



## Aqueous phase degradation of methyl paraben using UV-activated persulfate method



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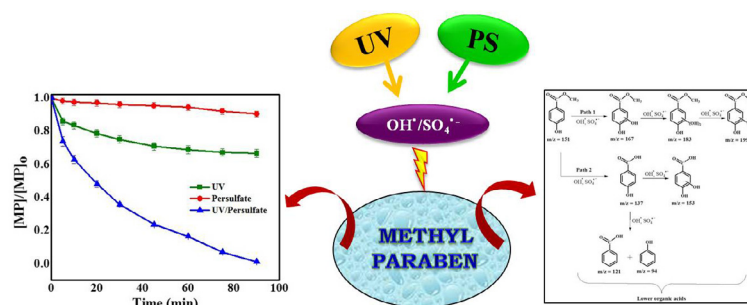
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### HIGHLIGHTS

- Aqueous phase MP degradation using UV/persulfate method was investigated.
- Degradation rate of MP followed pseudo-first-order kinetics.
- MP degradation was pH dependent.
- $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$  and humic acid exhibited inhibitory effect on MP degradation.
- Hydroxylation and hydrolysis were possible pathways of degradation of MP.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Methyl paraben (MP), a widely used preservative, exhibits endocrine-disrupting properties with estrogenic activities. The aqueous phase degradation of MP, using UV-activated persulfate method, was investigated in the present study. The combination of UV irradiation and persulfate anion successfully degraded MP showing 98.9% removal within 90 min. A quenching experiment using ethanol (EtOH) and *tert*-butyl alcohol (TBA) showed the presence of both radicals ( $\text{OH}^\bullet$  and  $\text{SO}_4^{\bullet-}$ ) in the system; near neutral pH  $\text{SO}_4^{\bullet-}$  radical was the major species. The influence of various factors such as persulfate dose, initial MP concentration, solution pH, and water matrix components on the degradation kinetics was examined in view of the practical applications of the developed process. The degradation rate of MP was considerably increased as the amount of persulfate increased. The degradation of MP in the UV/persulfate system was pH dependent and more promising near neutral pH (6.5) conditions. The presence of anions such as  $\text{Cl}^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{HCO}_3^-$  showed inhibitory effect towards MP degradation. The presence of humic acid also suppressed the degradation efficiency of MP. The reaction rate followed pseudo-first-order kinetics for all of the degradations. The degradation of MP by UV/persulfate treatment led to the production of seven transformation byproducts, which were identified using ultra-high-performance liquid chromatography-mass spectrometry (UPLC-MS). A degradation pathway for MP degradation was also proposed. The results of the present study reveal that the UV/persulfate process could be an effective approach to remove MP from aqueous solutions.

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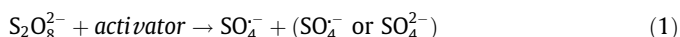
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## 1. Introduction

Pharmaceuticals and personal care products (PPCPs) pose a potential global threat to drinking water and aquatic ecosystems [1]. Alkyl and aryl esters of para-hydroxybenzoic acid, known as parabens, are a group of PPCPs with activities against yeasts, molds, and bacteria over a wide pH range. These antimicrobial properties of parabens encourage their use in pharmaceuticals, foodstuffs, and cosmetics as preservatives [2], which has led to their presence in approximately 80% of personal care products [3]. Parabens are known as endocrine-disrupting compounds (EDCs) and possess estrogenic activities [2,4]. The U.S. Environmental Protection Agency (USEPA) has classified parabens as emerging environmental contaminants [5]. Despite the restricted threshold limit of these chemicals in cosmetics by the European Union, parabens and their residues have frequently been detected in rivers [6,7], discharges of wastewater treatment plants and even in drinking water [8].

Among parabens, the amounts of methyl paraben (MP) in various cosmetic products are reported to be higher compared to others [4] and have the potential to cause breast cancer [9]. Biodegradation of parabens is likely in natural environments; however, they are characterized by slow reaction rates, which tend to be reduced as the alkyl chain length or degree of chlorination increase [2]. The presence of parabens in the discharge of wastewater treatment plants (WWTPs) indicates their incomplete removal through conventional treatment processes [2,10]. Thus, the development of an effective treatment methodology to eliminate such contaminants is the need of the hour. Advanced oxidation processes (AOPs), which are simple and cost effective, have gained much attention for the decontamination of wastewater containing a variety of refractory organic contaminants [11,12]. AOPs rely on the formation of reactive species, namely hydroxyl ( $\text{HO}^\cdot$ ) and sulfate ( $\text{SO}_4^\cdot$ ) radicals, which can be used to degrade and mineralize recalcitrant pollutants [13–15]. Photo-assisted AOP processes, such as UV/ $\text{O}_3$ , UV/ $\text{H}_2\text{O}_2$ , UV/ $\text{S}_2\text{O}_8^{2-}$ , and UV/ $\text{TiO}_2$ , have successfully been used for aqueous phase degradation of organic contaminants [16]. Sulfate radical ( $\text{SO}_4^\cdot$ ) assisted AOPs are efficient to remove organic contaminants in wastewater treatment and in situ chemical oxidation (ISCO). The  $\text{SO}_4^\cdot$  radical is considered to be an effective substitute for the  $\text{HO}^\cdot$  radical due to its high redox potential (2.5–3.1 V) and longer lifetime ( $3\text{--}4 \times 10^{-5}$  s) [17]. The persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ) is a strong, aqueous-stable, selective, and cost effective oxidant that operates at a wide pH range (1.2–12) [18,19]. Moreover, the persulfate anion is stable at ambient temperatures and generates  $\text{SO}_4^\cdot$  radicals by breaking peroxide bonds upon exposure to heat, UV light, bases, transition metals and ultrasound. (Eq. (1)) [20,21]. The sulfate ion is the final product of the  $\text{SO}_4^\cdot$  radical and is considered to be ecofriendly.



