Min, N., Yao, J., Amde, M., Tang, C., Wu, L., **Richnow, H.H.**, Chen, Y., Cui, Y., Li, H. (2021):
Compound specific isotope analysis to characterize degradation mechanisms of *p*-chloroaniline by persulfate at ambient temperature
Chem. Eng. J. **419** , art. 129526

http://dx.doi.org/10.1016/j.cej.2021.129526

Compound specific isotope analysis to characterize degradation mechanisms of *p*-chloroaniline by persulfate at ambient temperature

Ning Min, Jun Yao, Meseret Amde, Cengceng Tang, Langping Wu, Hans Hermann Richnow, Yafei Chen, Yongqiang Cui, Hao Li

PII: S1385-8947(21)01113-X
DOI: https://doi.org/10.1016/j.cej.2021.129526
Reference: CEJ 129526

To appear in: *Chemical Engineering Journal*

Received Date: 2 April 2020
Revised Date: 14 March 2021
Accepted Date: 17 March 2021

Please cite this article as: N. Min, J. Yao, M. Amde, C. Tang, L. Wu, H.H. Richnow, Y. Chen, Y. Cui, H. Li, Compound specific isotope analysis to characterize degradation mechanisms of *p*-chloroaniline by persulfate at ambient temperature, *Chemical Engineering Journal* (2021), doi: https://doi.org/10.1016/j.cej.2021.129526

Compound specific isotope analysis to characterize degradation mechanisms of *p*-chloroaniline by persulfate at ambient temperature

Ning Min[a], Jun Yao[a,*], Meseret Amde[a,b], Cengceng Tang[a], Langping Wu[c], Hans Hermann Richnow[d], Yafei Chen[a], Yongqiang Cui[a], Hao Li[a]

[a]School of Water Resources and Environment and Research Center of Environmental Science and Engineering, Sino-Hungarian Joint Laboratory of Environmental Science and Health, China University of Geosciences (Beijing), 29 Xueyuan Road, Haidian District, 100083 Beijing, China

[b]Department of Chemistry, College of Natural and Computational Sciences, Haramaya University, Dire Dawa, Ethiopia

[c]Department of Civil & Mineral Engineering University of Toronto 35 St. George Street. Toronto, ON M5S 1A4, Canada

[d]Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, Leipzig 04318, Germany

*Corresponding author:

E-mail: yaojun@cugb.edu.cn

Phone: +86-10-82321958

Fax: +86-10-82321958

Abstract

Compound-specific isotope analysis (CSIA) is a useful technique that has received an increasing attention for studying the degradation mechanisms of organic contaminants based on stable isotope fractionation concepts. This study reports the degradation mechanisms of *p*-chloroaniline (PCA) at different pH values (3, 5, 7 and 9) induced by persulfate (PS) based on ^{13}C isotope fractionation during its preferential oxidation with $SO_4^{\bullet-}$ and $^{\bullet}OH$. The results showed that the degradation of PCA followed first-order kinetics (rate constants, 0.026, 0.0362, 0.0754 and 0.0497 h^{-1} at pH = 3, 5, 7 and 9, respectively), with the fastest degradation under neutral conditions (pH 7). The degradation rate was found to be higher under alkaline conditions (pH 9) compared to acidic conditions (pH 3 and 5). A normal carbon isotope fractionation of PAC was observed under neutral and alkaline conditions (eg., ε_C = -0.8‰ ± 0.10 at pH 7 and ε_C = -1.0‰ ± 0.17 at pH 9). However, a reverse carbon isotope effect at pH 3 (ε_C = 0.6‰ ± 0.07) and pH 5 (ε_C = 1.1‰ ± 0.06) was observed, respectively. Based on the identified transformation products and the insights revealed by CSIA, the degradation pathways were proposed. The current findings are crucial in understanding the PCA degradation mechanisms with $SO_4^{\bullet-}$ and $^{\bullet}OH$ in aqueous systems.

Key words: *p*-Chloroaniline; Persulfate; Chemical oxidation; Compound-specific isotope analysis; Isotope fractionation

1. Introduction

The chloroaromatic compounds, *such as p*-chloroaniline (PCA), are widely used as an intermediate in a variety of chemical manufacturing for example agricultural chemicals, plastics, azodyes and pigments, and drugs[1]. It is also a secondary product of the smelting process used to extract non-ferrous metals, and hence, suspected to be present in wastewater and tailings associated with mining operations[2]. Researchers reported that PCA have been found in various systems including atmosphere, water body, sediments, and different types of soil and biological samples[3, 4]. PCA belongs to the persistent organic pollutants (POPs) and is included in the priority pollutant list of the US EPA and EU legislations[5] as it can impose significant risks on our health and the environment[6, 7]. Therefore, knowledge about its fate in the environment and degradation mechanisms is important for an efficient removal of PCA.

In recent years, a promising technique based on radical oxidation reactions, *in situ* chemical oxidation (ISCO), has been used for the removal of organic contaminants in various environmental systems[8]. Persulfate (PS) is one of the widely used oxidants in ISCO [9]. Oxidation using sulfate free radical ($SO_4^{\bullet-}$), produced by activating PS, is an emerging advanced oxidation technology. PS decomposes to $SO_4^{\bullet-}$ (Eq. 1)[10], which can further form hydroxyl radicals ($^{\bullet}OH$) under different pH conditions (Eq. 2 and 3)[11, 12]. Under acidic conditions, $S_2O_8^{2-}$ react to $HS_2O_8^{-}$ which can further form $SO_4^{\bullet-}$ and $HSO_4^{\bullet-}$ in subsequent reactions according to Eq. 4 and 5[10, 13, 14]. The high standard oxidation-reduction potential of $SO_4^{\bullet-}$ ($E^o = 2.5\text{-}3.1$ V) which is close to that of $^{\bullet}OH$ ($E^o = 2.8$ V) reveals its strong oxidizing properties under acidic, neutral, and alkaline conditions[15-18]. According to the previous studies, $SO_4^{\bullet-}$ can be applied for degrading organic pollutants effectively, including phthalate esters, benzene, ethylbenzene, toluene, xylene, polychlorinated biphenyls, polycyclic-aromatic hydrocarbons, and others [4, 19-21].

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad (1)$$

All pHs: $$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \quad (2)$$

Alkaline pH: $$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \qquad (3)$$

Acidic pH: $$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \qquad (4)$$

$$HS_2O_8^- + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ \qquad (5)$$

$$SO_4^{\bullet-} + H^+ + e^- \rightarrow HSO_4^{\bullet-} \qquad (6)$$

In addition, activated PS can act as a new and efficient oxidant reagent (Eq. 7 - 12)[22-27] and can efficiently remove chloroaniline substances in aqueous solutions[28, 29]. Recently, visible-light and solar-light have been used to activate PS to generate $SO_4^{\bullet-}$ and ${}^{\bullet}OH$ for making the photoactivation of PS for removal of organic pollutants by energy-efficient. Despite the increasing application of PS for the removal of PCA from contaminated industrial and mineral processing wastewaters[30-33], the mechanisms of the PS based degradation are still unclear. Conventionally, GC-MS identification of the molecular structures of transformation products (TPs) have been used to investigate the degradation mechanisms of PCA to characterize degradation mechanisms [34-36].

However, since the same product may be produced by different reaction pathways, it is challenging to characterize the degradation mechanisms of PCA using PS at different pH. Therefore, mechanisms involved in PCA degradation should be further invested to understand its environmental processes and design effective remediation approaches.

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet-} \qquad (7)$$

$$HSO_5^{-} + H_2O \rightarrow SO_4^{\bullet-} + {}^{\bullet}OH \qquad (8)$$

$$S_2O_8^{2-} + \text{heat/UV} \rightarrow 2SO_4^{\bullet-} \qquad (9)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{\bullet-} + OH^{-} \qquad (10)$$

$$HSO_5^{-} + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{\bullet-} + SO_4^{2-} \qquad (11)$$

$$HSO_5^{-} + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{2-} + {}^{\bullet}OH \qquad (12)$$

Techniques such as gas chromatography-mass spectrometer or liquid chromatography-mass spectrometer technology have been applied to study the degradation mechanism of organic pollutants. Due to the reaction mechanism relying on the chemical fingerprint of degradation products is often uncertain, the research conclusions cannot reach a consensus. This uncertainty brings difficulties to the degradation mechanism study and it is not conducive to in-depth study of the environmental behavior of organic pollutants. The compound specific isotope analysis (CSIA) technology determines the stable isotope ratio of a specific element of a single compound, and the result is not interfered by other reactants, products and elements, thus improving the reliability and accuracy of the results.

CSIA has been increasingly applied to identify and analyze the sources of pollutants, evaluate the transformation mechanisms, and estimate the extent of biodegradation of organic pollutants in the environment. Its application on investigating the fate of organic pollutants has becoming a research hotspot in the field of Environmental Science and Engineering[37, 38]. When the target organic pollutants are degraded, the reaction rate of the lighter isotopes of atoms at the reacting positions is slightly different from that of the heavier ones, which may result in a change in the isotope composition of a specific element in the residual fraction, leading to isotope fractionation. In order to further explore the reaction mechanism, the kinetic isotope effect (KIE) can be used to evaluate the extent of isotope fractionation, which refers to the ratio of the rate constant of the reaction with light isotopes to heavy ones. KIE is considered to be a useful tool for providing information about the reaction mechanism, which is achieved by determining the bond changes that occur during the first reaction rate-limiting step[39]. CSIA has been successfully applied to study the degradation mechanisms of organic pollutants, such as phthalates, polycyclic aromatic hydrocarbons and polychlorinated biphenyls[40, 41]. However, it is rarely used to study the degradation mechanism of p-chloroaniline. Previous studies on the degradation of PCA by PS under normal temperature conditions have mostly focused on the inference of the degradation mechanism using its degradation products[42, 43]. In the literature, there are limited reports on CSIA of PCA by PS oxidation, and no study has been reported on CSIA during PS oxidation of PCA in different pH at ambient temperature, to the best of our knowledge.

Accordingly, this study aimed to study the potential of 13C-CSIA to characterize the reaction processes involved in PS-based PCA oxidation at different pH conditions, ,as well as to evaluate the degradation kinetics of PCA in PS natural-light activation system at different pHs and to identify the PCA transformation products using GC-MS. Carbon isotope enrichment factor, ε_C, was determined under the studied conditions and the possible degradation pathways have been proposed based on the results obtained from all experimentations.

2. Materials and methods

2.1. Chemicals

Analytical grade PCA standard (purity, 99.5%), sodium persulfate ($Na_2S_2O_8$), dipotassium hydrogen phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), conc. sulfuric acid (H_2SO_4, 95–98%), sodium hydroxide (NaOH, 98%), 5,5-dimethyl-1-pyrrolinen-oxide, starch indicator (I_2, 1%), potassium iodide (KI, 99.5%), Sodium thiosulfate ($Na_2S_2O_3$, 99.5%) and tert-butyl alcohol (TBA) were obtained from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Methanol and dichloromethane (HPLC grade) were supplied by Beijing MREDA technology Co., Ltd. (Beijing, China). Deionized water prepared by a Milli-Q system (Millipore, Billerica, MA, USA) was used throughout the experiments.

