

Degradation and mineralization of tetracycline and oxytetracycline by Fenton process: effect of inorganic anions

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ABSTRACT

In this study, the effect of inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^-) on degradation and mineralization of tetracycline (TC) and oxytetracycline (OTC) with Fenton process was investigated. For this purpose, concentrations of 1, 10 and 100 mM of inorganic anions were used in this study. Tetracycline and oxytetracycline degradation is 100% at the inorganic anion concentrations studied. The degree of mineralization of TC was 66%, 64%, 64%, 62%, 65% and 43% at control, 1 mM Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^- , respectively. The degree of mineralization of OTC was 49%, 47%, 49%, 47%, 47% and 40% at control, 1 mM Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^- , respectively. The degree of mineralization of TC was 66%, 71%, 70%, 71%, 74% and 74% at control, 10 mM Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^- , respectively. The degree of mineralization of OTC was 49%, 58%, 55%, 50%, 50% and 68% at control, 10 mM Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^- , respectively. The degree of mineralization of TC was 66%, 76%, 65%, 60%, 74% and 43% at control, 100 mM Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^- , respectively. The degree of mineralization of OTC was 49%, 45%, 48%, 43%, 42% and 63% at control, 100 mM Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^- , respectively. When tetracycline and oxytetracycline mineralization were compared, tetracycline mineralization was higher. Inorganic anions affected the mineralization of tetracycline and oxytetracycline. While inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^-) did not affect degradation of tetracycline and oxytetracycline up to 100 mM concentration, mineralization was affected in both directions (increasing and decreasing) at different ion concentrations.

Keywords: Fenton process; Degradation; Mineralization; Inorganic anions

1. Introduction

Since antibiotics can inactivate or kill pathogenic bacteria, they are widely used to prevent diseases and promote growth in livestock and fish farming [1,2]. Tetracyclines (TCs) rank second worldwide in both production and usage among all antibiotics as broad-spectrum antibiotics against both gram-positive and gram-negative bacteria [3,4]. TCs are difficult to biodegrade and are excreted by humans and animals through urine and feces due to poor metabolization or adsorption [5]. Therefore, large amounts of tetracycline were directly discharged into the environment, and

they have been frequently detected worldwide in different aquatic environments such as surface water, sewage water, groundwater, sea water [6]. The emergence of TCs in the environment could pose a potential risk to human health and the ecosystem through the development of antibiotic-resistant bacteria or pathogens [7,8]. Therefore, antibiotics should be removed from aquatic environments [9]. Due to their stable nature, tetracene rings and antibiotic properties against bacteria, TCs are difficult to eliminate efficiently using conventional biological wastewater treatment [10,11]. Recently, advanced oxidation technologies (AOTs) have been shown to be highly effective at in

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removing recalcitrant and non-biodegradable organic contaminants that are resistant to traditional treatment [12–15]. The hydroxyl radical, which is non-selective and has a high oxidation potential of 2.80 V, can degrade organic molecules to harmless products (CO_2 and H_2O) by abstracting a hydrogen atom or adding it to double bonds [16,17]. Among the AOPs, Fenton stands out for its oxidation, high oxidation power, fast oxidation kinetics, cost effectiveness and ease of use [18]. Fenton process oxidizes organic pollutants using hydroxyl radicals ($\cdot\text{OH}$) produced from hydrogen peroxide (H_2O_2) – ferrous sulfate reaction in an acidic environment [19].

Various inorganic anions such as chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) are usually found in surface water, groundwater and wastewater. The inorganic anions present in the water body can have a significant effect on the overall reaction rates in the Fenton process [20–22]. The effect of inorganic anions on the degradation of organic pollutants such as dyes and pesticides was studied in the Fenton process [23–28]. Although the effect of inorganic ions on the degradation of TCs has been investigated for the photo-Fenton process, UV, UV/ H_2O_2 [4,29–31], it is seen that the studies on the effect of inorganic ions in removing TCs with dark-Fenton are not sufficient. Inorganic anions can change the overall efficiency of the Fenton system in different ways. Therefore, it is imperative to investigate the effect of inorganic anions in water treatment using Fenton. The aim of this study is to determine the effect of Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , HCO_3^- anions on degradation and mineralization of TC and oxytetracycline (OTC) with Fenton process.

2. Materials and methods

2.1. Experimental system

All experimental studies were carried out in amber-colored 250 mL glass bottles to minimize the light effect in TC and OTC degradation. pH was adjusted to 3 at the beginning of the experiment and pH adjustment was not made during the reaction. Initially, TC and OTC concentration was kept at 100 mg/L. In studies conducted with TC, the H_2O_2 concentration was 100 mg/L and the Fe^{2+} concentration was 30 mg/L. In studies with OTC, H_2O_2 concentration was 25 mg/L and Fe^{2+} concentration was 30 mg/L.

