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Degradation of Caffeine in Aqueous Solutions by Cobalt Activation of Peroxydisulfate under Ultrasound Irradiation

Yunleiyu Guo[1,2,*]

[1]*Linyi Hengtai New Energy Co., Ltd, Linyi, China*
[2]*Linyi Hengyuan New Energy Development Co. Ltd, Linyi, China*
[*]*Corresponding author*

Abstract: *Degradation of the Caffeine in aqueous solution using sulphate radicals under ultrasound irradiation was investigated. The experiments were conducted with only ultrasonication(US), cobalt activated peroxydisulfate(PS/Co^{2+}), ultrasonication activated peroxydisulfate(US/PS) and cobalt activated peroxydisulfate under ultrasound irradiation($US/PS/Co^{2+}$). It was found that the optimal removal of Caffeine (CAF) in aqueous solution was $US/PS/Co^{2+}$, which 57.4% of the CAF can be degradated at 8 h. The effect of CAF initial concentrations of the aqueous solution on the sonochemical degradation rate was also discussed. In our experiments, 100% CAF can be removal within 3 h at the condition of 10 mM PS, 0.5 mM Co^{2+} under ultrasound irradiation at pH 2.2.*

Keywords: *Pharmaceuticals and personal care products, caffeine, sonochemical degradation, sodium peroxydisulfate*

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have gained growing attention in the last decade because of their possible threats to aquatic environment and human health. The presence and potential risks of PPCPs in different water matrixes such as rivers[1], lakes [2]and domestic sewage[3]have been reported. Among the PPCPs, caffeine(CAF) has been detected with high frequency for its widely used in coffe, tea, chocolate, soft drinks and pharmaceuticals. In the Lake Simcoe watershed of Canada, the concentration of CAF varied from 5.1 to 76.8 ng L^{-1}[4], CAF has also been detected in the inffluent at a level of 3.4 to 6.6 μgL^{-1} in the wastewater treatment plants of Beijing[5]. For its widespread occurrence, CAF can act as a tracer of water pollution. Therefore, it is of interest to develop efficient water treatment method for removing CAF from aquatic environments.

Advanced oxidation processes (AOPs) are generally recognized as the most effective methods for the degradation of hazardous, refractory and non-biodegradable organic pollutants, for the generation of active oxygen species. AOPs such as ozonation[6], Fenton's Reagent[7], photocatalysis[8], have been successfully used for the degradation of the organic compounds. Recently, a innovative advanced oxidation technology using sodium peroxydisulfate ($Na_2S_2O_8$, PS) to generate sulfate radicals($SO_4^{\bullet -}$) has gained great concerns and has been found to be more efficient and powerful oxidant than hydroxyl radicals in water treatment [9,10]. PS can generate sulfate radicals with higher standard redox potentials (1.82 V). The peroxydisulfate anion can be activated by ultrsound, heat, base, transition metals, and quinone activation. Among the various methods, transition metals, particularly Co^{2+}, are the best activator[11].

As one kind of AOPs, ultrasonics (US) has been investigated to degrade non-biodegradable pollutants for the simplicity of the system and no production of toxic by-products. The chemical effects of sonication, such as the formation, growth, and implosive collapse of bubbles in a liquid, all of which produce unusual chemical and physical environments, arise from acoustic cavitation. The collapse of the bubbles during the adiabatic compression leads to the generation of intensive local temperature and pressure. Sonication in aqueous solution can generate HO·at the bubble surface or in bulk solution, which could degradate most of the organic pollutants.

However, in most cases, the degradation efficiency of ultrasonic cavitation process are limited to low level, and energy use efficiency is very low due to energy losses during transfer processes. The combination of ultrasound and persulfate ($S_2O_8^{2-}$) has recently received much attention as a potential

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alternative for the treatment of recalcitrant or hazardous compounds. This combination was proved to be effective for the enhanced removal of humic acid[12], 1,1,1-trichloroethane[13], In this scenario, persulfate can be activated to generate stronger oxidant sulfate radicals.

In this study, the degradation of CAF using sulfate radicals activated by cobalt ions under ultrasound irradiation was investigated. The effect of CAF initial concentrations of the aqueous solution on the sonochemical degradation rate was also discussed.

2. Experiment results and discussion

CAF (USP/BP grade) and cobalt sulfate ($CoSO_4 \cdot 7H_2O$, analytical grade) were obtained from Shanghai Jingchun Biochemical Technology Co., Ltd. (Shanghai, China). PS (analytical grade) was purchased from Tianjin Chemical Reagent Company, China. All other chemicals were of analytical grade and used without further purification. The water used in all experiments was purified by a Milli-Q system.

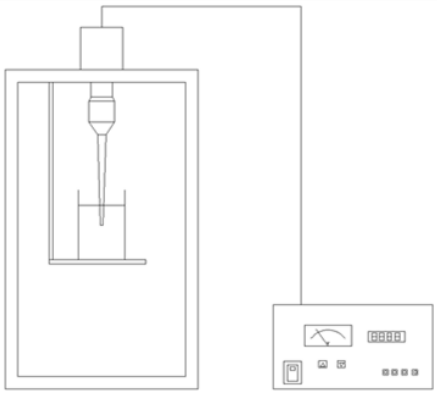

Figure 1: The device of ultrasonic.