2.2. Experimental procedures

Batch experiments of PS oxidation reactions were carried out at ambient temperature (~20 °C) in a of 500-mL polytetrafluoroethylene (PTFE) vials using a solution volume of 500 mL under natural-light, which were constantly stirred with a magnetic stirrer. Stock solutions of PCA (0.8 mM) was prepared prior to each batch experiment and stored in the dark. $Na_2S_2O_8$ was used to generate $SO_4^{\bullet-}$ in experiments at pH 3, 5, 7 and 9, using 10 mM phosphate buffer solution to stabilize the pH. The pH was adjusted using H_2SO_4 and NaOH solutions. To reach the detection limit of the isotope measurements, 0.8 mM of PCA was applied as initial concentration. The molar ratio of PCA and PS in the reaction solution was 1:50 as used before in similar experiment [44]. Control experiments were simultaneously conducted under the same conditions without adding PS. The reaction liquid were removed at different time intervals, and the remaining PCA was extracted using 5 mL dichloromethane by liquid-liquid extraction.

To investigate the degradation kinetics of PCA, 0.5 mL methanol, free radical quencher, was added to 2 mL of the solution in brown glass vials to stop the radical oxidation reaction. At different time intervals, 0.5 mL reaction solution was transferred to a brown vial for concentration determination.

2.3. Analysis techniques

2.3.1 Concentration determination

The amount of PCA was determined at 239 nm using a UltiMate 3000 HPLC system (Thermo Fisher Scientific, Massachusetts USA) equipped with a UV detector. A reversed-phase C_{18} column (250 mm length x 4.6 mm internal diameter, 5.0 µm particle size) was used for separation and the column temperature was 30 °C. A mixture of methanol and ultrapure water (65:35, *v/v*) supplied at a flow-rate at 1 mL min^{-1} was employed as the mobile phase.

2.3.2 Persulfate, TOC and Cl$^-$ determination

Persulfate concentration was determined using a colorimetric method using iodide as reported elsewhere[45]. A TOC analyzer (Shimadzu, model TOC-L CPHCN, Japan) was used to determine the total organic carbon (TOC) during the whole reaction period[46]. The samples were quenched by using 1 M sodium thiosulfate aqueous solution before TOC analysis. Cl$^-$ was quantified using an ion chromatograph (Dionex ICS-3000, USA) with a 25 mA suppressor current, A Thermo Fisher Scientific AS23 analytical column (4 × 250 mm), and 10 mM sodium carbonate and 0.8 mM sodium bicarbonate as eluent (1 mL/min) [42].

2.3.3 Dominant radicals identification

In order to identify the dominant radicals in the PS/natural-light system, quenching experiments were carried out to identify the possible radicals generated during the whole reaction process[23]. Methanol (MeOH) was used as the radical scavengers for both $^{\bullet}OH$ and $SO_4^{\bullet-}$, and tert-butyl alcohol (TBA) were selected as the radical scavengers for $^{\bullet}OH$.[47, 48]. Electron paramagnetic resonance (ESR) analysis were also conducted to identify the radical species using 5,5-dimethyl-1-pyrrolinen-oxide (DMPO) as a spin-trapping agent[49]. In brief, a suspension containing 1 mL 0.1 M DMPO solution was spiked into the reaction solutions at different time intervals and further shaken for 1 min[50]. The above suspension was then filtered through a 0.22 μm syringe filter and analyzed on a Bruker EMS Plus X-band ESR spectrometer at room temperature[51].

2.3.4 GC-MS analysis and toxicity estimation

An Agilent GC-MS (7890B-5977B) system was applied to determine PCA and its TPs . The compounds were separated by a HP-5 column (30 m x 0.25 mm x 0.25 μ m) (Agilent, USA) with helium (1 mL/min). The heating program of the oven was begun at 60 °C and held for 1 min, and increased to 180 °C at 15 °C min^{-1} and held for 2 min, and increased to 290 °C at 15 °C min^{-1} and held for 2 min. The injection temperature was 220 °C and 1 μL sample was injected into the GC at a split ratio of 5:1.

The University of Washington laboratory safety method was used to determine the toxicity of the TPs formed in PCA/PS/natural-light experiments[52, 53]. Based upon fish LC50 constituents of the leachate are divided into five categories as listed in Table 1 and then, the equivalent toxicity of the TPs was calculated (Eq. 13). In addition, quantitative structure-activity relationship (QSAR) analysis was used to evaluate and identify the acute and chronic toxicity of TPs produced in the PCA/PS/natural-light experiments based on the ecological structure-activity relationship (ECOSAR) prediction model[54].

Table 1 here

$$Toxicity(\%) = \sum X\% + \frac{\sum A\%}{10} + \frac{\sum B\%}{100} + \frac{\sum C\%}{1000} + \frac{\sum D\%}{10000} \qquad (13)$$

Where X, A, B, C and D are percentage of the TP constituents associated with each toxicity categories.

2.3.6 Specific oxidant efficiency

In order to explore the ability of PS to degrade *p*-chloroaniline, the index of specific oxidant efficiency (SOE) was used in this study[55]. SOE is the amount of Chemical Oxygen Demand (COD) removed per unit mass of PS consumed, calculated by Eq. 14, which indicate the system performance. COD concentrations were determined using a DR6000 UV-vis spectrophotometer (HACH, Beijing, China)[56].

$$SOE = \frac{(COD_0 - COD_t)}{(PS_0 - PS_t)} \tag{14}$$

2.3.5 Carbon isotope analysis

DELTA V gas chromatography - isotope ratio mass spectrometry (GC-IRMS, Agilent, USA) was used to measure the stable carbon isotope composition of PCA, and 1ul of samples were injected in a splitless mode. The stable range for reliable measurement of PCA carbon isotope compositions is shown in SI, Section 1. Sufficient separation and well resolved peak were achieved using a HP-5 column (30 m x 0.25 mm x 0.25 µm) (Agilent, USA). The heating program and other GC parameters were the same as those used in the above GC-MS (Section 2.3.2). All samples were analyzed in triplicates to ensure the reproducibility. The standard deviation of all isotope measurement was typical for CSIA (δ^{13}C: ± 0.5‰)[39].

2.4. Data evaluation

Rayleigh equation, expressed in Eq. 15[57, 58], was used to evaluate the carbon isotope fractionation of PCA during the oxidation reactions.

$$\ln \frac{\delta_t + 1}{\delta_0 + 1} = \varepsilon \times \ln f \qquad (15)$$

where δ_t and δ_0 are the corresponding carbon isotope compositions of PCA at sampling time t and 0, ε is the isotope enrichment factor for the degradation process and f is the remaining fraction of non-degraded PCA at time t ($f = C_t / C_0$).

In order to further study the reaction mechanisms and degradation pathways, the apparent kinetic isotope effects (AKIE) considering the reactive positions were calculated by Eq. 16[59].

$$AKIEc = \frac{1}{1 + \frac{n}{x} z \varepsilon_{c(‰)}/1000} \qquad (16)$$

Where ε_c is the obtained carbon isotope enrichment factor according to Rayleigh equation, n is the number of carbon atoms in the studied molecule, x is the number of carbon atoms at reactive positions and z is the number of carbon atoms in intramolecular competing positions.

3. Results and discussion

3.1. Degradation kinetics of PCA at different pHs

pH has a significant effect on the oxidation of organic pollutants with $SO_4^{\bullet -}$[60, 61]. Therefore, the oxidation experiments were conducted using $Na_2S_2O_8$ to generate $SO_4^{\bullet -}$ at different pH (3, 5, 7 and 9) with 40 mM and 0.8 mM initial concentrations of $Na_2S_2O_8$ and PCA, respectively. The results showed that the pH of the reaction system has a significant effect on the degradation rate of PCA (Table 2). It is noteworthy that only little loss of PCA was observed in control experiments without PS. Control experiment without any oxidant in the reaction system showed almost stable concentration and carbon isotope values of PCA, suggesting that photolysis of PCA can be negligible under all studied pHs (Fig. S2 and Fig. S3).

The degradation of PCA followed first order kinetics ($R^2 \geq 0.925$) in all experimental conditions (Table 2), which is essentially consistent with the previous reports[62, 63]. Although a second order reaction, the rate constants (k) can describe the PS/PCA reaction and were determined to be 0.020, 0.0362, 0.0754 and 0.0497 h^{-1} at 3, 5, 7 and 9 pH values, respectively (Table 2)

Table 2 here

Figure 1 here

The degradation rate of PCA with PS at pH 7 is faster (half-life = 9.19 h) than in acidic (half-life = 26.66 h at pH 3, half-life = 19.15 h at pH 5) and alkaline conditions (half-life = 13.95 h at pH 9) (Table 2 and Fig.1).

The reason for this observation may be attributed to the reaction rate between HPO_4^{2-} and $SO_4^{\bullet-}$ ($k = 1.2*10^6$) is higher than that of $^{\bullet}OH$ ($k = 1.5*10^5$). In addition, under acidic conditions, hydrogen ions can scavenge sulfate radicals (Eq. 6) [56, 64]. Therefore, the removal rate of PCA under alkaline condition was higher than that under acidic condition, which might be because of the quenching effect of phosphate on $^{\bullet}OH$ is less than on the $SO_4^{\bullet-}$. Albeit, more $^{\bullet}OH$ is generated at pH 9 than at pH 7 (see Eq. 3), it is likely that more $^{\bullet}OH$ would be scavenged at pH 9 due to its non-specificity and the strong competition for it between the SO_4^{2-} and PCA; thereby resulting a decrease in the PCA degradation rates at pH 9 [10]. Considering that the concentration of the buffer solution is relatively low, the degradation of PCA by secondary radicals generated from phosphate buffer can be ignored. In acidic solution, additional SO_4^{2-} could be formed due to the possible acid-catalyzation [65, 66]. However, the higher rate of $SO_4^{\bullet-}$ formation could favor reactions between the radicals (Eq. 17 and 18) over radical with PCA reactions (the predominant free radical at different pH are shown in Table 2) [67]. Therefore, strong acidic condition is not conducive to the degradation of PCA, and the half-life at pH 3 reached to 26.66 h. Liang et al. [10] also reported similar results on the effect of pH on the degradation of trichloroethylene in PS system, and they observed a highest degradation rate at pH 7. This also indicated that the initial pH values have a major effect on the rate constants of PCA decay.

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \qquad (17)$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \qquad (18)$$

3.2. Decomposition of persulfate and radical identification

Since the main source of the free radicals ($^{\bullet}OH$ and $SO_4^{\bullet-}$) in the PS/ natural-light system is PS, the concentrations of PS during the reaction at different pHs were monitored. As shown in the Fig. 2, PS is gradually consumed under all pH conditions (at pH 3, 5, 7 and 9, PS consumption was about 53.5%, 63.55%, 69.08 and 67.02%, respectively). Similar to the trend of PS being consumed, the degradation rate of PCA decreased from neutral to alkaline to acidic condition in the PCA/PS/natural -light system.

To identify the types of free radicals in the PCA/PS/natural-light system under different pH conditions, free radical scavengers (TBA and MeOH) were added to the system[23, 68]. Methanol can react quickly with $^{\bullet}OH$ (k=9.7 × $10^8 M^{-1}S^{-1}$) and $SO_4^{\bullet-}$ (k=1.1 × $10^7 M^{-1}S^{-1}$), and hence, it can be used as a quencher for the two free radicals [23, 47]. The reaction rate of TBA with $^{\bullet}OH$ (k=6.0 × $10^8 M^{-1}S^{-1}$) is three-order faster than that of $SO_4^{\bullet-}$ (k=4.0 × $10^5 M^{-1}S^{-1}$), thus TBA is added to the reaction system as a quencher of $^{\bullet}OH$. The inhibition of the degradation rate of PCA by TBA is relatively low under acidic conditions (pH 3 and pH 5) suggesting that $SO_4^{\bullet-}$ is the major radical species (Fig. 3).