These values were chosen based on preliminary laboratory results. In addition, possible concentrations (1–10–100 mM) of inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , HCO_3^-) that can be found in the aquatic environment were tested. The reaction time was 60 min for both TC and OTC. TC, OTC and total organic carbon (TOC) analyzes were performed by taking samples at the 5th, 10th, 20th, 30th and 60th min of the reaction. The experimental setup is shown in Fig. 1.

2.2. Reagents

Tetracycline (TC) hydrochloride salt (CAS No. 64-755) and oxytetracycline (OTC) hydrochloride salt (CAS No. 2058-46-0) were obtained from Sigma-Aldrich. Hydrogen peroxide (H_2O_2), ferrous sulphate heptahydrate ($\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), sodium chloride (NaCl), sodium sulphate (Na_2SO_4), sodium nitrate (NaNO_3), sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) were obtained from Merck. The pH of the solution was adjusted using diluted 98% H_2SO_4 (0.2 N) and NaOH (0.2 N).

2.3. Analytical methods

TC and OTC analysis were performed by high performance liquid chromatography (HPLC) (Shimadzu). The HPLC was equipped with diode array detector and an AllureBiPh column (5 μm , 150 mm \times 4.6 mm). The mixture of acetonitrile/ammonium dihydrogenphosphate (80/20, v/v) was used as the mobile phase at a constant flow rate of 1.2 mL/min. The wavelength for TC and OTC detection was 269 nm. The retention time for TC and OTC was found to be 3.90 and 2.95 min, respectively. TOC analysis was done with the TOC analyzer (TOC-VCPh, Shimadzu).

3. Results and discussion

3.1. Effect of chloride

Cl^- is an important anion that affects the Fenton oxidation [12]. In the control study where Cl^- was not used, TC degradation was 100%. The effect of Cl^- on TC degradation using 1, 10, and 100 mM Cl^- was investigated and it was found that the removal curves overlapped over time and removal efficiencies were similar to the control study (Fig. 2). OTC removal was 100% without Cl^- and at

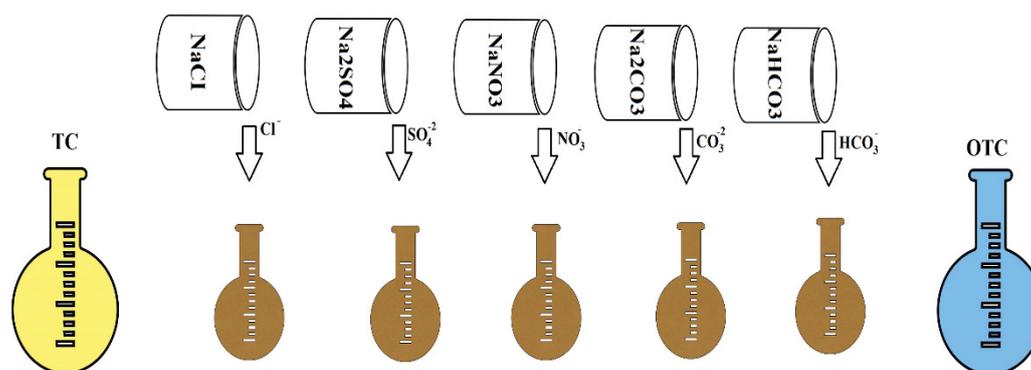


Fig. 1. Experimental setup.

