, and 2.6 nm, respectively. All other reagents were of analytical grade and all sample solutions were prepared using deionized water.

2.2. Procedure

The catalysts were prepared by impregnation method. Briefly, a fixed amount of GAC was immersed into cobalt nitrate solution of different concentration, and the suspension was stirred for 24 h at constant temperature. Then the samples were dried at 120℃ for 12 h and calcined for 4–6 h under N_2 flow. The Co content was about 0.5, 1, 5, and 10 wt%.

The degradation experiments were performed in a cylindrical reactor containing 200 mL of the AO7 solution with magnetic stirring at about 500 rpm. The vessel was wrapped with foil in order to avoid any photochemical effects. The UV lamp ($\lambda = 254$ nm, 5 W, Liang Xing Electrical, Zhongshan) was placed vertically in the middle of the reactor and immersed about 30% into the solution. A stock solution of AO7 was prepared fresh with deionized water before each run and the initial concentration (C_0) was fixed at 50 mg/L except for the experiments concerning initial AO7 concentration. About 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used to adjust the initial pH (pH_0) of the dye solution. Then catalyst and PS were added into the stirred solution and the UV lamp was switched on before the reaction started. All experiments were conducted at constant temperature (20 ± 2℃) using cooling water. At pre-selected time intervals, samples were withdrawn and filtered through 0.22 μm membranes (Millipore Co.) before analysis.

2.3. Analytical methods

The pH of the solution was measured by FE20 pH meter (Metteler-Toledo Instruments Co. Ltd., Shanghai). The absorbance of AO7 was measured at $\lambda_{max} =$ 485 nm using a Rayleigh UV-9100 spectrophotometer (Rayleigh Co., China). UV–Vis spectra from 200 to 800 nm were recorded with a UV-1700 spectrophotometer (Shimadzu). COD was determined using a closed reflux spectrophotometric method based on the Standard of the People's Republic of China for Environmental Protection (HJ-T 399-2007).

3. Results and discussion

3.1. Decolorization of AO7 under different systems

To investigate the effect of Co loading on the catalytic activity, five catalysts with different Co content supported by GAC (0, 0.5, 1, 5, and 10%) were used to activate PS and remove AO7 in the dark condition. As shown in Fig. 1, the decolorization efficiency of AO7 increased from 25.5 to 43.2% with the increase of Co content varied from 0 to 1%. However, the decolorization efficiency of AO7 changed very little with further increase of Co content (1–10%). Based on the results obtained, 1% Co-GAC was chosen in the UV/Co-GAC/PS process.

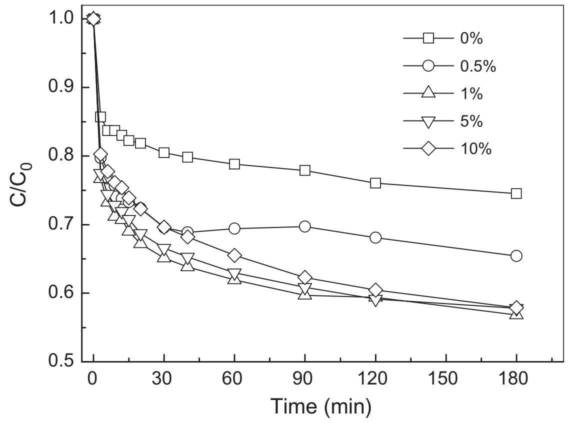

Fig. 1. Effect of different Co content supported by GAC on the decolorization of AO7 ($C_0 = 50$ mg/L, [PS] = 0.2 g/L, [catalyst] = 0.5 g/L, $T = 20 \pm 2$℃, pH_0 7).

As presented in Fig. 2, there was a slight color removal (4.6%) under UV irradiation alone. The degradation efficiency of organic dyes by direct photolysis is dependent upon reactivity and photosensitivity of the dye. Most commercially used dyes are usually designed to be light resistant, which makes them extremely difficult to be degraded under UV light in the absence of an additional agent [23]. As the oxidation ability of PS was quite limited ($E^0 = 2.01$ V) [8], the decolorization efficiency of AO7 with PS alone was almost the same as UV alone. When PS was combined with UV, the decolorization efficiency of AO7 increased to some extent (9.9%), indicating activation of PS by UV was not remarkable. Moreover, the adsorption of Co-GAC only was also confirmed, and the color removal of AO7 was about 35.8%.