At pH 3 and pH 5, the inhibition rate of TBA was 0.003 and 0.009. While methanol exhibited greater inhibitory effect on the degradation of PCA, the inhibition rates are 0.022 and 0.032, respectively. The results therefore indicate that the $SO_4^{\bullet-}$ plays a leading role under acidic conditions. Under neutral conditions (pH 7), the inhibition rates of TBA and methanol on PCA degradation were 0.0537 and 0.0615, respectively, which indicated that both of the free radicals coexisted in the system. Under alkaline conditions (pH 9), the inhibition rates of TBA and methanol on PCA degradation were 0.0426 and 0.0447, respectively, indicating that the $^{\bullet}OH$ is the dominant free radical.

Figure 3 here

Due to the fact that DMPO can capture $^{\bullet}OH$ and $SO_4^{\bullet-}$ to generate DMPO-OH and DMPO-SO_4 secondary products, respectively, the two products can be detected by the electron paramagnetic resonance (EPR) spectrometer analyzing the type of existing free radicals in the system[49-51]. The results shown in Fig. 4 demonstrate that under acidic (pH 3 and pH 5) and alkaline conditions (pH 9), the dominant free radicals in the PCA/PS system are $SO_4^{\bullet-}$ and $^{\bullet}OH$, respectively, and the two radicals coexist in neutral conditions (pH=7) which is in agreement with the results of quenching experiments (Fig. 3).

Figure 4 here

3.3. Potential reaction products of PCA and toxicity estimation

At different pH values, the PS become activated to yield $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals, which attack different chemical bonds of many organic pollutants[69], and various intermediate products also form during the processes. The possible intermediates formed during PCA oxidation with the free radicals, $SO_4^{\bullet-}$ or $^{\bullet}OH$, were identified by GC-MS and the results are presented in (Fig. S4). The main secondary product was identified to be 4-amino-phenol at pH 3 and pH 5, which was not reported in previous studies (Fig. S4a). At pH 7 and pH 9, the main possible intermediate products were tentatively identified as 2-amino-5-chlorophenol, (Fig. S4b). Accordingly, 1-chloro-4-nitroso-benzene and p-benzoquinone were tentatively identified to be the main intermediate products at all studied pHs (Fig. S4c and Fig. S4d)[41, 70-74].

The toxicity of PCA before and after the degradation of PS was also calculated to be 2.09% and 1.455%, respectively, which imply a good toxicity reduction during this process.

Table 3 here

3.4. Main inorganic products and degree of mineralization

The concentration of Cl^- was used as the main inorganic product in the aqueous solution to further clarify the degradation mechanism of PCA in the PCA/PS/natural-light system. The various profiles of PCA and TOC were investigated and the results are shown (Fig. 5). The results demonstrate that the Cl^- concentration is relatively low at pH 7 and pH 9 (Fig. 5A). Gradual increase in the Cl^- concentration was observed at pH 3 and pH 5. The degradation rates of TOC increased with time, and the degradation rate of TOC in neutral (pH 7) and alkaline conditions (pH 9) are higher than that in acidic conditions (pH 3 and pH 5) (Fig. 5B). However, the degradation rate of PCA was significantly higher than that of TOC, which indicate that only part of the PCA was completely mineralized and the other part may be converted into other products (Fig. 5C).

Figure 5 here

3.5. Carbon isotope fractionation during the chemical oxidation

The carbon isotopic ratio of PCA were analyzed during the oxidation process. The obtained isotopic ratio values ($\delta^{13}C$) showed a more positive trend during the reaction process and with progressing reaction and decreasing amounts of the residual reactant in neutral and alkaline conditions (Fig. 6). The enrichment of ^{13}C in residual PCA molecule in neutral and alkaline conditions indicate that the process of oxidative degradation of PCA by $^{\bullet}$OH was associated with a normal carbon isotope effect. In control experiment for 300 h, no PCA degradation were observed and constant $\delta^{13}C$ (pH 7: −28.1 ± 0.1‰, and pH 9: –28.1 ± 0.1‰) were obtained (Fig. S3), proving that the isotope fractionation was caused by $^{\bullet}$OH degradation. The ε_C values were calculated to be –0.80 ± 0.07‰ and –1.0 ± 0.06‰, at pH 7 and pH 9, respectively (Table 2), which indicate a normal isotope effect.

While, the obtained isotopic ratio values ($\delta^{13}C$) showed a more negative trend during the reaction process and with progressing reaction and decreasing amounts of the residual reactant in acidic condition (Fig. 7). The enrichment of ^{13}C in residual PCA molecule in condition indicate that the process of oxidative degradation of PCA by $SO_4^{\bullet-}$ was associated with a reverse carbon isotope effect. In control experiment for 300 h, no PCA degradation were observed and constant $\delta^{13}C$ (pH 3: −27.5 ± 0.1‰ and pH 5: –27.7 ± 0.1‰) were obtained. The ε_C values were calculated to be 0.6 ± 0.1‰ and 1.1 ± 0.17‰ at pH 3 and pH 5, respectively (Table 2).

Figure 6 here

The carbon isotope enrichment factors of PCA at the considered pH values were quantified using Rayleigh equation (Fig. 7), and high correlation coefficients, $R^2 \geq 0.9251$, was exhibited by the Rayleigh regression of PCA for $\delta^{13}C$. The hydrolysis of PCA would potentially cause ^{13}C enrichment in the residual fraction associated with a normal carbon isotope effect. The control experiments however show no decrease in PCA concentration or enrichment of $\delta^{13}C$ (Fig. S2 and Fig. S3) demonstrating the hydrolysis do not take place under acidic and alkaline conditions in the time frame of the experiment. Thus, the isotope fractionation was due to the free radical-based oxidative degradation reaction with a normal isotope effect when •OH is dominant and an inverse isotope effect when $SO_4^{\bullet-}$ is the primary reacting radical.

Figure 7 here

Even though, the inverse C isotope fractionation is not common in free radical-based degradations of organic pollutants and rarely reported in the literature[75-77], the observed inverse C isotope fractionation of PCA might be understood as an indication for increased bonding to C in the rate-limiting step of the reaction [78]. However, previous study has shown that direct photolysis of atrazine can cause inverse C isotope fractionation, which may be due to the magnetic isotope effect produced by the interaction of spin-carrying nuclei with unpaired electrons [79]. In addition, Elsner et al. [80] reported that changes in solution pH and the ion species in the reaction system can affect magnetic isotope effects, significantly. Thus, the acidic conditions (pH 3 and pH 5) and different free radicals may affect magnetic effects of PCA.

3.6. Apparent kinetic isotope effects of PCA with $^{\bullet}OH$ and $SO_4^{\bullet-}$

The main intermediate products in the PCA/PS reaction system are different in acidic (pH, <7) and alkaline (pH, >7) conditions as showed in Fig. S4. Based on the main identified intermediate products, chloro-4-nitroso-benzene and p-benzoquinone have been found in all study conditions, the attack of $SO_4^{\bullet-}$ on the N–H bond of PCA to produce intermediate which then attacked by $^{\bullet}OH$ and deamination to form 1-chloro-4-

nitroso-benzene and *p*-benzoquinone are assumed to be the reaction mechanism in all studied pHs[30]. The possible degradation pathway is shown in Scheme 1.

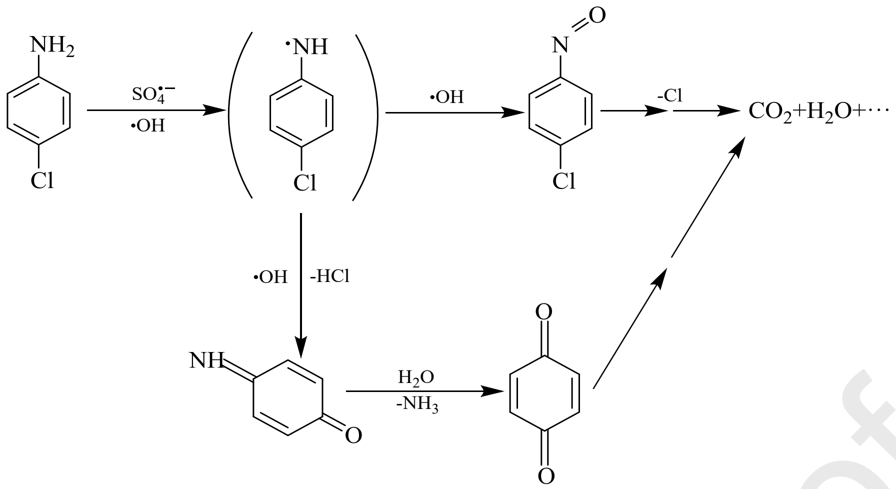
According to the identified intermediate product, 4-amino-phenol, in acidic condition, the main reaction mechanism is assumed to be through the attack of C–Cl bond on the benzene ring of PCA by the $^{\bullet}OH$. As shown in Scheme 2[81], direct photolysis of PCA may lead to the heterolytic dechlorination of excited state of PCA species and generate 3,4-iminocyclohexa-2,5-dienylidene which then subsequently react with H_2O, that is the addition of H_2O, to form 4-amino-phenol. A reverse carbon isotope effect was observed under acid condition in this study, the $SO_4^{\bullet-}$ might attack the C-Cl bond in a complex reaction forming a radical by cleaving the C-Cl bond and the radical further react with water forming an alcohol. When the rate limiting step is the formation of the HO-C bond lighter isotope of the potential intermediate may react faster leading to a small inverse isotope effect in the overall reaction. This hypothesis might explain the reverse isotope fractionation during dechlorination in acidic PS systems.

The possible secondary product, 2-amino-5-chlorophenol has been found under neutral and alkaline conditions in this study. The abstraction of H from the aromatic ring is a typical preferential reaction of •OH with a high rate constant, and has been observed in reaction with OH radicals before[30, 42]. We speculate that the reaction mechanism under neutral and alkaline conditions is dominant and lead to low normal isotope effect (Scheme 3).

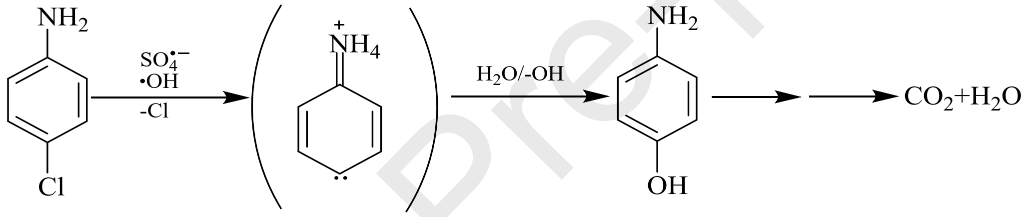
Hydroxyl radicals can react with organic contaminants in aqueous solutions by the following three pathways. (i) The $^{\bullet}$OH addition to an aromatic ring or other unsaturated bond of the target compound leading to the radical adducts formation (RAF) which is considered to be the kinetically favored reaction of •OH with aromatic rings. (ii) The hydrogen abstraction by H atom transfer from the target compound to •OH and formation of a radical which is subsequently hydroxylated. (iii) The single transfer of an electron to the substrate catalyzed by $^{\bullet}$OH (SET) [82]. The 2-amino-5-chlorophenol detected in the PS/PCA reaction system shows the addition of $^{\bullet}$OH to the benzene ring of PCA. Therefore, we speculate that radical adducts formation (RAF) is the main reaction mechanism under PS/PCA alkaline conditions. Previous studies have shown that the $AKIE_C$ for the oxidation reaction of C-H bond cleavage, yield in the range of 1.01-1.03 [83]. Apparent kinetic isotope effect for carbon (^{13}C-AKIE) has been calculated based on the obtained carbon isotopic fractionation [78, 84]. For PCA, $AKIE_C$ was computed using $n = 6$, $x = 1$ and $z = 1$ and the $AKIE_C$ values at different pH are summarized in Table 2. Compared with other literature values, the ^{13}C-AKIE values of PCA in the PS/PCA system at neutral and alkaline conditions (pH 7 and 9) were all within the expected KIE range of C-H bond cleavage (KIE_C: 1.01–1.03), which suggest that the C-H bond cleavage is the initial reaction step [85, 86]. The side reaction to chloro-4-nitroso-benzene and coupling products (scheme 1 and 3) are unlikely to yield primary carbon isotope effects.