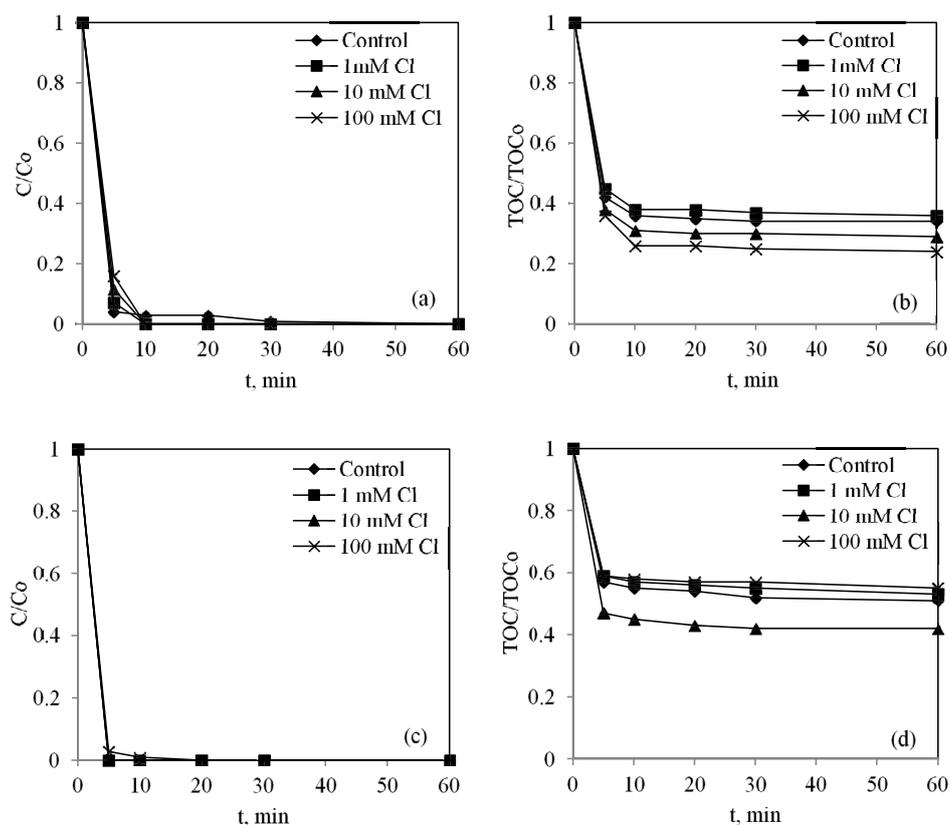
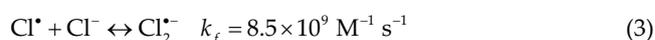
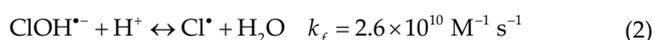
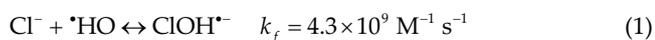


Fig. 2. Effect of Cl^- on (a) TC degradation, (b) TC mineralization, (c) OTC degradation, and (d) OTC mineralization.

all chloride concentrations (1, 10 and 100 mM). When the degradation of TC and OTC was compared, it could be said that the concentration change was almost similar depending on the time, although the degradation rate of OTC was slightly higher at the beginning. The inhibition of oxidation with the Fenton process due to the increasing concentration of Cl^- was generally attributed to two reasons: (i) Chloride can generate radicals (Cl^\bullet , $\text{Cl}_2^{\bullet-}$ and $\text{ClOH}^{\bullet-}$) that prevent the reaction between the hydroxyl radical and organic matter. (ii) Chloride forms complexes with iron (FeCl^+ , FeCl_2^+ and FeCl_2^{\bullet}) and affects the reactivity of iron species [26,32]. In this study, it was observed that the inhibition effect of the Cl^- up to 100 mM concentration on the degradation of TC and OTC by the Fenton process was tolerated. On the contrary, Yu et al. [33] reported that the presence of low concentrations (50 mM) of Cl^- shows a mild inhibitory effect on the degradation of sulfamethoxazole (SMX), and higher Cl^- (100 mM) concentrations significantly accelerate the degradation of SMX. Fang et al. [34] found that Cl^- affects the distribution pattern and selectivity of free radicals and can increase the overall concentration of radical species. In the presence of chloride, Cl^\bullet , $\text{Cl}_2^{\bullet-}$ and $\text{ClOH}^{\bullet-}$ are formed [Eqs. (1)–(3)] [35,36].



When $\text{pH} > \text{pKa}$ (7.2), $\text{ClOH}^{\bullet-}$ is the dominant radical, whereas at $\text{pH} < \text{pKa}$ (7.2), the dominant radical species are Cl^\bullet and $\text{Cl}_2^{\bullet-}$ [35]. The redox potential of the Cl^\bullet and $\text{Cl}_2^{\bullet-}$ are 2.41 and 2.09 V, respectively [32]. Since the initial pH value was 3 and the change in pH during the reaction was negligible, the active radicals in the medium were expected to be Cl^\bullet and $\text{Cl}_2^{\bullet-}$. Due to their high redox potential, Cl^\bullet and $\text{Cl}_2^{\bullet-}$ are considered to be reactive species like hydroxyl radical and thus, might have prevented the inhibition effect of the Cl^- ion. However, these reactions are complex, not fully understood, and there is a lack of information regarding the degradation rate constant of pharmaceutically active compounds with reactive chloride species [37]. Lebig-Elhadi et al. [38] reported that chloride could have inhibitory or beneficial effect according to experimental conditions and the nature of the pollutant. Yuan et al. [39] reported that Cl^\bullet and $\text{Cl}_2^{\bullet-}$ can react with dye and intermediates via an electron oxidation, H-stripping, and bonding to unsaturated C–C bonds. These reaction pathways are similar to TC and OTC reaction pathways. Thus, the mechanism of action of the Cl^\bullet and $\text{Cl}_2^{\bullet-}$ can be considered to be similar, but the intermediates formed need to be determined. In the control study without the Cl^- , 66% of TC was mineralized. Similar mineralization value was obtained at 1 mM Cl^- concentration compared to the control study, the mineralization value increased at higher Cl^- concentration values.

