



Sonodegradation of amitriptyline and ibuprofen in the presence of $Ti_3C_2T_x$ MXene



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ABSTRACT

This study, which investigated the sonodegradation of selected pharmaceutical active compounds (PhACs) (amitriptyline (AMT) and ibuprofen (IBP)) with MXene, was carried out in an aqueous solution. To investigate the practicality of the degradation process, the experiments were conducted in various water quality conditions, including pH, temperature, natural organic matter, and ionic strength. Based on the experimental results, the produced hydrogen peroxide, which could be a representative of the produced OH radicals, was a vital factor that affected the degradation performance of both PhACs. To confirm the importance of OH radicals, the effect of a OH radical promoter (H_2O_2) and scavenger (t-BuOH) was also studied. In addition, the synergism between ultrasonication (US) and MXene was evaluated with the rate constants of US only, MXene only, and a US/MXene combined system. Mineralization of the PhACs was also investigated, and removal of AMT was higher than that of IBP, which could be attributed to the physicochemical properties of the compounds and enhanced adsorption by the well-dispersed MXene. Overall, utilization of MXene by means of ultrasonication could enhance the removal performance of PhACs in water.

1. Introduction

There have been advances in the pharmaceutical industry as a result of the increasing need for medication for various purposes, such as treatment of a wide range of diseases, prevention of diseases, and, ultimately, improvement of the quality of life (Hester et al., 2020). Endocrine-disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs), which are now easily accessible to the public, have saved a number of people, but they have had a negative impact on the environment as well. Over the last two decades, a large amount of EDCs and PhACs have been discharged into the environment without being properly treated, and accordingly, concentrations of the discharged compounds in water systems have increased (Al-Hamadani et al., 2017b; Jun et al., 2019; Kim et al., 2018). Furthermore, several studies have emphasized that conventional water treatment processes are not very efficient to completely remove the released EDCs and PhACs present in influents (Cerreta et al., 2020; Manoli et al., 2019; Yang et al., 2017).

Through water systems, such as surface water and ground water, the concentrated discharged compounds could ultimately take a toll on

animals, plants and human beings (Kolpin et al., 2002; Li et al., 2019). Specifically, ibuprofen (IBP), which is frequently used as an anti-inflammatory analgesic, has been found to be discharged from water treatment plants at a concentration of 0.002–24.6 $\mu\text{g/L}$ (Buser et al., 1999; Méndez-Arriaga et al., 2008). The other selected PhAC, amitriptyline (AMT), which is widely prescribed as an antidepressant, has been detected in surface water, leading to long-term exposure of living organisms to the compound in water systems (Baker and Kasprzyk-Hordern, 2011; Baker et al., 2012; Kasprzyk-Hordern et al., 2008; Lajeunesse et al., 2012). Various treatment processes have been used to remove PhACs and EDCs from water, such as adsorption (Guillossou et al., 2020; Jung et al., 2013), coagulation/sedimentation (Adams et al., 2002), membrane processes (Heo et al., 2013, 2012), disinfection (Vieno et al., 2007), UV/ H_2O_2 (Yuan et al. 2009), and Fenton oxidation (Mohapatra et al. 2013). However, efficiencies of the conventional treatments are considered low, and it is known that the disinfection process could produce by-products (Al-Hamadani et al., 2017a; Westerhoff et al., 2005).

Ultrasonic (US) treatment has been studied as one of the advanced technologies. It is prominent for removing contaminants with complex

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structure. US treatment is basically conducted by highly reactive OH radicals by dissociating water molecules through ultrasonication. Water molecules are dissociated through a series of processes: formation, growth, and collapse of cavitation bubbles caused by sonication in water (Im et al., 2014). Acoustic cavitation can form and grow cavitation bubbles and, when the bubbles collapse, extremely high temperatures (~ 5000 K) and pressures (~ 1000 atm) can be produced, resulting in the production of reactive free radicals such as OH, O, and HO_2 (Al-Hamadani et al., 2016, 2017a). The free radicals can oxidize various contaminants, thus degrading the contaminants in water. Due to its advantages, including high efficiency, convenient operation, and environmental-friendliness, US treatment has been widely studied for adaptability in water treatment (Chu et al., 2017). However, US treatment generally causes high usage of energy, which may lead to poor cost efficiency compared to other water treatments. Since US treatment has this critical drawback, a variety of studies have been conducted on sonocatalysts in order to improve their US degradation rates (Im et al., 2015; Jun et al., 2019; Lee et al., 2018).

