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Technical Note

Feasibility study of ultraviolet activated persulfate oxidation of phenol

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ABSTRACT

Using ultraviolet photolytic persulfate activation to produce two sulfate radicals ($SO_4^{-\bullet}$) exhibits a potential for destroying organic contaminants in wastewater treatment applications. This study investigated both the feasibility of using a UV/SPS (sodium persulfate) process to treat phenol in aqueous phase and the effect of pH on degradation efficiency and TOC removal. The results revealed that a high initial persulfate concentration (i.e., 84 mM) and a lower initial phenol concentration (i.e., 0.5 mM) resulted in rapid and complete phenol degradation within 20 min. For all three pHs evaluated (i.e., 3, 7 and 11), complete phenol degradation was also achieved after 30 min of treatment by UV/SPS oxidation processes (i.e., under an SPS/phenol molar ratio of 84/0.5) with pseudo-first-order rate constants ($k_{obs,\ phenol}$) of 0.14–0.16 min^{-1} (average half-life ($t_{1/2}$) = 4.5 min). UV–Vis spectrum scanning of the aqueous solution during treatment identified the development of brown color in the wavelength range of 400–460 nm. The colored intermediate compounds that formed were suspiciously similar to those observed during Fenton treatment. However, a more aggressive oxidation at pH 11 showed a rapid and more complete removal of TOC in aqueous phase. Therefore, it is recommended that UV photolytic persulfate activation under basic pH be a preferred condition for treatment of phenol.

1. Introduction

The persulfate anion ($S_2O_8^{2-}$, E^o = 2.01 V) is a strong oxidant that can be activated to generate an even stronger oxidant known as a sulfate radical ($SO_4^{-\bullet}$, E^o = 2.4 V) (Huie et al., 1991). Commercial TOC analyzers commonly utilize ultraviolet photolytic or thermal persulfate activation (e.g., 100 °C) to mineralize organic compounds and allow superior carbon liberation (Visco et al., 2005). In situ chemical oxidation using persulfate or activated persulfate is also an increasingly popular remediation technology that can be applied to a wide range of organic contaminants. Using UV photolytic persulfate activation to produce two $SO_4^{-\bullet}$ in accordance with Eq. (1) exhibits great potential for destroying organic contaminants in wastewater treatment applications. Herrmann (2007) has reported that the extinction coefficients of UV photolytic persulfate activation at 248, 308, and 351 nm are 27.5 ± 1.1, 1.18 ± 0.05, and 0.25 ± 1.01 mol^{-1} cm^{-1}, respectively, and that the formation of photo fragments (e.g., $SO_4^{-\bullet}$) decreases as photolytic wavelength increases.

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\bullet} \quad \text{(Dogliotti and Hayon, 1967)} \qquad (1)$$

Phenol and its derivatives are commonly found in wastewater resulting from the manufacture of various products, such as petrochemicals, textiles, paint, and pharmaceuticals (ATSDR, 2008). Advanced oxidation processes (AOPs), such as Fenton reaction, Fenton-like reaction, UV/Fenton, UV/H_2O_2, and UV/O_3, have been reported to decompose phenol effectively (Esplugas et al., 2002; Kušić et al., 2006a,b). However, even though complete degradation of phenol can be achieved, mineralization of phenol is still a challenging issue. For example, Kušić et al. (2006b) investigated phenol degradation using various Fenton-type processes and reported complete phenol removal for each of the applied processes. However, residual TOC from applied Fenton-type processes ranged from 45% to 60%, and complete mineralization had not yet been achieved. Moreover, partial mineralization in Fenton-based AOP treatments of phenol may lead to the generation of highly toxic intermediate products such as catechol, hydroquinone, benzoquinone, and maleic acid (Mijangos et al., 2006; Yalfani et al., 2009). Application of UV light in conjunction with a Fenton reaction has been demonstrated to be capable of accelerating the degradation of phenol and also enhancing mineralization efficiency (Esplugas et al., 2002; Kušić et al., 2006a,b).

Alternatively, a UV/$S_2O_8^{2-}$ process acting in a reaction mechanism similar to Fenton-based AOP has been demonstrated to be effective in degrading organic contaminants (Hori et al., 2005, 2007; Lau et al., 2006; Criquet and Leitner, 2009; Salari et al., 2009). For example, Hori et al. (2007) demonstrated that fluorotel-

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omer unsaturated carboxylic acid completely disappeared within 5 min by using a UV/$S_2O_8^{2-}$ process (note: the UV wavelength region was 220–460 nm from the xenon–mercury lamp, and the sensitive wavelength was 220–310 nm). Lau et al. (2006) also demonstrated that a UV (254 nm)/$S_2O_8^{2-}$ oxidation process at acidic, neutral, and basic pH ranges effectively mineralized butylated hydroxyanisole. Moreover, Huang and Huang (2009) investigated a two-stage oxidation process using UV (254 nm)/$S_2O_8^{2-}$ to degrade bisphenol A into intermediate products, followed by using H_2O_2/Fe(II, III)) to ensure complete mineralization of bisphenol A, and reported a TOC removal of around 90%. The present work investigated both the feasibility of using a UV/$S_2O_8^{2-}$ process in treating phenol in aqueous phase and the effect of pH on degradation efficiency and TOC removal.

2. Materials and methods

2.1. Chemicals

Phenol (99.2%) and phosphoric acid (86.0%) were purchased from J.T. Baker; sodium persulfate ($Na_2S_2O_8$, SPS, 99.0%) was purchased from Merck; sulfuric acid (95–97%) was purchased from Fluka; sodium bicarbonate (99.7%), sodium hydroxide (99.0%), and sodium thiosulfate (99.5%) were purchased from Riedel-de Haën; methanol (99.9%) was purchased from ECHO Chemical; potassium iodide (99.5%) were purchased from Union Chemical Work. The water used was purified using a Millipore reverse osmosis purification system.