When the values of the complex formed in HPLC were examined (data not given), two different complexes and a slight increase in the values of these two different complexes were observed. The increase in the mineralization value due to the increase in Cl^- showed that the size of the formed complexes did not affect the mineralization degree. OTC mineralization was lower compared to TC. Depending on the increase in chloride concentration value, the change in the mineralization value showed that it differs from TC. In the control study, mineralization of OTC was 49%. The mineralization degrees of OTC at 1, 10 and 100 mM Cl^- concentrations were 47%, 58% and 45%, respectively. There was a slight increase in complex values due to the increase in chloride concentration. However, both complexes had a higher value compared to TC. It has been observed that the magnitude of the complex values reduces the mineralization of OTC. In the study where the chloride concentration was 10 mM, mineralization was approximately 10% higher than in other cases. This could be explained by the fact that the value of second complex formed at this Cl^- concentration value was relatively lower and that certain Cl^- concentration relatively increased the mineralization of OTC. It is known that chloride ions are always a serious concern because of the possibility of chloro-organic compounds forming in water supplies because these compounds are toxic and pose a threat to human health and the ecosystem [40]. The degradation and mineralization of TC and OTC were similar over time under all operating conditions. The reason why

mineralization is lower than degradation is that mineralization takes place in a more complex way and the intermediate products formed do not fully convert to CO_2 and H_2O .

3.2. Effect of the sulfate

The sulfate ion inhibits the Fenton process with the effect of preventing the radicals formed in the medium and the complexes it has formed [41]. Khan et al. [42] reported that sulfate ions have low or no reactivity towards hydroxyl radical. Increasing the sulphate ion concentration slightly decreased the initial TC degradation rate. TC degradation was 100% in control study and studies involving sulfate ion (Fig. 3). Sulfate ion did not prevent TC degradation by Fenton process. TC mineralization degree which was approximately 65% was similar in control study, 1 and 100 mM sulphate ion concentration values. At 10 mM sulfate ion concentration value, the mineralization degree was 70%. Compared to the others, the mineralization degree was higher. Both complex values formed were relatively less at this concentration value. The difference in this mineralization degree depends on the size of the complex values formed. In the study with control, 1, 10 and 100 mM sulfate ion, OTC degradation was 100%. Degradation of OTC by Fenton process was not affected up to 100 mM sulphate ion concentration. This showed that the presence of sufficient Fe^{2+} and H_2O_2 concentrations in the working medium prevented the inhibition due to SO_4^{2-} . OTC mineralization