The single electron transfer is the dominating probably the mechanisms of $SO_4^{\bullet-}$ with p-chloroaniline (scheme 2) leading to slightly inverse C isotope effects. The reaction mechanism. $SO_4^{\bullet-}$ may attack at the amino group which may not lead to a primary carbon isotope effect or we speculate on a complex dechlorinating reaction where bond change at carbon atom is not rate limiting in the transition stage. Inverse C isotope effects has been observed in photochemical reaction due to cleavages of halogen-carbon bonds[87]. The increased C−C bond strength of the isotopically substituted reaction intermediates may support chlorine elimination in the transition stage and lead to inverse isotope fractionation.

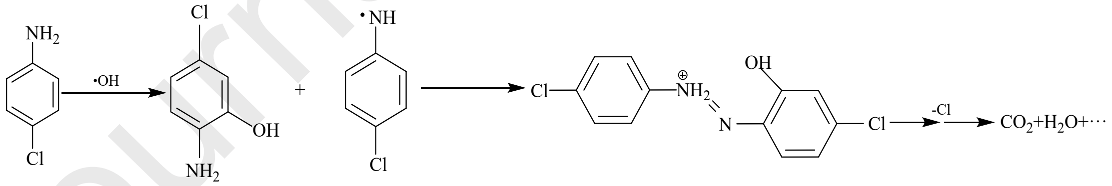
In previous studies, the researchers simply detecting the types of degradation products in the reaction system and speculating on the possible degradation pathways in the reaction process, which could not distinguish the chemical bond breaks of target pollutants under different pHs and reaction conditions[42, 43, 47, 88]. Compound specific isotope analysis have been used to characterize degradation mechanisms of p-chloroaniline by persulfate in different pHs at ambient temperature. The carbon isotope fractionation characteristics and apparent kinetic isotope effects have been used to characterize the chemical bond cleavage and degradation mechanism of PCA in the PS/PCA/natural -light system, which more clearly reflects the environmental fate of PCA in the studied system (Scheme 1, Scheme 2 and Scheme 3).



Scheme 1. Pathways of oxidation degradation of PCA by PS at ambient temperature in acidic conditions (pH 3, pH 5, pH 7, pH 9).



Scheme 2. Pathways of oxidation degradation by PS of PCA at ambient temperature in acidic condition (pH 3, pH 5).



Scheme 3. Pathways of oxidation degradation by PS of PCA at ambient temperature in neutral and alkaline conditions (pH 7, pH 9).

The isotope fractionation study suggest that SET is the dominating pathway at acidic conditions and at neutral and alkaline conditions the mechanism shift to the RAF pathway. This implies that the formation of •OH become dominant which is in-line with the hypothesis that RAF is a kinetically favored reaction.

3.7. Specific oxidant efficiency (SOE) and cost evaluation

The specific oxidant efficiency (SOE) result show that the COD removal rate per PS consumption are 0.20 g/mM, 0.21 g/mM, 0.39 g/mM and 0.31 g/mM under pH 3, 5, 7 and 9 in the PCA/PS/natural-light system, respectively, which indicate that the PCA/PS/natural-light system has a higher specific oxidant efficiency in neutral condition.

The cost evaluation of persulfate processes was made and the price of persulfate is 0.12 dollar /g (based on the price obtained from Aladdin Chemical Reagent Co., Ltd). Under the conditions for persulfate process in this study, the total cost of persulfate process was 1.88 RMB, for removing 0.8 mM PCA. This study aims to study the isotope fractionation characteristics of PCA in the PCA/PS/solar-light system, and then to study its degradation mechanism. In order to obtain sufficient and stable carbon isotope signal values, the initial concentration of PCA is set at 0.8 mM, and the concentration of PCA in the environmental medium will not reach such a high level. In addition, persulfate is easier to store and transport than hydrogen peroxide. Therefore, it is economical and feasible to degrade PCA with sodium persulfate [89, 90].

4. Conclusion

In this work, the degradation of PCA by PS was investigated at ambient temperature in different conditions (pH, 3, 5, 7 and 9). The study results indicated that the pH of the reaction system greatly affects the degradation rate of PCA, and the degradation process can be described by first-order kinetics. The optimum condition for the degradation of PCA was pH 7. Four main intermediates were detected by GC-MS and identified as 1-chloro-4-nitroso-benzene, p-benzoquinone, 4-amino-phenol, and 2-amino-5-chlorophenol, respectively. CSIA was used to evaluate the free radical degradation of PCA. Small ^{13}C isotope enrichment in the residual PCA at pH 7 and pH 9, and small inverse ^{13}C isotope fractionation was obtained at pH 3 and pH 5. Combining the intermediate products and carbon isotope fractionation, the possible degradation mechanisms in PS/PCA system have been discussed. Carbon isotope fractionation model is of great importance to assess the degradation pathways of pollutants (e.g. PCA) during in situ remediation. The results of this work provide an important basis for understanding the degradation mechanisms of PCA with $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals produced from persulfate in aqueous solutions at ambient temperature.

Acknowledgements

This work is supported in part by grants from the National Science Foundation of China (41720104007, 41430106) and project of the Major National R & D Projects for Chinese Ministry of Science and Technology (2019YFC1803500).

Conflict of interest

The authors have no competing interest to declare.

References

[1]. H.Y.Liang, Y.Q. Zhang, S.B. Huang, and I. Hussain, Oxidative degradation of pchloroaniline by copper oxidate activated persulfate. Chem. Eng. J. 218 (2013) 384-391. https://doi.org/10.1016/j.cej.2012.11.093.

[2]. N.Boon, J. Goris, P. De Vos, W.Verstraete, E. M.Top, Genetic diversity among 3-chloroaniline- and aniline-degrading strains of the Comamonadaceae. Appl Environ Microbiol. 67 (2001) 1107-1115. https://doi.org/1128/AEM.67.3.1107-1115.2001

[3]. D. D. Dantzger, C. M. Jonsson, H. Aoyama, Mixtures of diflubenzuron and pchloroaniline changes the activities of enzymes biomarkers on tilapia fish (Oreochromis niloticus) in the presence and absence of soil. Ecotoxicol Environ Saf. 148 (2018) 367-376. https://doi.org/10.1016/j.ecoenv.2017.10.054 [4].

[4] X. Zhang, M. Feng, R. Qu, H. Liu, L. Wang, Z. Wang, Catalytic degradation of diethyl phthalate in aqueous solution by persulfate activated with nano-scaled magnetic CuFe 2 O 4 /MWCNTs. Chem. Eng. J. 301 (2016) 1-11. https://doi.org/10.1016/j.cej.2016.04.096

[5]. L. Zhu , L. V. M L ,X, Dai. The stability of aerobic granular sludge under 4-chloroaniline shock in a sequential air-lift bioreactor (SABR). Bioresour. Technol. 140 (2013) 126-130. https://doi.org/10.1016/j.biortech.2013.04.017

[6]. H. Radianingtyas,G. K. Robinson, A.T, Bull, Bacterial community structure and physiological state in a biofilm reactor degrading 4-chloroaniline. Appl Microbiol Biotechnol. 62(4) (2003.) 423-429. https://doi.org/10.1007/s00253-003-1311-x

[7]. A. F. Pizon , A. R. Schwartz , L. M. Shum , Toxicology laboratory analysis and human exposure to p-chloroaniline. Clin. Toxicol. (2009)132-136. https://doi.org/10.1080/15563650801971390

[8]. J. M. Monteagudo, A. Durán, R. González, A. J. Expósito. *In situ chemical oxidation of carbamazepine solutions using persulfate simultaneously activated by heat energy, UV light, Fe2+ ions, and H2O2.* Appl. Catal. B-Environ. 176(2015). 120-129. https://doi.org/10.1016/j.apcatb.2015.03.055

[9]. C. Min，G. Zeng，D. Huang，L. Cui，L. Yang. *Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review.* Chem. Eng. J. 284(2016) 582-598. https://doi.org/10.1016/j.cej.2015.09.001

[10]. C.Liang, Z.S. Wang, and C.J. Bruell, *Influence of pH on persulfate oxidation of TCE at ambient temperatures.* Chemosphere, 66(2007) 106-13. https://doi.org/10.1016/j.chemosphere.2006.05.026

[11]. X. Jiang，Y. Wu，W. Peng. *Degradation of bisphenol A in aqueous solution by persulfate activated with ferrous ion.* Environ Sci Pollut Res Int, **20**(2013) 4947-53. https://doi.org/10.1007/s11356-013-1468-5

[12]. C.L.Su, a.H.-W. *Identification of Sulfate and Hydroxyl Radicals in Thermally Activated Persulfate.* Ind. Eng. Chem. Res. , 48(2009) 5558–5562. https://doi.org/10.1021/ie9002848

[13] D. An, P. Westerhoff, M. G. Zheng, M. Y. Wu, Y. Yang, C. A. Chiu, *UV-activated persulfate oxidation and regeneration of NOM-Saturated granular activated carbon.* Water Res, 73(2015) 304-10. https://doi.org/10.1021/cr60217a001

[14]. D. A. HOUSE, *Kinenics and mechanism of oxidations by peroxydisulfate* Chem. Rev., **62(**1961) 185-203. https://doi.org/10.1021/cr60217a001

[15]. Romero, A., et al., *Diuron abatement using activated persulphate: Effect of pH, Fe(II) and oxidant dosage.* Chemical Engineering Journal, 2010. **162**(1): p. 257-265.

[16]. C. Liang，I. L. Lee，I. Y. Hsu，C. P. Liang，Y. L. Lin. *Persulfate oxidation of trichloroethylene with and without iron activation in porous media.* Chemosphere, 70(2008) 426-35. https://doi.org/10.1016/j.chemosphere.2007.06.077

[17]. R. Xiao，Z. Luo，Z. Wei，S. Luo，R. Spinney，W. Yang，D. D. Dionysiou. *Activation of peroxymonosulfate/persulfate by nanomaterials for sulfate radical-based advanced oxidation technologies.* Curr. Opin. Chem. Eng., 19(2018) 51-58. https://doi.org/10.1016/j.coche.2017.12.005

[18]. C.Liu , B. Wu, and X.e. Chen, *Sulfate radical-based oxidation for sludge treatment: A review.* Chem. Eng. J. 335(2018) 865-875. https://doi.org/10.1016/j.cej.2017.10.162

[19]. A.Tsitonaki, B. J. Petri, M. Crimi, H. Mosber. *In Situ Chemical Oxidation of Contaminated Soil and Groundwater Using Persulfate: A Review.* Crit. Rev. Environ. Sci. Technol. 40(2010) 55-91. https://doi.org/10.1080/10643380802039303

[20]. S. Wacawek , H. V. Lutze, K. Grübel. Chemistry of persulfates in water and wastewater treatment: A review. Chem. Eng. J. 2017, 330(2017):44-62. https://doi.org/10.1016/j.cej.2017.07.132

[21]. J.Wang, S. Wang, *Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants.* Chem. Eng. J. **334(**2018) 1502-1517. https://doi.org/10.1016/j.cej.2017.11.059

[22]. Q. Yang，Y. Ma，F. Chen，F. Yao，D. Wang. *Recent advances in photo-activated sulfate radical-advanced oxidation process (SR-AOP) for refractory organic pollutants removal in water.* Chem. Eng. J. 378(2019) 122149. https://doi.org/10.1016/j.cej.2019.122149

[23]. Z. Y. Wang, N.Y. Gao, X. Lu, N. An, *Degradation kinetic of phthalate esters and the formation of brominated byproducts in heat-activated persulfate system* . Chem. Eng. J. 359(2018) 1086-1096.