When Co-GAC catalyst was combined with UV or PS, the decolorization efficiency of AO7 increased to some extent, but with no significant enhancement (Fig. 2). The decoloriazation efficiency of AO7 was 39.3% in UV/Co-GAC process, showing that only a small amount of active radicals can be produced during the catalytic UV process in the absence of oxidant [9]. The decolorization efficiency achieved was 43.9% under Co-GAC/PS process, illustrating that PS could be activated by Co-GAC. When UV was introduced into the Co-GAC/PS process, the decolorization efficiency of AO7 reached 96.2%, which is much higher than the dark condition. The decolorization efficiency of AO7 obtained by UV/Co-GAC/PS was remarkably higher than the sum of the decolorization efficiencies when AO7 was individually removed by UV and Co-GAC/PS process. Obviously, a clear synergetic effect existed in the combination of UV and Co-GAC/PS process for the decolorization of AO7.

3.2. Effect of PS concentration on the decolorization of AO7

The oxidant PS plays an important role in the reaction, as it is the source of the $SO_4^{-\cdot}$, so the effect of PS concentration on AO7 decolorization efficiency was investigated. As presented in Fig. 3, the decolorization efficiency of AO7 increased from 43.2 to 73.5% with the increase of PS concentration varied from 0.2 to 1.0 g/L. Further increase of the concentration of PS to 1.5 g/L, the decolorizaiton efficiency of AO7 improved slightly to 76.5%. It is due to the reason that with more PS in the system, more reactive radicals would be generated to degrade AO7. On the other hand, the side reactions of $SO_4^{-\cdot}$ and $SO_4^{-\cdot}$, $SO_4^{-\cdot}$ and PS became

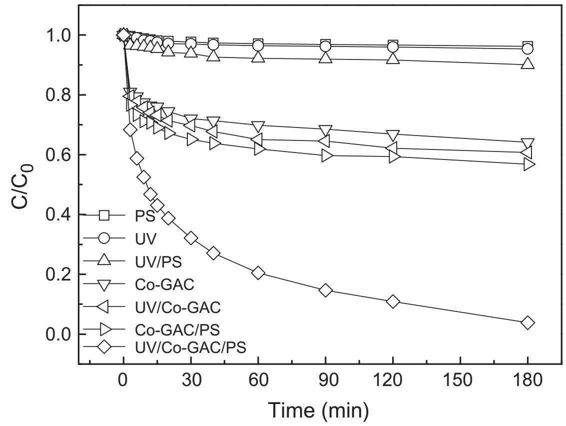

Fig. 2. Decolorization of AO7 under different systems ($C_0 = 50$ mg/L, [PS] = 1.0 g/L, [catalyst] = 0.8 g/L, $T = 20 \pm 2$℃, pH_0 7).

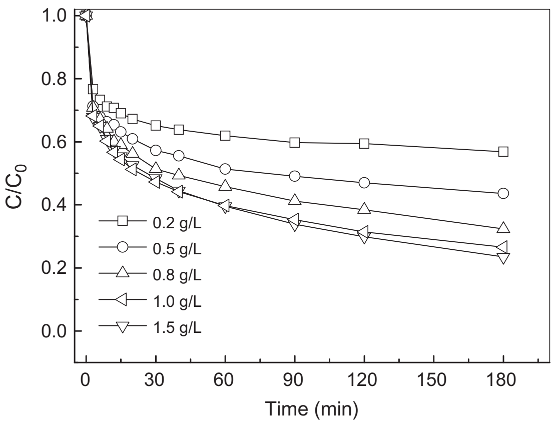

Fig. 3. Effect of PS concentration on the decolorization of AO7 ($C_0 = 50$ mg/L, [catalyst] = 0.8 g/L, $T = 20 \pm 2$℃, pH_0 7).

more significant with the increase of PS concentration, which would consume more PS via Eqs. (3) and (4) [7,24]. But considering the decolorization efficiency, 1.0 g/L was chosen as the optimal PS concentration for subsequent experiments.

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

$$SO_4^{-\cdot} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-\cdot} \quad (4)$$

3.3. Effect of initial pH on the decolorization of AO7

In order to investigate the influence of initial pH on the degradation of AO7, experiments were conducted at pH 3, 5, 7, and 9. It was shown in Fig. 4 that as the initial pH value decreased from 9 to 3, the decolorization efficiencies only increased from 95.8 to 98.7%. The insignificant effect of initial pH on the decolorization efficiency may be due to the fact that the pH value of the dye solution would drop with the progress of the reaction and finally incline to be around 3 at initial pH higher than 3 [7]. When sulfate radicals were generated by decomposition of PS via Eqs. (1) and (2), it could react with H_2O or OH^- to produce hydroxyl radical.