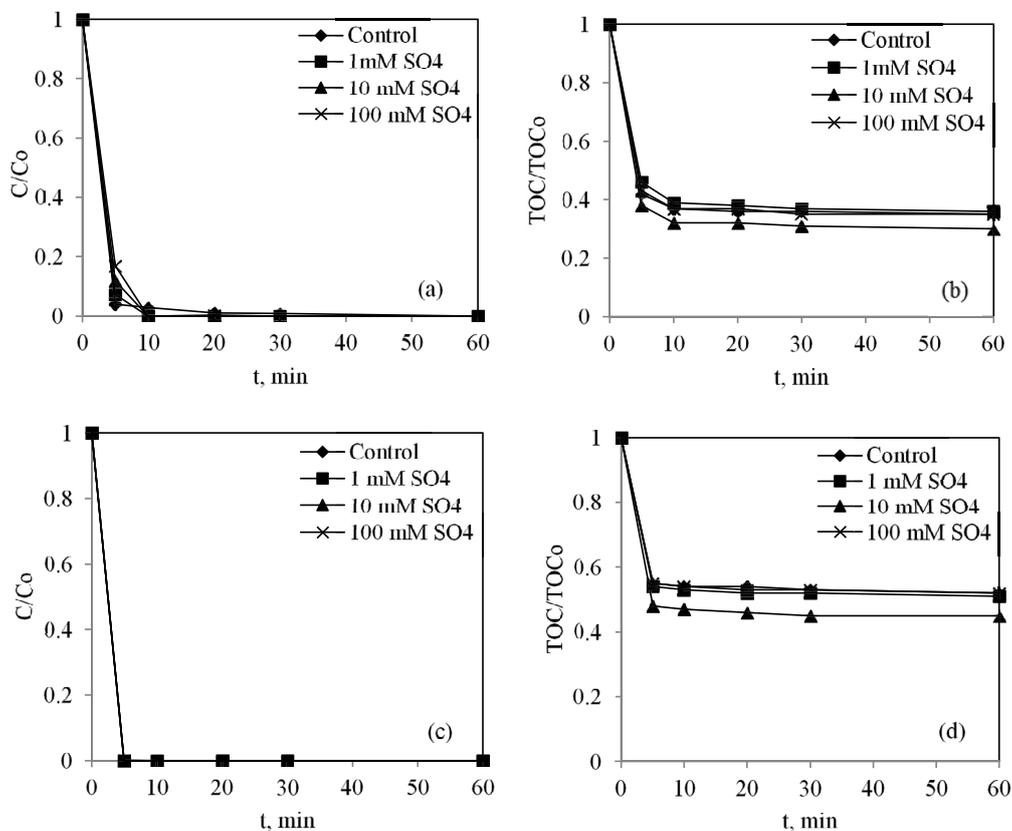


Fig. 3. Effect of SO_4^{2-} on (a) TC degradation, (b) TC mineralization, (c) OTC degradation, and (d) OTC mineralization.

was 48%, 49%, 55% and 48% at control, 1, 10 and 100 mM sulphate concentrations, respectively. Mineralization was slightly more at 10 mM sulphate concentration. TOC removal efficiency indicated that TC and OTC transformed into intermediate products without complete mineralization. Compared with TC mineralization, OTC mineralization was lower. This was due to the greater number of complexes formed during OTC mineralization.

3.3. Effect of the nitrate

There are two different views with the effect of NO_3^- ion. Some studies suggest that NO_3^- ion does not form complexes with Fe(II) and therefore does not affect yield [25,41]. Some studies also show that it reacts easily with reactive radical species and as a result there is a decrease in efficiency [40,43,44]. In order to determine the effect of NO_3^- on TC degradation by Fenton process, 1, 10 and 100 mM NO_3^- concentration values were used. TC degradation was achieved in both control and all NO_3^- concentrations and efficiency was 100% under all operating conditions (Fig. 4). It was reported that low concentration of NO_3^- (1 and 10 mM) did not affect benzotriazole (BTA) oxidation, but 100 mM NO_3^- inhibited the reaction [45]. In this study, NO_3^- had no effect on TC degradation. The results correspond with results obtained by Cao et al. [3] who investigated zero-valent iron activated peroxymonosulfate of TC and reported that NO_3^- has the lowest reaction rate with $\cdot\text{OH}$ and it almost has no inhibition effect

on TC degradation. The mineralization degree of TC was 64%, 62%, 71% and 60%, at the control, 1, 10 and 100 mM NO_3^- concentrations, respectively. Mineralization was more in the study with 10 mM NO_3^- . The fact that the resulting first complex value was lower at 10 mM NO_3^- concentration increased the mineralization value. In this study, complexes were formed with the NO_3^- . This result contradicts with studies indicating that NO_3^- ion does not form complexes [25,41]. OTC degradation was 100% under all working conditions. NO_3^- concentration did not affect OTC degradation up to a concentration of 100 mM. The degree of mineralization of OTC was 47%, 47%, 50% and 43% for control, 1, 10 and 100 mM NO_3^- , respectively. Compared to the control study, the mineralization value did not change up to a concentration of 1 mM NO_3^- , while a slight increase in the concentration of 10 mM NO_3^- was observed. At 100 mM NO_3^- concentration, the degree of mineralization was slightly reduced. The less mineralization degree of OTC compared to TC is due to the more complexes formed.

3.4. Effect of the carbonate

The CO_3^{2-} had no significant effect on TC and OTC degradation up to a concentration of 100 mM (Fig. 5). Both TC and OTC degradation were 100%. The results showed that the degradation of TC and OTC were completed in both CO_3^{2-} -free and CO_3^{2-} -containing studies by Fenton process. It is stated that the oxidation efficiency will decrease