[24]. C.Tan , N. Gao, Y. Deng. Degradation of antipyrine by heat activated persulfate. Sep. Purif. Technol.109(2013) 122-128. https://doi.org/10.1016/j.seppur.2013.03.003

[25]. J. Sharmaa, I.M.Mishraa, D. D. Dionysiou, V. Kumarac, *Oxidative removal of Bisphenol A by UV-C/peroxymonosulfate (PMS): Kinetics, influence of co-existing chemicals and degradation pathway.* Chem. Eng. J. 276(2015) 193-204. https://doi.org/10.1016/j.cej.2015.04.021

[26]. M.M. Ahmed, S. Chiron, *Solar photo-Fenton like using persulphate for carbamazepine removal from domestic wastewater.* Water Res, 48(2014) 229-36. https://doi.org/10.1016/j.watres.2013.09.033

[27]. M.M.Ahmed. *Solar photo-Fenton using peroxymonosulfate for organic micropollutants removal from domestic wastewater: Comparison with heterogeneous TiO 2 photocatalysis.* Chemosphere, 117(2014) 256-261.

[28]. M. A. Fagier, E. A. Ali, K. S. Tay, M. R. B. Abas, Mineralization of organic matter from vinasse using physicochemical treatment coupled with Fe2+-activated persulfate and peroxymonosulfate oxidation. Int. J. Environ. Sci. Technol. 13(4) (2016) 1189-1194. https://doi.org/10.1007/s13762-016-0963-x

[29]. D. Zhang, L. Wu, J. Yao,H. H. Herrmann, Carbon and hydrogen isotope fractionation of phthalate esters during degradation by sulfate and hydroxyl radicals. Chem. Eng. J. 347 (2018) 111-118. https://doi.org/10.1016/j.cej.2018.04.047

[30]. I. Hussain,Y. Zhang, S. Huang, X, Du. Degradation of p-chloroaniline by persulfate activated with zero-valent iron. Chem. Eng. J. 203 (2012) 269-276. https://doi.org/10.1016/j.cej.2012.06.120

[31]. W. S. Chen, C. P. Huang, Mineralization of aniline in aqueous solution by electrochemical activation of persulfate. Chemosphere. 125 (2015) 175-181. https://doi.org/10.1016/j.chemosphere.2014.12.053

[32]. Yang, S, *Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature.* J Hazard Mater, 2011. **186**(1): p. 659-66.

[33]. Y.Q.Zhang, X.Z. Du, W.L. Huang, *Temperature effect on the kinetics of persulfate oxidation of p-chloroaniline.* Chinese Chemical Letters, 22(2011_ 358-361.

[34]. B.V.Chang, T.H. Wang, S.Y. Yuan, *Biodegradation of four phthalate esters in sludge.* Chemosphere, 69(2007) 1116-1123. https://doi.org/10.1016/j.chemosphere.2007.04.011

[35]. C. C. Chen., H. Dewen., J. X, Zhou., *Photocatalytic Degradation of Diethyl Phthalate with Titanium Dioxide Suspension.* Environ. Sci. Technol, 2015. **24,(4)**: p. 181-184.

[36]. C. Ding, Z. Li, Z. Zhang, Q. Yu, Growth Condition and Degradation Dynamics of p-Chloroaniline Degrading Strain, International Conference on Environmental Science and Information Application Technology. (2009) 96-98. https://doi.org/10.1109/ESIAT.2009.152.

[37]. H. H. Richnow, I. Nijenhuis, *Stable isotope fractionation concepts for characterizing biotransformation of organohalides.* Curr. Opin. Biotechnol. 41 (2016) 108-113. https://doi.org/10.1016/j.copbio.2016.06.002

[38]. C. Vogt, C. Dorer, F. Musat , H. H. Richnow, *Multi-element isotope fractionation concepts to characterize the biodegradation of hydrocarbons — from enzymes to the environment.* Curr. Opin. Biotechnol. 2016. 41(2016) 90-98. https://doi.org/10.1016/j.copbio.2016.04.027

[39]. N. Zhang, S. Bashir, J. Qin, J. Schindelka, Compound specific stable isotope analysis (CSIA) to characterize transformation mechanisms of alpha-

hexachlorocyclohexane. J. Hazard. Mater. 280(2014). 750-7. https://doi.org/10.1016/j.jhazmat.2014.08.046

[40]. S. L. Badea., C. Vogt., S. Weber., *Stable Isotope Fractionation of γ-Hexachlorocyclohexane (Lindane) during Reductive Dechlorination by Two Strains of Sulfate-Reducing.* Environ. Sci. Technol. (2009) https://doi.org/10.1021/es801284m

[41] H. Liu, *Carbon isotopic fractionation during biodegradation of phthalate esters in anoxic condition.* Chemosphere, **138** (2015) 1021-1027. https://doi.org/10.1016/j.chemosphere.2014.12.063

[42] Y. Yuan, *Degradation of p-chloroaniline by persulfate activated with ferrous sulfide ore particles.* Cheml. Eng. J, **268** (2015) 38-46. https://doi.org/10.1016/j.cej.2014.12.092

[43]. X. Z. Du, *Oxidation degradation of p-chloroaniline in water by persulphate at ambient temperations.* Environ. Chem. Lett. 31(2012) 880-884.

[44]. D. Zhang, L. Wu, J. Yao, C. Vogt, H. H. Richnow, Carbon and hydrogen isotopic fractionation during abiotic hydrolysis and aerobic biodegradation of phthalate esters. Sci Total Environ. 660 (2019) 559-566. https://doi.org/10.1016/j.scitotenv.2019.01.003

[45]. N, Wahba, M.F.E.A, M. EL Sadr, *Iodometric Method for Determination of Persulfates.* Anal. Chem. 31(1959) 1870-1871. https://doi.org/10.1021/ac60155a059

[46]. B.Y. Yan, DD.C. Xu, Z.Q. Liu, J. Z. Tang, R. Huang, *Degradation of neurotoxin β-N-methylamino-L-alanine by UV254 activated persulfate: Kinetic model and reaction pathways.* Chem. Eng. J. 404(2021) 127041.

[47]. C. Yao , Y. Zhang , M. Du, Insights into the mechanism of non-radical activation of persulfate via activated carbon for the degradation of p - chloroaniline. Chem. Eng. J. 362(2019) 262-268. https://doi.org/10.1016/j.cej.2019.01.040

[48]. W. Li , H. Guo, C. Wang. ROS reevaluation for degradation of 4-chloro-3,5-dimethylphenol (PCMX) by UV and UV/persulfate processes in the water: Kinetics, mechanism, DFT studies and toxicity evolution. Chem. Eng. J. 390(2020) 124610.

[49]. C. Y. Zhu, F. Zhu, C. Liu, "Reductive Hexachloroethane Degradation by S2O8 with Thermal Activation of Persulfate under Anaerobic Conditions." Environ. Sci. Technol. (2018)7b06279-.

[50]. L. Fang, K. Liu , F. Li , New insights into stoichiometric efficiency and synergistic mechanism of persulfate activation by zero-valent bimetal (Iron/Copper) for organic pollutant degradation. J. Hazard. Mater. 403(2021) 123669. https://doi.org/10.1016/j.jhazmat.2020.123669

[51]. J. He, *Magnetic ball-milled FeS@biochar as persulfate activator for degradation of tetracycline.* Chem. Eng. J. 404(2021).

[52]. Q. Sui , W. Gebhardt , H. F. Schröder, Identification of New Oxidation Products of Bezafibrate for Better Understanding of Its Toxicity Evolution and Oxidation Mechanisms during Ozonation. Environ. Sci. Technol. 51(2017)

2262-2270.

[53]. A. Ranjbari, N. Mokhtarani, *Post treatment of composting leachate using ZnO nanoparticles immobilized on moving media.* Appl. Catal. B-Environ. 220(2018) 211-221. https://doi.org/10.1016/j.apcatb.2017.08.042

[54]. Y. Zhang, *Characterization of Mining-Related Aromatic Contaminants in Active and Abandoned Metal(loid) Tailings Ponds.* Environ. Sci. Technol. 54(2020) 23.15097-15107. https://doi.org/10.1021/acs.est.0c03368

[55]. N. Jaafarzadeh, , F. Ghanbari, M. Alvandi, *Integration of coagulation and electro-activated HSO 5 − to treat pulp and paper wastewater.* Sustainable Environment Research, 27(2017) 223-229. https://doi.org/10.1016/j.serj.2017.06.001

[56]. A. M. Soubh, *Zero-valent iron nanofibers (ZVINFs) immobilized on the surface of reduced ultra-large graphene oxide (rULGO) as a persulfate activator for treatment of landfill leachate.* Journal of Environmental Chemical Engineering, 6 (2018) 6568-6579.

[57]. K. M. Scott, X. Lu, C. M. Cavanaugh,J. S. Liu, Optimal methods for estimating kinetic isotope effects from different forms of the Rayleigh distillation equation. Geochimica et Cosmochimica Acta. 68(3) (2004) 433-442 https://doi.org/10.1016/S0016-7037(03)00459-9

[58]. J. Sun, J. Huang, A. Zhang, W. Liu, W. Cheng, Occurrence of phthalate esters in sediments in Qiantang River, China and inference with urbanization and river flow regime. J Hazard Mater. 248-249 (2013) 142-149. https://doi.org/10.1016/j.jhazmat.2012.12.057

[59]. L.Wu, J. Yao, P. Trebse, N. Zhang, H. H. Richnow, Compound specific isotope analysis of organophosphorus pesticides. Chemosphere. 111 (2014) 458-463. https://doi.org/10.1016/j.chemosphere.2014.04.037

[60]. F. O. Kehinde, H. Abdul Aziz, Influence of Operating Conditions on the Persulfate Oxidation of Textile Waste Water at Ambient Temperature. Applied Mechanics and Materials. 802 (2015) 454-459. https://doi.org/10.4028/www.scientific.net/amm.802.454

[61]. X. Xie,Y. Zhang, W. Huang, S. Huang, Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation. J. Environ. Sci. 24(5) (2012) 821-826. https://doi.org/CNKI:SUN:HJKB.0.2012-05-008

[62]. A. Suzuki, G.Teleki, Phthalate Esters as Environmental Contaminants. Nature. 238 (1972) 411-413. https://doi.org/10.1038/238411a0

[63]. A. Charles , D. R. P. Staples, F. Thomas , J. Adams, The environmental fate of phthalate esters- A literature review.pdf. Chemosphere. 35-4 (1997) 667-749. https://doi.org/10.1016/S0045-6535(97)00195-1

[64]. M. Ahmadi, F. Ghanbari, *Combination of UVC-LEDs and ultrasound for peroxymonosulfate activation to degrade synthetic dye: influence of promotional and inhibitory agents and application for real wastewater.* Environ. Sci. Pollut. Res. 25(2017) 6003-6014.