In the recent years, several AOPs have been tested to degrade parabens [22–24]. The degradation of MP has been investigated through several AOPs, such as photo catalysis [25], ozone oxidation [26], electrochemical [27], sonochemical [28], photodegradation processes [29,30] and heat activated persulfate method [31] using hydroxyl ( $\cdot\text{OH}$ ) and sulfate ( $\text{SO}_4^\cdot$ ) radicals as the main oxidants. However, to the best of the authors' knowledge, UV/persulfate-assisted degradation of methyl paraben has yet to be studied. The objective of this study was to investigate the degradation efficiency of methyl paraben using a UV-activated persulfate method. The effects of different parameters, such as the initial concentration of substrate (MP), persulfate dosage, solution pH, and water matrix components (humic acid and inorganic anions), were stud-

ied to explore their potential influence on the degradation kinetics of MP. In addition, the predominant radicals and reaction byproducts obtained after the treatment were identified using LC-MS. A degradation pathway was also proposed.

## 2. Materials and methods

### 2.1. Chemicals

Methyl paraben (purity 99%), sodium persulfate, sodium thiosulfate, sodium bicarbonate, and humic acid were procured from Sigma-Aldrich (USA). Sodium chloride (NaCl), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and *tert*-butanol were supplied by Junsei Chemicals (Japan), Merck (Germany) and Wako Pure Chemicals (Japan), respectively. Acetonitrile (HPLC grade) was purchased from Thermo Fisher Scientific (USA). All of the chemicals were of analytical reagent grade and were used as received without further purification (or unless otherwise mentioned). Milli-Q-Water was used for preparation of aqueous solutions and the HPLC mobile phase.

### 2.2. Photochemical experiments

Photodegradation experiments were conducted in a bench-scale photochemical apparatus (Fig. 1). The apparatus was equipped with a borosilicate glass vessel, a magnetic stirrer, and two low-pressure mercury UV lamps emitting monochromatic light (254 nm) as the irradiation source. Using potassium ferrioxalate actinometry, the photon flux ( $I_0$ ) was estimated to be  $0.44 \mu\text{E s}^{-1}$  [32]. A 100 mL aqueous solution of MP, in a 250-mL-capacity photoreactor, was irradiated at pH 6.5 and room temperature. It was then stirred thoroughly to homogenize the reaction solution. After the adjustment of initial pH of solution (except in the case of anions effect on MP degradation), the desired amount of persulfate was added to the reactor. The reaction was started by holding the reaction vessel under the irradiation region. The persulfate solutions were freshly prepared for each experiment. At specified time intervals, 1 mL aliquots were withdrawn and quenched immediately with a sodium thiosulfate solution (1 M), followed by filtration ( $0.20 \mu\text{m}$  syringe filter, Pall Life Sciences, USA). The filtrate was used for HPLC analysis to determine the residual concentrations of MP. The same procedure was followed to study the effects of various parameters on the degradation of MP. The effect of the components of the water matrix was assessed by adding known amounts of anions and humic acid to the solution before the addition of an oxidant. All of the experiments were conducted in duplicate, and the data reported in this paper are the average of duplicate measurements.

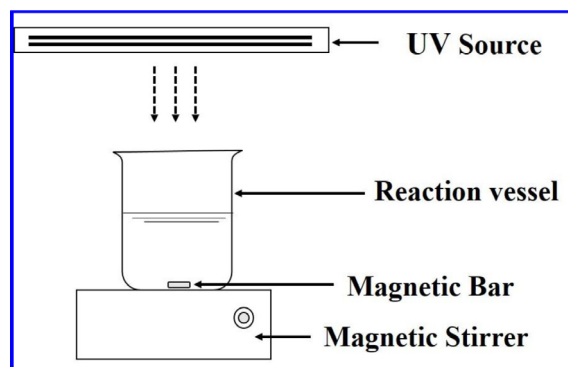


Fig. 1. The schematic diagram of photochemical apparatus.

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