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + {}^{\cdot}OH + H^+ \quad (5)$$

$$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH \quad (6)$$

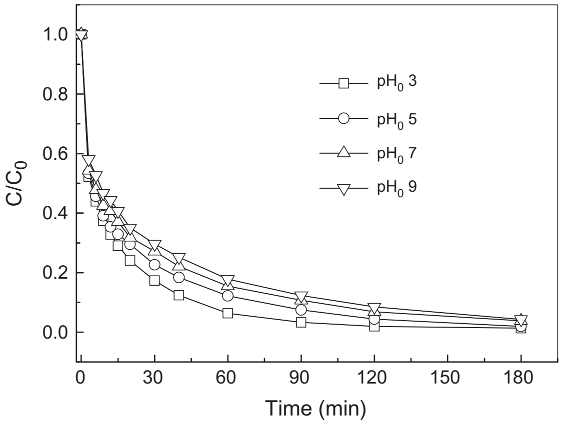

Fig. 4. Effect of initial pH (pH_0) on the decolorization of AO7 ($C_0 = 50$ mg/L, [PS] = 1.0 g/L, [catalyst] = 0.8 g/L, $T = 20 \pm 2$℃).

As seen in Eqs. (5) and (6), either H^+ would be produced or OH^- would be used, which brings up a reduction in pH. At the same time, H^+ would be further released by the dissociation of HSO_4^- [25], which was formed through the reaction of hydroxyl radical and sulfate radical (Eq. (7)) as well as the decomposition of PS in water (Eq. (8)) [25].

$$SO_4^{-\cdot} + {}^{\cdot}OH \rightarrow HSO_4^- + 0.5O_2 \quad (7)$$

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + 0.5O_2 \quad (8)$$

$$HSO_4^- \rightarrow SO_4^{2-} + H^+ \quad (9)$$

Therefore, pH would decrease to almost the same value and the decolorization of AO7 tended to be conducted under the similar conditions as the reaction proceeded. Thus, the similar decolorization efficiency was observed at different initial pH values, as illustrated in Fig. 4. This indicated that the UV/Co-GAC/PS process could be successfully applied at a wide range of initial pH, and the neutral pH 7 was selected as the initial pH for subsequent experiments.

3.4. Effect of catalyst dosage on the decolorization of AO7

The degradation of AO7 at different dosage of Co-GAC was investigated in this study. As presented in the Fig. 5, the degradation efficiency increased with the dosage of Co-GAC in the range from 0.5 to 1.0 g/L. As expected, the addition of Co-GAC significantly improved the removal efficiency of AO7. Co-GAC is multivalent oxide catalyst, which acts as a good provider of ≡Co(II) for the activation of PS. As an initiator, ≡Co(II) activates PS to generate $SO_4^{-\cdot}$, which induces the decomposition of AO7. Increasing Co-GAC dosage would correspond to a higher available ≡Co(II). This improved the decomposition of PS to generate more $SO_4^{-\cdot}$, and thus the higher degradation rate of AO7 can be achieved. Once PS was activated, the generated $SO_4^{-\cdot}$ and ·OH might initiate a series number of chain reactions during the UV irradiation. Despite different initial degradation rates of AO7 were observed when dosage of the catalyst increased from 0.8 to 1.0 g/L, the final removal efficiency was nearly the same. Therefore, 0.8 g/L was set as the catalyst dosage in the following experiments.

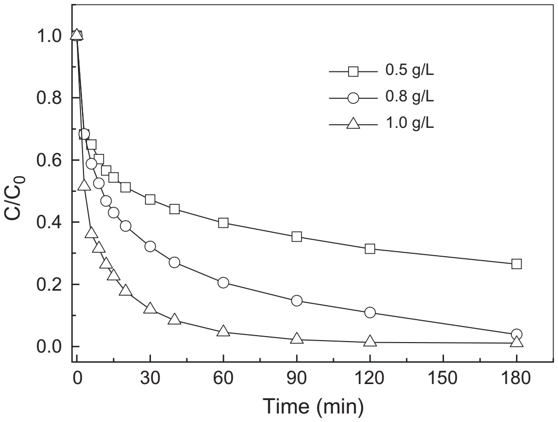

Fig. 5. Effect of catalyst dosage on the decolorization of AO7 ($C_0 = 50$ mg/L, [PS] = 1.0 g/L, $T = 20 \pm 2$°C, pH_0 7).