[65]. D. A. House, Kinetics and Mechanism of Oxidations by Peroxydisulfate. Chemical Reviews. 62(3) (1962) 185-203.

https://doi.org/10.1021/cr60217a001

[66]. J. E. McIsaac, J. O. Edwards, Kinetics and mechanisms of the oxidation of methanol and .alpha.-phenylethanol by peroxydisulfate ion. The Journal of Organic Chemistry. 34(9) (1969) 2565-2571. https://doi.org/10.1021/jo01261a018

[67]. H. Chen, R. Zhuang, J. Yao, F. Wang,Y. Qian, A comparative study on the impact of phthalate esters on soil microbial activity. Bull Environ Contam Toxicol. 9 (2013) 217-223. https://doi.org/10.1007/s00128-013-1033-4

[68]. Q. Zhong , Q. Lin , R. Huang. Oxidative degradation of tetracycline using persulfate activated by N and Cu codoped biochar. Chem. Eng. J. 380(2019)122608.

[69]. G. P. Anipsitakis, D. D. Dionysiou, Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt. Environ. Sci. Technol. 37(20) (2003) 4790-4797. https://doi.org/10.1021/es0263792

[70]. K. Othmen, P. Boule, B. Szczepanik, K. Rotkiewicz, G. Grabner, Photochemistry of 4-Chloroaniline in Solution. Formation and Kinetic Properties of a New Carbene, 4-Iminocyclohexa-2,5-dienylidene. The Journal of Physical Chemistry A. 104(42) (2000) 9525-9534. https://doi.org/10.1021/jp0010381

[71]. C. Richard, P. Krajnik, G. Grabner, Photolysis of 4-chlororesorcinol in water: competitive formation of a singlet ketene and a triplet carbene. Phys Chem Chem Phys. 12(42) (2010) 14322-14329. https://doi.org/10.1039/c0cp00756k

[72]. S. Net,R. Sempere, A. Delmont, A. Paluselli, B. Ouddane, Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ Sci Technol. 49(7) (2015) 4019-4035. https://doi.org/10.1021/es505233b

[73]. R. H. Waldemer,P. G. Tratnyek, R. L. Johnson, J. T. Nurmi, Oxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products. Environ. Sci. Technol. 41(3) (2007) 1010-1015. https://doi.org/10.1021/es062237m

[74]. F. Gosetti, M. Bottaro,V. Gianotti, E. Mazzucco, P. Frascarolo, D. Zampieri, C. Oliveri, A. Viarengo, M. C. Gennaro, Sun light degradation of 4-chloroaniline in waters and its effect on toxicity. A high performance liquid chromatography - Diode array - Tandem mass spectrometry study. Environ Pollut. 158(2) (2010) 592-598. https://doi.org/10.1016/j.envpol.2009.08.012

[75]. M. Skarpeli-Liati, A. Turgeon, A. N. Garr, W. A. Arnold, C. J. Cramer, T. B.Hofstetter, pH-dependent equilibrium isotope fractionation associated with the compound specific nitrogen and carbon isotope analysis of substituted anilines by SPME-GC/IRMS. Anal Chem. 83 (2011) 1641-1648. https://doi.org/10.1021/ac102667y

[76]. M. Skarpeli-Liati, M. Jiskra, A. Turgeon, A. N. Garr, W. A. Arnold, C. J. Cramer, R. P. Schwarzenbach,T. B. Hofstetter, Using nitrogen isotope fractionation to assess the oxidation of substituted anilines by manganese

oxide. Environ Sci Technol. 45(13) , T. B., (2011) 5596-5604. https://doi.org/10.1021/es200743t

[77]. S. G. Pati, K. Shin, M. Skarpeli-Liati, J. Bolotin, S. N. Eustis, J. C. Spain, T. B. Hofstetter, Carbon and nitrogen isotope effects associated with the dioxygenation of aniline and diphenylamine. Environ Sci Technol. 46(21) (2012) 11844-11853.

[78]. M. Ratti, S. Canonica, K. McNeill, J. Bolotin, T. B. Hofstetter, Isotope Fractionation Associated with the Photochemical Dechlorination of Chloroanilines. Environ Sci Technol. 49(16) (2015) 9797-9806. https://doi.org/10.1021/acs.est.5b03119

[79]. A. E. Hartenbach, T. B. Hofstetter, P. R. Tentscher, S. Canonica, M. Berg, R. P. Schwarzenbach, Carbon, Hydrogen, and Nitrogen Isotope Fractionation During LightInduced Transformations of Atrazine. Environ. Sci. Technol. 42(21) R. P., (2008) 7751-7756. https://doi.org/10.1021/es800356h

[80]. M. Elsner, M. A. Jochmann, T. B. Hofstetter, D. Hunkeler, A. Bernstein, T. C. Schmidt, A. Schimmelmann, Current challenges in compound-specific stable isotope analysis of environmental organic contaminants. Anal Bioanal Chem. 403(9) (2012) 2471-2491. https://doi.org/10.1007/s00216-011-5683-y

[81]. Ratti, M., *Isotope fractionation associated with the direct photolysis of 4-chloroaniline.* Environ Sci Technol, 49(7)(2015) 4263-73. https://doi.org/10.1021/es505784a

[82]. T.C. An, G. Y. Li.,P. V. Kamat., J. Peller., M. V. Joyce. Kinetics and Mechanism of •OH Mediated Degradation of Dimethyl E Environ. Sci. Technol. 48 (2013) 641- 648. https://doi.org/10.1021/es404453v

[83]. E. Martin, D. Hunkele, P. Rene´, Schwarzenbach, A New Concept Linking Observable Stable Isotope Fractionation to Transformation Pathways of Organic Pollutants. Environ. Sci. Technol. 39 (2005) 6896-6916. https://doi.org/10.1021/es0504587

[84]. M. Ratti, S. Canonica,K. McNeill, L.Bolotin, T. B. Hofstetter, Isotope Fractionation Associated with the Indirect Photolysis of Substituted Anilines in Aqueous Solution. Environ Sci Technol. 49(21) (2015) 12766-12773. https://doi.org/10.1021/acs.est.5b02602

[85]. D. Zhang，L. Wu，J. Yao，C. Vogt，H. H. Richnow, *Carbon and hydrogen isotopic fractionation during abiotic hydrolysis and aerobic biodegradation of phthalate esters.* Sci Total Environ, **660(**2019) 559-566. https://doi.org/10.1016/j.scitotenv.2019.01.003

[86]. J. Liu, L. Wu, K. Steffen, J. Yao, S Thomas, H. Hartmut, H.H. Richnow, Carbon and hydrogen stable isotope analysis for characterizing the chemical degradation of tributyl phosphate. Chemosphere, 212 (2018) 133-142. https://doi.org/10.1016/j.chemosphere.2018.08.034

[87]. X. Wang, X. Hu, H. Zhang, C. Fei, Y. Luo., Photolysis Kinetics, Mechanisms, and Pathways of Tetrabromobisphenol A in Water under Simulated Solar Light Irradiation. Environ Sci Technol, 49(11)(2015) 6683-90. https://doi.org/10.1021/acs.est.5b00382

[88]. Y. Zhang, Efficient pyrite activating persulfate process for degradation of p - chloroaniline in aqueous systems: A mechanistic study. Chem. Eng. J. 308(2017) 1112-1119.

[89]. Y. Xiao , L. Zhang , W. Zhang, *Comparative evaluation of iodoacids removal by UV/persulfate and UV/H2O2 processes.* Water. Res. 102(2016) 629-639. https://doi.org/10.1016/j.watres.2016.07.004

[90]. S.Wang, J. Wang, *Comparative study on sulfamethoxazole degradation by Fenton and Fe(ii)-activated persulfate process.* RSC Adv., 7(2017). 48670-48677. https://doi.org/10.1039/C7RA09325J

List of Tables

Table 1 Chemical Waste Toxicity Categories

Toxic Category	Fish(ppm) LC_{50}
X	<0.01
A	0.01-<0.1
B	0.1-<1
C	1.0-<10
D	10.0-100.0

Table 2. Degradation kinetic and carbon isotope fractionation parameters of PCA during chemical oxidation in PS/PCA system.

pH	Dominant radical/s	k (h^{-1})	Half-life (h)	R^2	ε_C (‰)	^{13}C-AKIE
3	$SO_4^{\bullet -}$	0.026	26.66	0.93	0.6±0.10	0.9996
5	$SO_4^{\bullet -}$	0.036	19.15	0.93	1.1±0.17	0.9993
7	$SO_4^{\bullet -}$, $^{\bullet}OH$	0.075	9.19	0.96	–0.8±0.07	1.01
9	$^{\bullet}OH$	0.050	13.95	0.93	–1.0±0.06	1.01

Table 3. Toxicity results of PCA and its transformation products produced in the PCA/PS/natural-light system and PCA using ECOSAR program

No.	Compounds	CAS	Formula	Acute toxicity(mg/L)			Chronic toxicity(mg/L)		
				Fish (LC_{50})	Daphnia (LC_{50})	Green Algae (EC_{50})	Fish (LC_{50})	Daphnia (LC_{50})	Green Algae (EC_{50})
1	2-amino-5-chlorophenol	28443-50-7	C_6H_6ClNO	-	-	-			
2	1-chloro-4-nitroso-benzene	100-00-5	$C_6H_4ClNO_2$	50.5	29.9	26.5	5.19	3.28	7.62
3	*p*-benzoquinone	106-51-4	$C_6H_4O_2$	0.095	0.0738	0.047	0.0091	4.87	0.011
4	4-amino-phenol	123-30-8	C_6H_7NO	-	-	-	-	-	-
5	*p*-chloroaniline	106-47-8	C_6H_6ClN	20.9	1.56	4.27	0.0236	0.019	1.31

List of Figures

Fig.1. Effect of pH on the degradation of PCA in PS system. [PCA]0 = 0.8 mM; [PS]0 = 40 mM.

Fig. 2. The decomposition of PS under different pH conditions in PCA/PS system. $[PCA]_0$ = 0.8 mM; $[PS]_0$ = 40 mM.

Fig. 3. Reaction of PCA in PCA/PS system with the presence of TBA or Methanol. $[PCA]_0$ = 0.8 mM; $[PS]_0$ = 40 mM. $[TBA\ or\ Methanol]_0/PCA=1000/1$

Fig. 4. Electron paramagnetic resonance (EPR) spectra at pH 3, pH 5, pH 7, pH 9 in PCA/PS system.

Fig. 5. Evaluation of the transformation products (A), degradation rates of TOC (B) and PCA (C) in the PCA/PS system under different pH. $[PCA]_0$ = 0.8 mM; $[PS]_0$ = 40 mM.

Fig. 6. PCA transformation during chemical oxidation at pH = 3, 5, 7, and 9. The remaining fraction of substrate (C_t/C_0 signified by black squares) vs carbon (red circles) isotope signatures are shown. Uncertainties of isotope analysis represent standard deviations of triplicate measurements.

Fig. 7. Rayleigh regression of carbon isotope data during the oxidation of PCA with PS at different pHs.