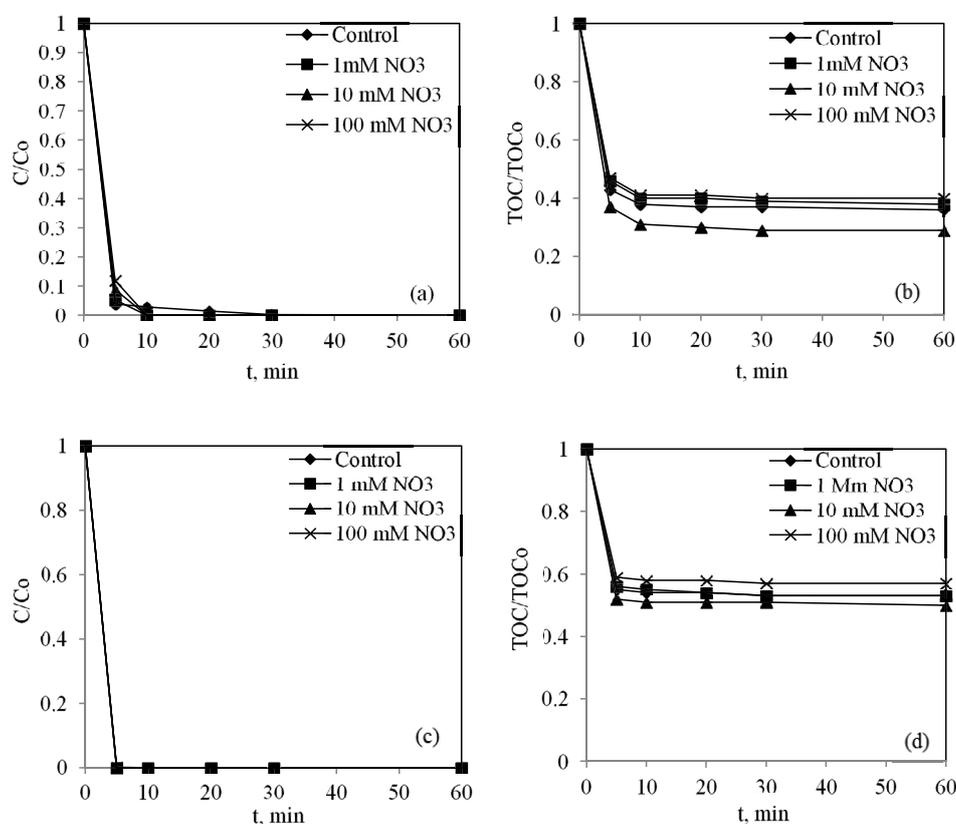


Fig. 4. Effect of NO_3^- on (a) TC degradation, (b) TC mineralization, (c) OTC degradation, and (d) OTC mineralization.

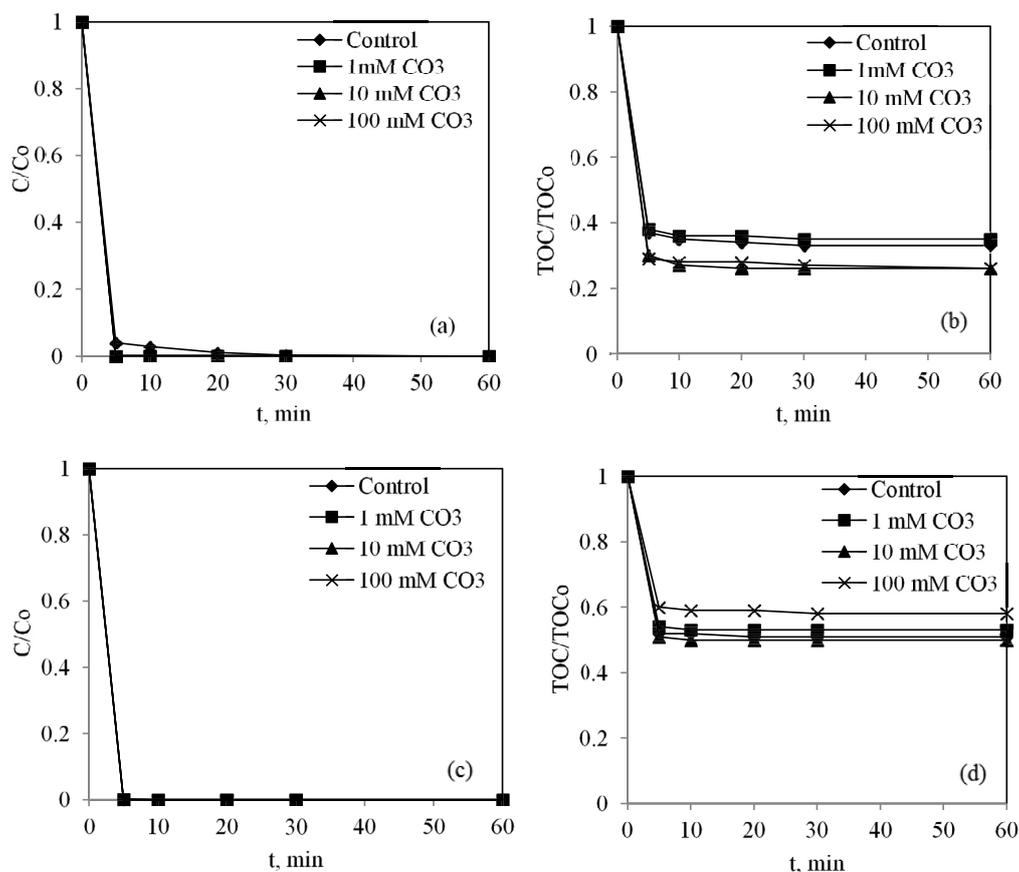


Fig. 5. Effect of CO_3^{2-} on (a) TC degradation, (b) TC mineralization, (c) OTC degradation, and (d) OTC mineralization.

