

Degradation of 2,4,6-trichlorophenol in aqueous solutions using peroxymonosulfate/activated carbon/UV process via sulfate and hydroxyl radicals



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ARTICLE INFO

Article history:

Received 17 August 2015

Received in revised form

23 November 2015

Accepted 29 November 2015

Available online 12 December 2015

Keywords:

2,4,6-Trichlorophenol

Sulfate radical

Activated carbon

Peroxymonosulfate

Reaction mechanism

ABSTRACT

In this study, the activation of peroxymonosulfate (PMS) was investigated by activated carbon (AC) along with UV for 2,4,6-trichlorophenol (TCP) degradation. The effects of operating parameters including pH, PMS concentration, AC dosage, initial TCP concentration and reaction time on TCP degradation were studied and optimized at pH 5.0, 8.0 mM PMS, 0.75 g/L AC and 75 min. Single step or two step additions of PMS made no marked difference in terms of TCP removal. The results of PMS decomposition showed that, AC/UV configuration was able to significantly activate PMS to degrade TCP compared to sole application of AC or UV. The contribution of UV in activation of PMS was more than that of AC. The rate constants of TCP degradation were in range of 0.0103–0.0512 min⁻¹ for initial TCP concentrations of 5–50 mg/L. Scavenging experiments revealed that sulfate radical was the dominant radical of its kind for degradation of TCP, although hydroxyl radical was also partly effective. The results indicated that contribution of free radicals in solution was higher than that of surface-bound radicals. Moreover, mineralization of TCP was evaluated by COD, TOC and chlorine release and related results were 50.2%, 31.2% and 55%, respectively.

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1. Introduction

Protection of the environment from pollution by synthetic organic compounds released from human activities has become an issue of growing concern during recent decades. Chlorophenol compounds are used in various industries with high volumes. Toxicity and persistence to biodegradation are dependent on the C–Cl bond and the position of chlorine atoms relative to the hydroxyl group [1]. 2,4,6-trichlorophenol (TCP) is one of chlorophenol compounds that is widely used in agriculture as a herbicide, fungicide and a glue preservative [2]. This chemical is toxic, resistant to biodegradation and bio-accumulative which has been classified as a priority pollutant in the environment based on the list of US Environmental Protection Agency [1,3,4]. TCP is carcinogenic to animals which can cause blood and liver cancers through oral exposure (drinking water or food) [5]. TCP may also be considered as a by-product of disinfection in chlorination system which

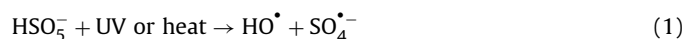
has been frequently detected in receiving waters [3,4]. Although the use of TCP in agriculture has been banned, TCP is still a precursor in production of several fungicides. TCP along with other chlorophenols have been found in industrial wastewaters such as pulp and paper, dye and pigment, pharmaceuticals and also in municipal waste incineration [6,7]. TCP belongs to the recalcitrant pollutants which is persistent to conventional biological and physico-chemical methods. Biological methods are not capable of eliminating TCP from polluted water since TCP is toxic for microorganisms [8]. Recently, Advanced Oxidation Processes (AOPs) have been proposed as effective processes for degradation and mineralization of recalcitrant pollutants in polluted water. These processes are based on in situ generation of hydroxyl radical (HO[•]) which is a powerful oxidant with $E^0 = 2.7$ V. AOPs involve Fenton reagent, UV/H₂O₂, UV/TiO₂, ozonation, electrooxidation, etc. which have different mechanisms for the generation of hydroxyl radical [9,10].

In recent years, the application of sulfate radical has been increased in degradation of organic compounds and wastewater treatment. It is suggested as an alternative of hydroxyl radical thanks to its high redox potential (2.5–3.1 V) [11,12]. Sulfate radicals have a longer lifetime (3–4 × 10⁻⁵ s) than hydroxyl radicals

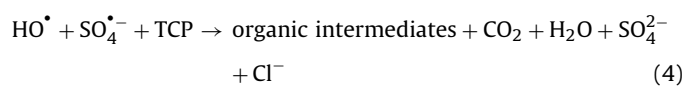
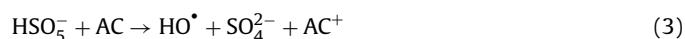
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(2×10^{-8} s); therefore, they have more chances of reacting with organic pollutants [13]. Sulfate radicals are produced by activation of persulfate ($S_2O_8^{2-}$) and peroxymonosulfate (HSO_5^-). Peroxy-monosulfate (PMS) is often activated by heat [14], UV [15,16] and transitional metals (Co, Fe, etc.) [17]. Peroxymonosulfate produces both sulfate and hydroxyl radicals in presence of UV and heat [14].



Activated carbon (AC) is one of the most applicable materials in water and wastewater treatment. It has been widely used as an adsorbent, a heterogenic catalyst and support because of its huge specific surface area, inexpensiveness and pore volume [18]. Activated carbon can activate PMS through the mechanism of electron transfer from surface (Eqs. (2) and (3)). The produced hydroxyl and sulfate radicals can degrade TCP to mineral compounds and organic intermediates (Eq. (4)) [19].