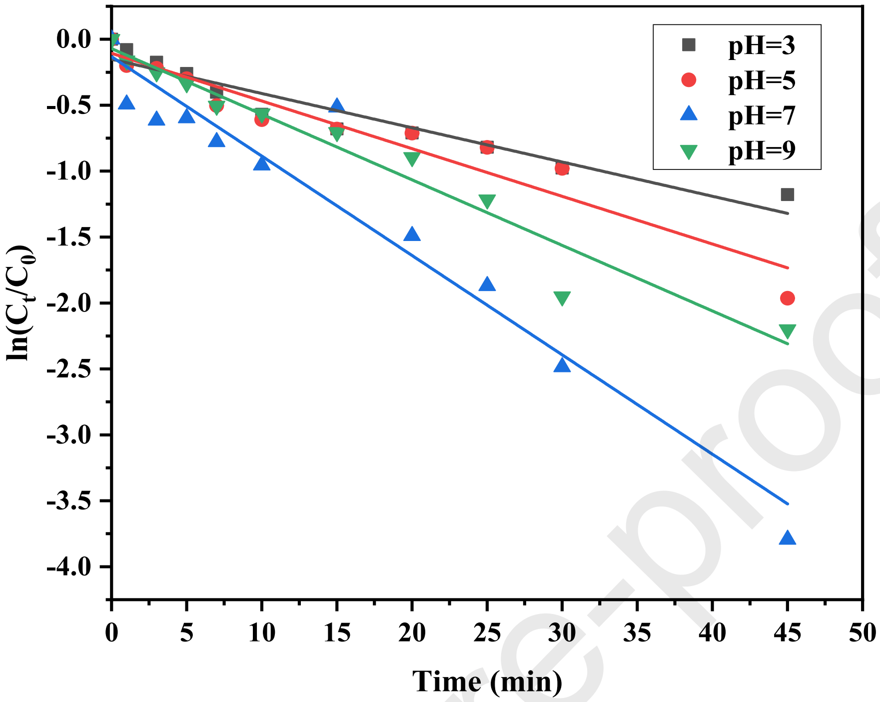


Fig.1. Effect of pH on the degradation of PCA in PS system. $[PCA]_0 = 0.8$ mM; $[PS]_0 = 40$ mM.

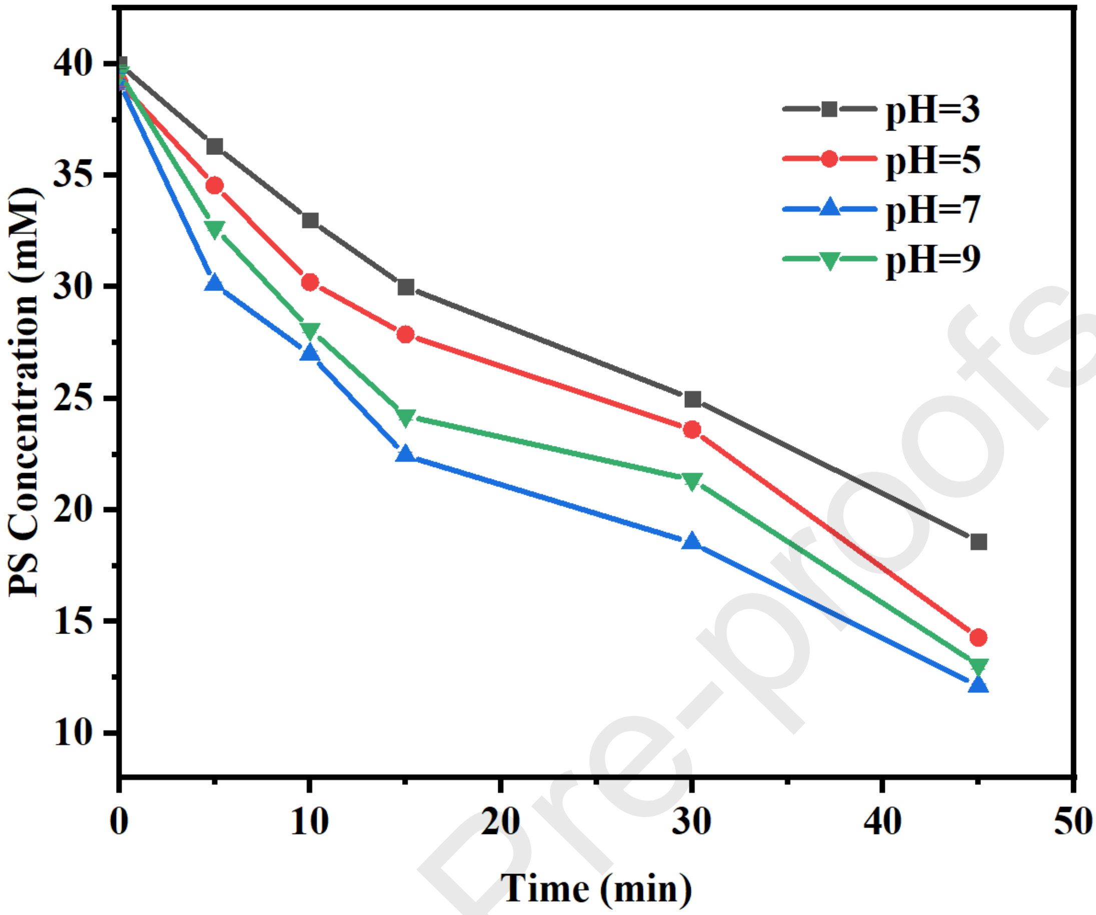


Fig. 2. The decomposition of PS under different pH conditions in PCA/PS system.

[PCA]0 = 0.8 mM; [PS]0 = 40 mM.

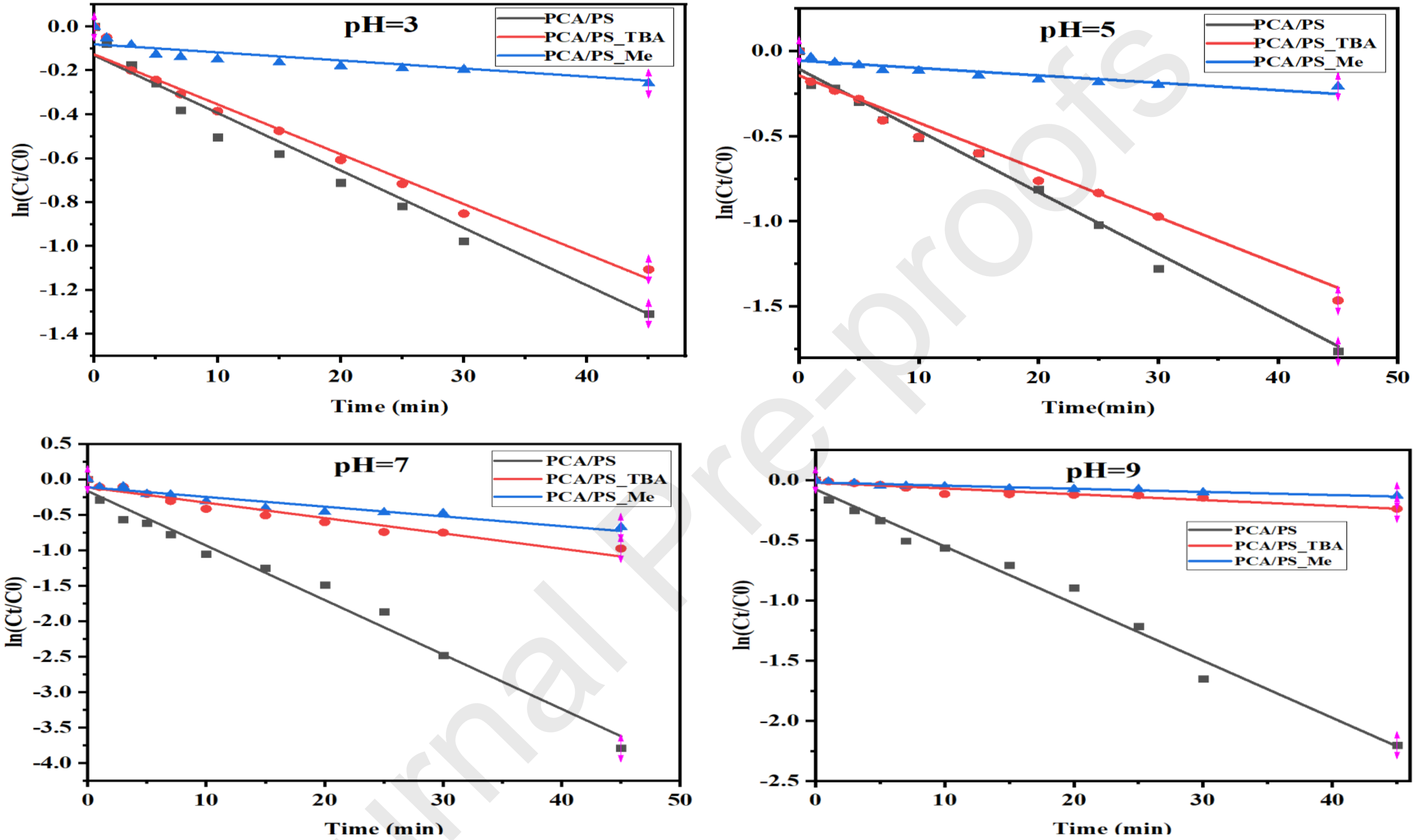


Fig. 3. Reaction of PCA in PCA/PS system with the presence of TBA or methanol. $[PCA]_0 = 0.8$ mM; $[PS]_0 = 40$ mM. $[TBA\ or\ methanol]_0/PCA=1000/1$.

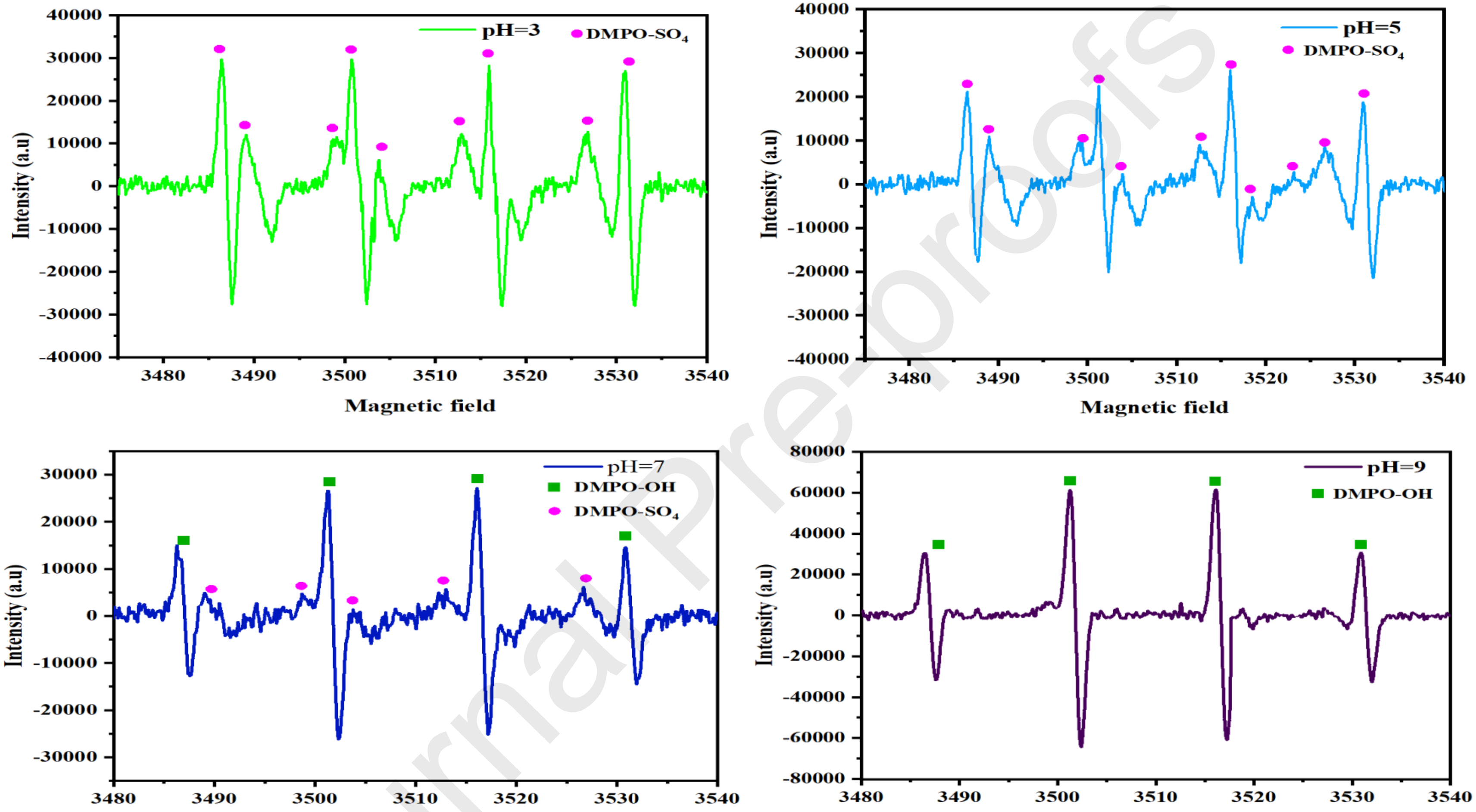


Fig. 4. Electron paramagnetic resonance (EPR) spectra at pH 3, pH 5, pH 7, pH 9 in PCA/PS system.