2.2. Experimental procedure

All experiments were conducted in a 3 L reaction flask in an air-conditioned room (25 ± 2 °C). A quartz tube was placed vertically in the middle of the reactor; the tube contained a 15 W mercury lamp (UV-C, 254 nm, Sparkie GLQ-D287 supplied by Biddy Photronic Co., Taiwan). The top of the reaction flask was covered with a reaction flask head that was sealed with stainless steel clamp.

Initial efforts focused on investigating the feasibility of a UV/SPS process in degrading phenol at various SPS/phenol molar ratios (i.e., 8.4 or 84 mM of SPS to 0.5 or 5 mM of phenol). The phenol solutions were prepared by adding the required amount of pure phenol and mixing for a few minutes in the reaction flask. Phenol degradation reactions were initiated by added a predetermined amount of SPS to the reaction flask, and the resulting solution was continuously stirred in an open batch system for 1 h. The pH electrode was installed through one of sample ports on the top cover. When UV was used for persulfate activation, the UV lamp was turned on as soon as SPS was added. Seven samples (5 mL each) were collected periodically using a gas-tight syringe (SGE Analytical Science) and were used for analyzing phenol, SPS, and UV–Vis absorbance spectrum. TOC analysis was conducted at the end of each experiment. Control tests to observe phenol degradation in the presence of UV or SPS were also conducted.

Further experiments to investigate the influence of pH (i.e., 3, 7 and 10) on the degradation rate of phenol were conducted at a fixed SPS/phenol molar ratio of 84/0.5. The procedure in these experiments was similar to that described earlier with the exception that the solution pH was maintained during the course of reaction within a pH unit ±0.2 of the designated pH. This was accomplished with a pH controller (pH/ORP controller PC-310, Suntex Instruments) which pumped 0.5 N H_2SO_4 or NaOH at a rate of 1 mL min^{-1} through two Teflon tubes inserted in a port on the top cover of the reaction flask. The variation in volume (accounting for acid/base additions and samples taken) was limited to <2%. All experiments were conducted in duplicate and averages were reported.

2.3. Analysis

For analysis of phenol and SPS, aqueous samples were filtered using a polytetrafluoroethylene filter (0.2 μm, Toyo stainless syringe holder). The concentration of phenol was measured using a high-performance liquid chromatographer (Agilent 1100) equipped with UV–Vis detector set at a wavelength of 254 nm in accordance with operational conditions reported by Liang and Su (2009). Persulfate anion concentration was determined by iodometric titration with sodium thiosulfate (Kolthoff and Stenger, 1947). Color change was determined by using a UV–Vis spectrophotometer (Jasco V-530) and 1-cm light path in quartz cuvettes at a wavelength 455 nm (Pintar and Levec, 1992; Mijangos et al., 2006) and to scan the whole wavelength range of 200–1000 nm. TOC analysis was performed using a TOC analyzer (Aurora 1030 W, O.I. Analytical). The pH was measured using a pH meter (Thermo Orion 720A$^+$) equipped with a ROSS pH combination electrode.

3. Results and discussion

3.1. Influence of the SPS/phenol molar ratio

Tests were conducted to determine what effect the SPS/phenol molar ratio had on degradation of phenol in UV photolytic persulfate activation, and the results obtained are shown in Fig. 1. Two SPS/phenol molar ratios (84/0.5 and 8.4/0.5) achieved complete phenol degradation after 20 and 60 min (respectively) of treatment. The pseudo-first-order degradation rate constants of phenol ($k_{obs,\ phenol}$) are presented in Table 1. It can be seen that the $k_{obs,\ phenol}$ increased with increased persulfate concentrations. However, oxidation rate efficiency decreased as initial phenol concentration was increased (i.e., 0.5 to 5 mM) (see Fig. 1a). These results are similar to other studies investigating UV/H_2O_2 and UV/SPS systems, which revealed that the contaminant degradation rates increased as initial contaminant concentrations decreased (De et al., 1999; Modirshahla and Behnajady, 2006; Salari et al., 2009). This can be explained by considering that the molar extinction coefficient of the phenol at 254 nm is very high, so a rise in its concentration induces an inner filter effect, and hence the solution becomes more impermeable to UV radiation (Modirshahla and Behnajady, 2006). Persulfate decomposition under all experimental conditions with the presence of phenol exhibited less than a 10% reduction of initial persulfate concentrations (data not shown). However, the control test of UV/SPS in the absence of phenol showed a $k_{obs,SPS}$ of 1.0×10^{-2} min^{-1} ($R^2 = 0.99$).

UV–Vis spectral changes of phenol during reaction in the UV/SPS/phenol system are displayed in Fig. 1b. Before treatment, the UV–Vis spectrum of phenol exhibited a main absorption band in the UV region (<350 nm). However, as soon as the activated reaction started, the intensity of the visible band in the wavelength region of 400–460 nm rapidly rose. The absorption region confirms the development of color, which is in agreement with the color measurements reported by Mijangos et al. (2006), who indicated that colored intermediate compounds were generated in the course of Fenton oxidation of phenol and that the absorption peak of these compounds occurred at a wavelength of 455 nm. They also reported that these highly colored intermediate compounds may include *p*-benzoquinone (yellow), *o*-benzoquinone (red), and hydroquinone (colorless), and the mixed solution of all intermediate compounds revealed brown color. Furthermore, Fig. 1c shows absorbance variation at 455 nm during the UV/SPS oxidation process. The control test of phenol under UV light showed almost no color change (i.e., SPS/phenol = 0/0.5). However, when SPS was added and SPS/phenol molar ratios were 8.4/0.5, 8.4/5, and 84/5,