Sonication as shown in Fig. 1 was performed under air atmosphere with a 22 kHz ultrasonic generator (Model GA92-IIDB, Wuxi Shangjia Biotechnology Co., China), which was equipped with a titanium probe (8 mm of diameter). Sonication was applied in pulsed mode (2 s on 2 s off) and the sonication time was expressed as the sum of pulse-on times. The titanium probe was placed about 1 cm below the surface of the solution during sonication. Prior to the sonication, the pH values of the solution were adjusted to a desired level using diluted solution of H_2SO_4 or NaOH and appropriate amount of PS was added. All the experiments were carried out in a 100 mL cylindrical reaction cell, in which was added 50 mL of the test solution. At preselected time intervals, samples were taken by syringe and filtered through 0.45 μm membranes. Then aliquots of 20 μL were injected manually for HPLC analysis (LC-10AT, Shimadzu, Japan). AC18 reverse phase column (4.6×150 mm) was used for separation. The concentration of caffeine was determined by a UV-Vis spectroscopy at 273 nm. Methanol and water were used as mobile phase (30:70, v/v) at a flow rate of 1.0 mL/min. The degradation ratio of caffeine was calculated as follows:

$$R\%=C_t/C_0\times 100\% \quad (1)$$

Here R% is the degradation ratio of caffeine, C_0 and C_t is the initial concentration and remained concentration of caffeine.

A series of experiments were performed in order to compare the effects of different treatment methods, including US, PS activated by ultrasonic irradiation (PS/US), PS activated by cobalt ion(PS/Co^{2+}), and PS activated by cobalt under ultrasonic irradiation ($US/PS/Co^{2+}$). The experimental results were shown in Fig. 2.

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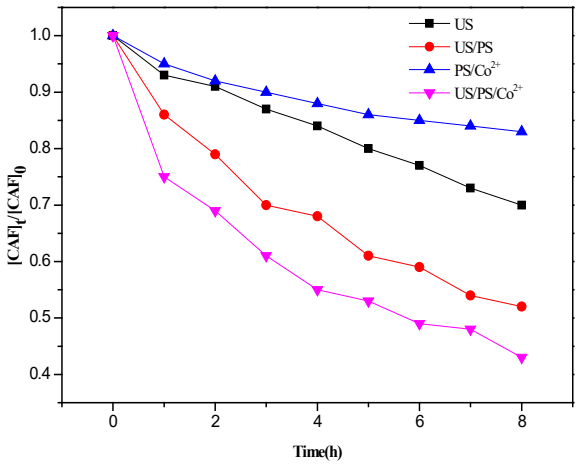

Figure 2: The effect of different removal methods on CAF degradation ratio. Experimental conditions: [CAF] = 20 mg/L, [PS] = 10 mM, [Co^{2+}] = 0.5 mM, pH=2.2, ultrasound power: 200 W.

It was observed obviously that CAF was hardly to be removal by US and PS actived by cobalt, only 30.1% and 16.8% was degradated for 8 h. However, the degradation ratio of CAF increased to 48.4% on the condition of PS activated by US, it can be accelerated remarkably by adding PS. The optimum removal efficiency was obtained with US/PS/Co^{2+} treatment method, in the same case, 57.4% of the CAF was removal in the experiment of combinate US with PS activated by cobalt. It means that the optimum and efficient treatment method for removal the CAF in aqueous solution was ultrasound coupled PS activated by cobalt.

The effect of CAF initial concentration on the CAF degradation ratio was investigated. The results were shown in Fig. 3. The degradation ratio was inversely proportional to the initial CAF concentration. The degradation ratios of CAF were 100%, 67.5%, 18.2% and 14.3% after 3 h when the initial concentrations of CAF were 5 mg L^{-1}, 10 mg L^{-1}, 20 mg L^{-1}, and 50 mg L^{-1}, respectively. The results were a common phenomenon [14]. When the concentration of initial CAF increased, the amount of active oxygen species such as HO· and $SO4^{\bullet-}$ radicals in aqueous solution would be constant. So the CAF degradation rate was decreased.

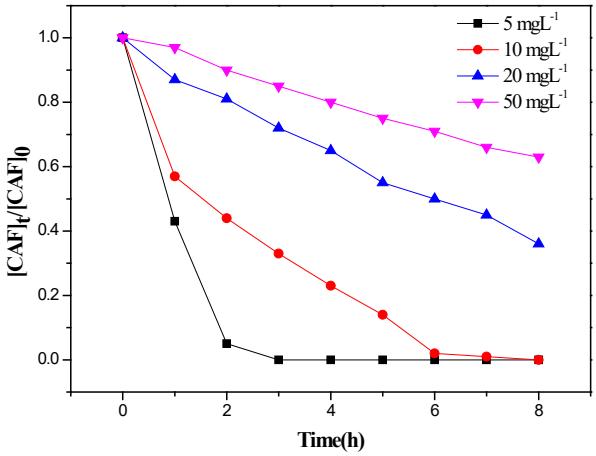

Figure 3: The effect of CAF initial concentration on the CAF degradation ratio. Experimental conditions: [PS] = 10 mM, [Co^{2+}] = 0.5 mM, pH=2.2, ultrasound power: 200 W.

3. Conclusion

The degradation of the CAF in aqueous solution using sodium peroxydisulfate activated by cobalt sulfate combined with sonication was investigated. The results showed that ultrasound coupled PS activated by cobalt ion can accelerate the removal of CAF remarkably and the efficient treatment method for treating the CAF in aqueous solution. The degradation ratio of CAF decreased generally with increasing the CAF initial concentration.

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