with the addition of the CO_3^{2-} , since the CO_3^{2-} is formed and it has a lower redox potential (1.59 V) [46,47]. In this study, the CO_3^{2-} did not reduce the oxidation efficiency up to 100 mM concentration. It was reported in a previous study that CO_3^{2-} had a high reaction rate for OTC (2.9×10^8 1/M.s) [30]. Zhang et al. [48] found that although the rate constants of target antibiotics with CO_3^{2-} are lower than those with $\cdot\text{OH}$, the higher selectivity of the carbonate radical makes it less susceptible to scavenging effects. It has been reported that CO_3^{2-} reacts with organic matter by electron transfer and hydrogen abstraction [49]. Jeong et al. [50] reported that in the 10–100 mg/L CO_3^{2-} concentration range, the TC degradation mechanism is preferred by the addition of an electron to the aromatic ring rather than the hydroxyl radical. TC mineralization increased slightly in studies where CO_3^{2-} concentration was 10 and 100 mM. Complexes were also formed with the CO_3^{2-} . There was no relationship between the increase in mineralization and the size of the complexes formed. The increase in mineralization could be due to its high selectivity and longer survival time. It has been reported that CO_3^{2-} shows high reactivity to elective rich compounds such as phenols and N-containing compounds [30]. The TC structure preferably contains electron rich groups such as the phenol moiety and the dimethylammonium group, which can be attacked by CO_3^{2-} [51]. OTC mineralization was observed to decrease as the CO_3^{2-} concentration increased

to 100 mM. The value of the complexes formed at this concentration decreased. Therefore, the decrease in OTC mineralization was due to the decrease in the mineralization of itself and intermediate products that occur due to the pH change.

3.5. Effect of the bicarbonate

Due to its high solubility, HCO_3^- is widely distributed in natural waters and in biological systems where it forms the main biological buffer [52]. TC and OTC degradation took place completely in the presence of HCO_3^- and 100% was removed (Fig. 6). HCO_3^- ion reacts with $\cdot\text{OH}$ radical to form $\text{CO}_3^{\cdot-}$ and $\text{HCO}_3^{\cdot-}$ [22]. The $\text{HCO}_3^{\cdot-}$ has a lower oxidation potential compared to the $\cdot\text{OH}$ [44]. In this study, TC and OTC degradation were not affected by HCO_3^- ion up to 100 mM concentration. TC mineralization was of similar magnitude to the control study at 1 mM HCO_3^- concentration. When the HCO_3^- concentration increased to 10 mM, the mineralization increased, but it decreased at 100 mM HCO_3^- concentration. The resulting complex values were slightly lower at 10 mM HCO_3^- concentration. Therefore, the effect of the formed complexes on mineralization was very low. The change in the transformation paths since the increase in pH with the addition of HCO_3^- was more effective in the increase in mineralization. OTC mineralization also increased at 10 mM HCO_3^- concentration, similar to TC