Few studies have demonstrated that activated carbon (AC) can activate both hydrogen peroxide and PMS [19,20]. However, there is not much data available in case of activation of PMS by AC for degradation and mineralization of organic compounds. For such purpose, there is no survey dealing with the application of PMS/AC/UV in degradation of TCP yet and also the determination of reaction mechanism has not been studied by scavenging experiments. In the current study, we investigated the performance of PMS/AC/UV system in degradation of TCP with a focus on operating parameters. The reaction mechanisms of AC and UV with PMS, as well as that of PMS decomposition are discussed further. Finally, mineralization of TCP was analyzed by COD, TOC and chlorine release parameters.

2. Materials and methods

2.1. Chemicals

2,4,6-trichlorophenol ($Cl_3C_6H_2OH$) was purchased from ACROS Organic Inc. with purity of 98%. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used as a source of peroxymonosulfate which was provided from Aldrich Inc. Ethanol, methanol (HPLC grade), water (HPLC grade), *tert*-butanol and activated carbon were supplied from Merck Company. Potassium dichromate and ferrous ammonium sulfate were obtained from Fluka and Merck Company respectively. All chemicals were analytical grade reagents and were used as received without further purification. Double distilled water was used in the present study.

2.2. Experiments

Degradation studies for the performance evaluation of PMS/AC/UV for TCP removal from aqueous solutions were carried out in the batch condition. For these experiments, 200 mL of TCP solution was poured in cylindrical quartz reactor of 300 mL. Then a certain amount of AC was added to the solution. The solution pH was adjusted with 0.1 M H_2SO_4 or 0.1 M NaOH solution to range the pH from 3.0 to 11.0. A UV-C lamp (6W, Philips) was used as a source of irradiation with maximum emission of 253.7 nm. The UV-C light intensity was measured with a Lux-UV-IR radiometer (Leybold Didactic GMBH-666-230). The gap between UV lamp

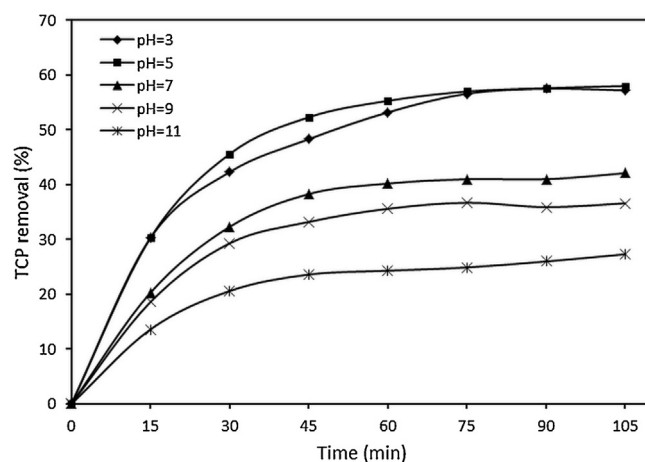


Fig. 1. The effect of pH on TCP degradation in PMS/AC/UV system under condition: PMS = 8 mM, 0.50 g AC, 50 mg/L TCP.

and cylindrical quartz reactor was 2 cm. The light intensity was 1.35 ± 0.1 mW/cm² during all experiments. After that, a certain amount of PMS was slowly added to the solution and then, the mixture was magnetically stirred with speed of 200 rpm under the temperature of 25–28 °C. Samples were taken at regular intervals of fifteen minutes during the experiments. In order to evaluate the effect of oxidant and catalyst, the same experiments were also conducted for PMS and AC separately. Scavenging experiments were carried out in the presence of ethanol, methanol, *tert*-butanol (0.5 M) and iodide potassium with concentration of 10 mM.

2.3. Analytical method

COD values were determined by colorimetric method using low range COD ampoules (HACH Chemical) with a spectrophotometer (DR 5000, Hach). TOC values were measured by a TOC Analyzer (Shimadzu, Japan). Chloride ions were determined based on Standard Method (titration with silver nitrate) [21]. PMS was determined by iodometric method which was titrated by sodium thiosulfate. Concentration of TCP was measured by High Performance Liquid Chromatography (HPLC) (KNAUER, Germany), where a C-18 column and a mobile phase of methanol/water (70:30, v/v) were used at a flow rate of 1 mL min⁻¹. An injection volume of 20 μL was utilized and TCP values were measured by employing a UV detector at 280 nm.

3. Results and discussions

3.1. The effect of solution pH

The solution pH is a key factor in chemical processes for water remediation. Fig. 1 shows the effect of pH on TCP removal under condition of PMS = 4 mM and 0.75 g AC. As can be clearly seen, with the increase of pH values, removal efficiency was significantly reduced. Consequently, TCP removals were 53.2%, 55.3%, 40.2%, 35.6% and 24.3% at pH of 3.0, 5.0, 7.0, 9.0 and 11.0, respectively. In alkaline condition, degradation of TCP is reduced due to self-decomposition of PMS which occurs in form of non-radical [22]. Moreover, at acidic condition, active sites of AC are charged by protons enabling it to adsorb chloride function of TCP. Hence, TCP degradation availability on AC surface at lower pH is more than that at higher pH. The redox potentials of HSO_5^- and $SO_4^{\bullet-}$ are higher in acidic condition rather than in alkaline condition [11]. Several researchers have reported that PMS has the best performance in

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