3.5. Effect of reaction temperature on the decolorization of AO7

The effect of reaction temperature at 12, 22, 32, and 42°C on AO7 decolorization was investigated. AO7 is not self-decomposed at elevated temperature (45°C) according to our experiment results (<5%). Therefore, the main degradation of AO7 was attributed to $SO_4^{-\bullet}$, derived from activation of PS by UV and catalyst. It can be seen from Fig. 6 that the decolorization rate increased with the increasing temperature. As the temperature had a limited effect on the decolorization efficiency, the room temperature of 22°C was chosen in the sequent experiments.

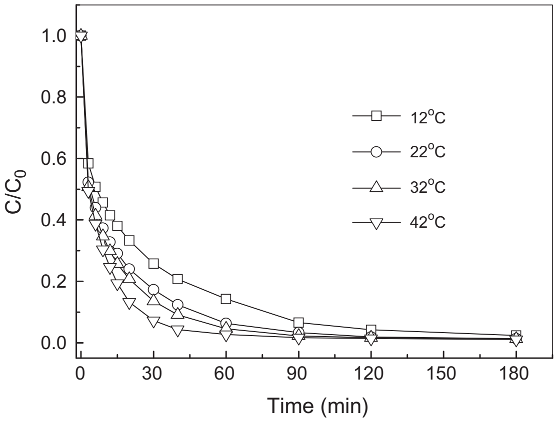

Fig. 6. Effect of reaction temperature on the decolorization of AO7 ($C_0 = 50$ mg/L, [PS] = 1.0 g/L, [catalyst] = 0.8 g/L, pH_0 7).

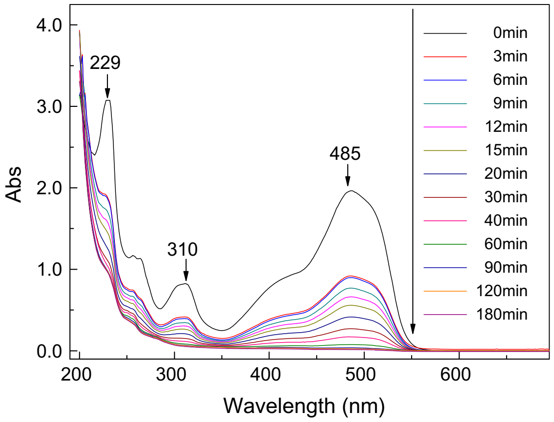

Fig. 7. UV–Vis spectra of AO7 in the UV/Co-GAC/PS process.

3.6. UV–Vis spectra and mineralization efficiency of AO7 in the UV/Co-GAC/PS process

To clarify the changes of molecular and structural characteristics of AO7 in the UV/Co-GAC/PS process under optimum conditions, representative UV–Vis spectra changes in the solution as a function of reaction time were observed in Fig. 7. It was presented that absorption spectrum of AO7 in aqueous solution was mainly characterized by three bands. One main band in the visible was shown at 485 nm originating from an extended chromophore, comprising both aromatic rings, connected through the azo bond. The other two bands in the ultraviolet region located at 229 and 310 nm were associated with benzene-like structures in the molecule [7,26,27]. The disappearance of the visible band with the reaction time was correlated with the fragmentation of the azo links which led to decolorization of AO7. As the reaction proceeded, the absorbance peak at 229 and 310 nm also diminished, indicating that the benzene and naphthalene rings were destroyed by oxidant and degraded to small molecule organics and eventually CO_2 and H_2O [28]. To verify the degradation of AO7, the values of COD before and after treatment were monitored. The COD removal efficiency was 38.5% after 180 min reaction.

4. Conclusion

This study showed that the combination of UV and Co-GAC catalyst with PS process is efficient for the AO7 degradation. The effects of various experimental conditions on the removal of AO7 were investigated in order to optimize the process. Under the optimal condition of initial pH_0 value 7, PS concentration 1.0 g/L, the catalyst loading 0.8 g/L in the UV/Co-GAC/PS system, the decolorization efficiency was 96.2% and COD removal was 38.5% within 180 min. It indicates that UV/Co-GAC/PS process is effective in degradation of AO7 in neutral pH solution, and consequently it appears as a promising process for dye wastewater treatment.

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