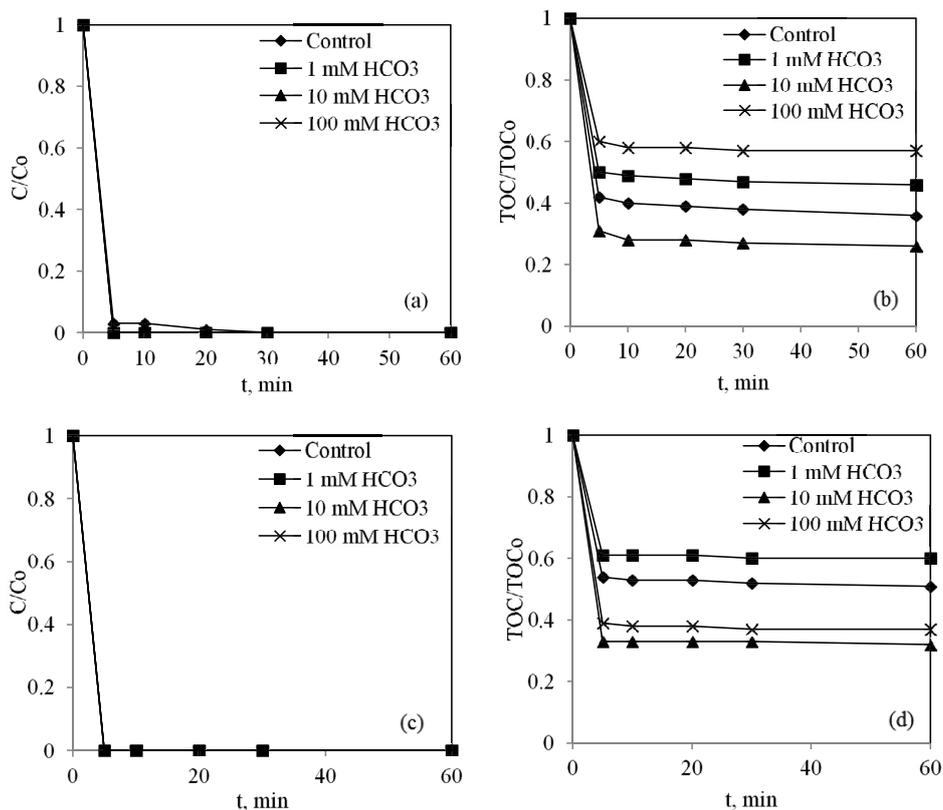


Fig. 6. Effect of HCO₃⁻ on (a) TC degradation, (b) TC mineralization, (c) OTC degradation, and (d) OTC mineralization.

Table 1
Comparison of the effects of inorganic anions

Inorganic anion concentration	TC						OTC					
	Degradation, % (Mineralization, %)						Degradation, % (Mineralization, %)					
	Control	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	CO ₃ ²⁻	HCO ₃ ⁻	Control	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	CO ₃ ²⁻	HCO ₃ ⁻
1 mM	100 (66)	100 (64)	100 (64)	100 (62)	100 (65)	100 (43)	100 (49)	100 (47)	100 (49)	100 (47)	100 (47)	100 (40)
10 mM	100 (66)	100 (71)	100 (70)	100 (71)	100 (74)	100 (74)	100 (49)	100 (58)	100 (55)	100 (50)	100 (50)	100 (68)
100 mM	100 (66)	100 (76)	100 (65)	100 (60)	100 (74)	100 (43)	100 (49)	100 (45)	100 (48)	100 (43)	100 (42)	100 (63)

mineralization. OTC mineralization was partially decreased at 100 mM HCO₃⁻ concentration compared to 10 mM HCO₃⁻ concentration. However, this reduction in OTC mineralization is quite small compared to TC.

3.6. Comparison of the effects of inorganic anions (Cl⁻, SO₄²⁻, NO₃⁻, CO₃²⁻, HCO₃⁻) on degradation and mineralization of TC and OTC

TC and OTC degradation were unaffected up to 100 mM concentration of Cl⁻, SO₄²⁻, NO₃⁻, CO₃²⁻ and HCO₃⁻. TC and OTC were completely degraded. Mineralization of organic compounds is environmentally important because the ultimate goal of AOPs is the oxidation of organic pollutants to mineral compounds [40]. While the main contaminant can be completely removed during advanced oxidation, by-products can be created, and some of them may be more toxic than the original substance.

Therefore, monitoring the mineralization scope is important to evaluate the performance of different technologies [38]. TC mineralization was similar in studies conducted with control, 1 mM Cl⁻, SO₄²⁻, NO₃⁻ and CO₃²⁻ (Table 1). In the study containing 1 mM HCO₃⁻, there was a decrease of approximately 22% in TC mineralization. There was a slight increase in mineralization at 10 mM ion concentration compared to the control study. The effect of ions on mineralization was almost the same. TC mineralization at 100 mM concentration of SO₄²⁻ and NO₃⁻ was similar to the control study. There was an increase in TC mineralization in the presence of Cl⁻ and CO₃²⁻ and this increase was approximately the same for both ions. In the case of the HCO₃⁻, there was a decrease in TC mineralization and this decrease was the same as compared to the decrease in 1 mM HCO₃⁻ concentration. OTC mineralization at 1 mM Cl⁻, SO₄²⁻, NO₃⁻ and CO₃²⁻ ion concentration is the

same as compared to the control study. OTC mineralization decreased approximately 9% in case of 1 mM HCO_3^- . Similar results were obtained when 10 mM NO_3^- and CO_3^{2-} concentration and control study were compared in terms of OTC mineralization. In the presence of 10 mM Cl^- and SO_4^{2-} concentration, there was an increase of approximately 5%–10% in OTC mineralization. This increase in mineralization in the presence of HCO_3^- was 19%. The OTC mineralization obtained at 100 mM SO_4^{2-} concentration and in the control study was the same. OTC mineralization was partially reduced in the presence of 100 mM Cl^- , NO_3^- and CO_3^{2-} . In the presence of 100 mM HCO_3^- , there was an increase of 14%.

4. Conclusions

Oxidation of organic compounds is known to be affected by inorganic anions found in water. In this study, the effect of different inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^-) on degradation and mineralization of TC and OTC was investigated. Both TC and OTC degradation were not affected by the inorganic anions studied (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} and HCO_3^-) and their different concentrations (1, 10 and 100 mM). TC and OTC degradation was 100%. TC and OTC mineralization was affected by the presence of inorganic anions studied. OTC is less mineralized compared to TC due to the more complexes formed. The effect of inorganic anions on mineralization showed differences in terms of both ion and ion concentration.

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