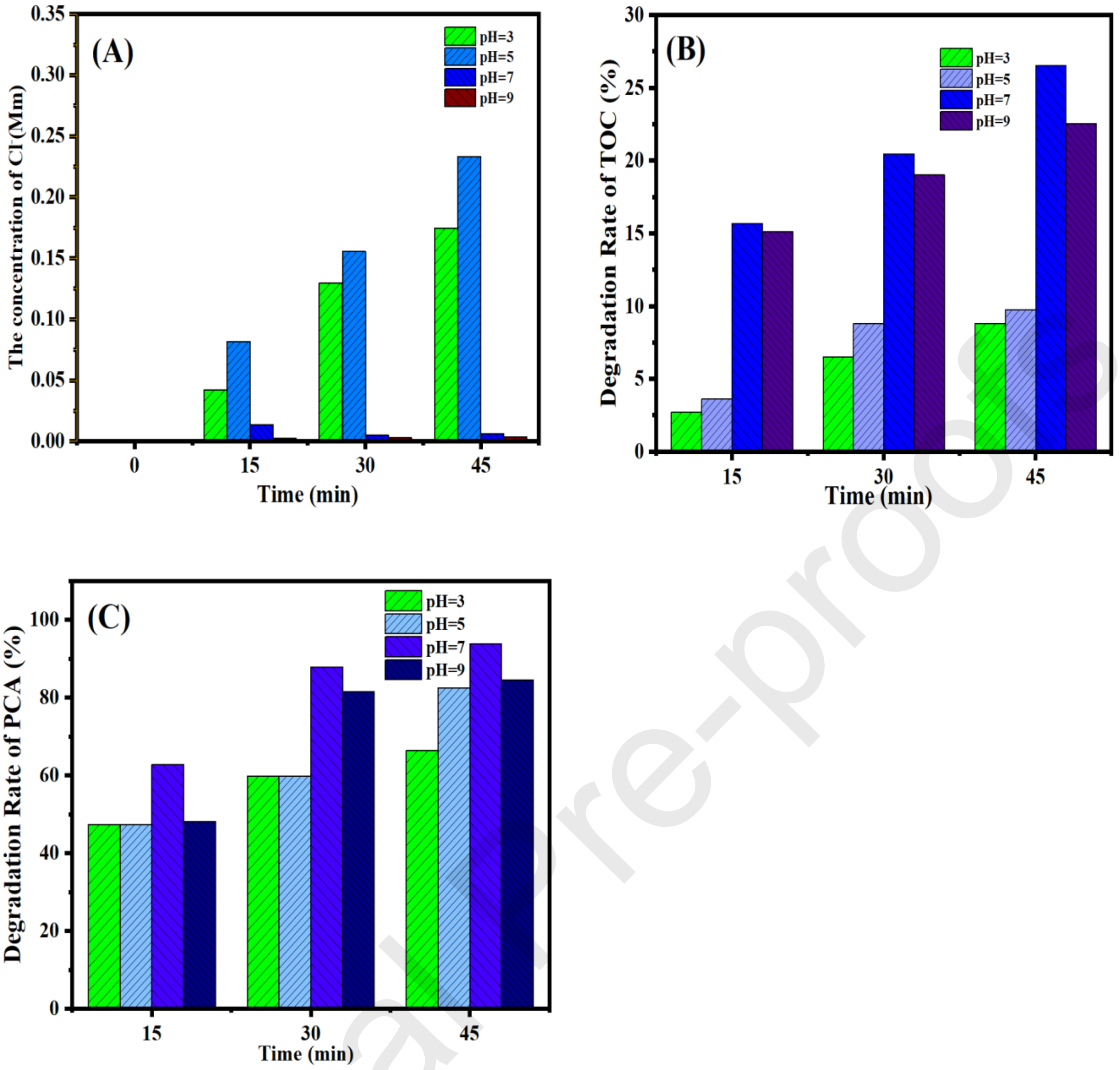


Fig. 5. Evaluation of the transformation products (A), degradation of TOC (B) and PCA (C) in the PCA/PS system under different pH. $[PCA]_0 = 0.8$ mM; $[PS]_0 = 40$ mM

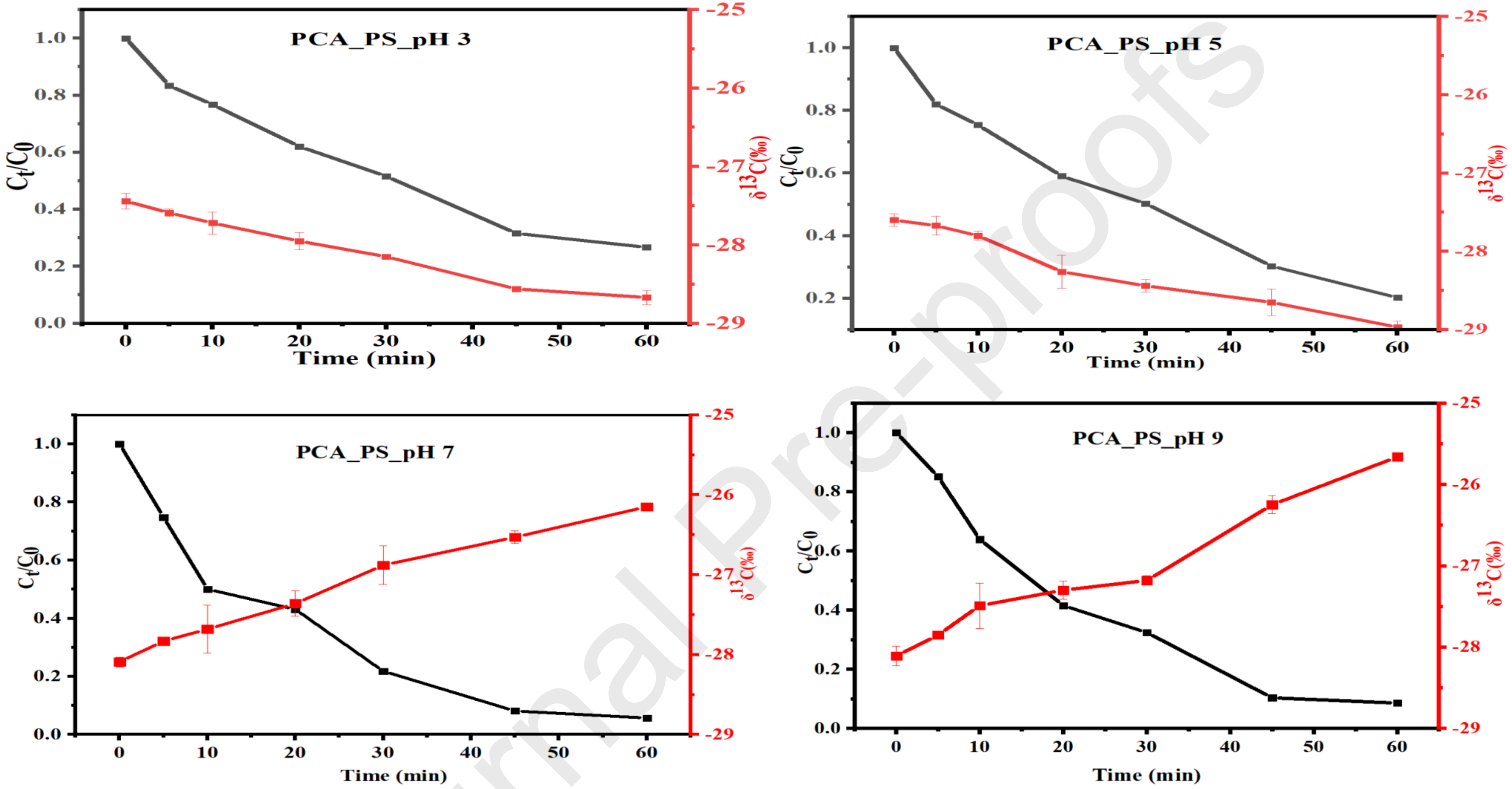


Fig. 6. PCA transformation during chemical oxidation at pH = 3, 5, 7, and 9. The remaining fraction of substrate (C_t/C_0 signified by black squares) vs carbon (red circles) isotope signatures are shown. Uncertainties of isotope analysis represent standard deviations of triplicate measurements.

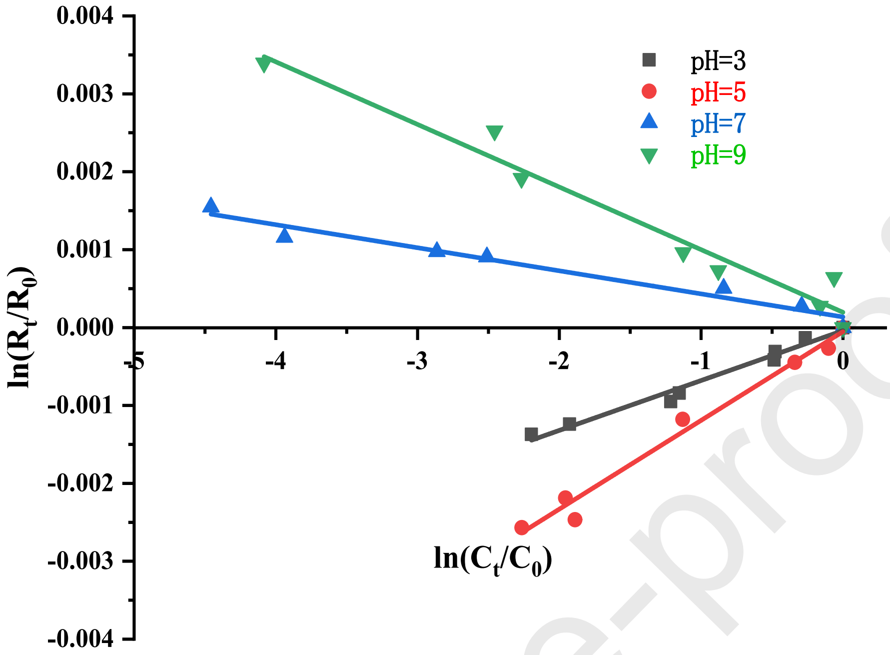


Fig. 7. Rayleigh regression of carbon isotope data during the oxidation of PCA with PS at different pHs.

Research Highlights

- In light activated PS system, PCA degradation is fastest under neutral conditions.
- Isotopic substitution support Cl removal and cause inverse isotope fractionation.
- $AKIE_C$ values of PCA indicate C-H bond cleavage in alkaline and neutral conditions.
- The reaction mechanism is by •OH addition to the PCA aromatic ring.