By adding sonocatalysts in US reactions, they can play an important role of promoting the production of cavitation bubbles by providing additional nuclei to the bubbles, thus supporting the generation of more free radicals (Al-Hamadani et al., 2018; Im et al., 2015; Jun et al., 2019b). Several sonocatalysts have been used to enhance the efficiency of US degradation, such as single-walled carbon nanotubes (Al-Hamadani et al., 2016, 2017a; Im et al., 2013), graphene oxide (Al-Hamadani et al., 2018), powdered activated carbon (Im et al., 2014), metal-organic framework (Jun et al., 2019b), glass beads (Al-Hamadani et al., 2016), fly ashes (Al-Hamadani et al., 2017b), and TiO_2 nanotubes (Im et al., 2015). Adding the abovementioned materials as sonocatalysts could improve the sonodegradation of organic pollutants by increasing the production of free radicals and mostly dispersing the catalysts, which could boost their adsorption effect (Chu et al., 2017). MXene is a new family of two-dimensional materials fabricated by etching "A" layers from a "MAX" structure, thus obtaining compounds with the formula $\text{M}_{n+1}\text{X}_n\text{T}_x$, such as $\text{Ti}_3\text{C}_2\text{T}_x$, where "A" represents an A-group element, such as Si, Al, or Sn, "M" is a transitional metal (e.g., V, Nb, or Ti), and "X" is N or C (Jeon et al., 2020). To the best of our knowledge, only a few studies have been

conducted on the utilization of MXene to improve the degradation of organic pollutants, such as PhACs, by ultrasonication.

The main purpose of this study is to investigate the effect of several experimental conditions on sonodegradation of the selected PhACs with MXene. The synergism between ultrasonication and MXene was also evaluated. Synergetic indices were first evaluated by calculation with pseudo-first-order kinetic constants of US only, MXene only, and the US/MXene combined process. All the other experiments were conducted in a US/MXene combined system, and the experimental conditions included pH and temperature of solution, ionic strength, natural organic matter (NOM), and existence of OH radical promoter and scavenger.

2. Materials and methods

Details regarding chemicals, used in this study, and measurement method of PhAC and H_2O_2 concentration are provided in the supplementary information (SI, Section 1).

2.1. US reactor and specific experimental conditions

All the US experiments were conducted with a custom-designed US system comprising a water circulation chiller (HS-28A, 22–240 V, 50 Hz, HAILEA) and a circulation pump (HX 6530, 50 W, 220–240 V, HAILEA). The US reaction tank ($\Phi 110 \times 170$ mm, effective volume 1 L) consisted of dual stainless-steel walls, mounting plates, and circulation fittings to control the water temperature. A stainless-steel transducer module (Fulltech, Taiwan) was attached to an ultrasonic generator (Flexonic Mirae Ultrasonic Tech., model FX-4FREQ, Korea). Mechanical stirring was controlled using an overhead stirrer (HS-50A, WiseStir[®]) at a constant speed.

The US frequency and power of this system were optimized, with the combination of 35 kHz and 50 W L^{-1} , which was found to produce the highest amount of H_2O_2 , selected for this study. 45 mg L^{-1} of MXene was used for each experiment, and detailed experimental conditions were set as follows: (i) initial pH of PhAC solution of 3.5, 7, or 10.5; (ii) addition of 0.2, 1, or 5 mM of H_2O_2 as a OH radical promoter and of t-BuOH as a OH radical scavenger; (iii) solution temperature of 293, 303, or 313 K; (iv) addition of 3 or 9 mg L^{-1} of HA; and (v) ionic strength of NaCl of 300, 600,

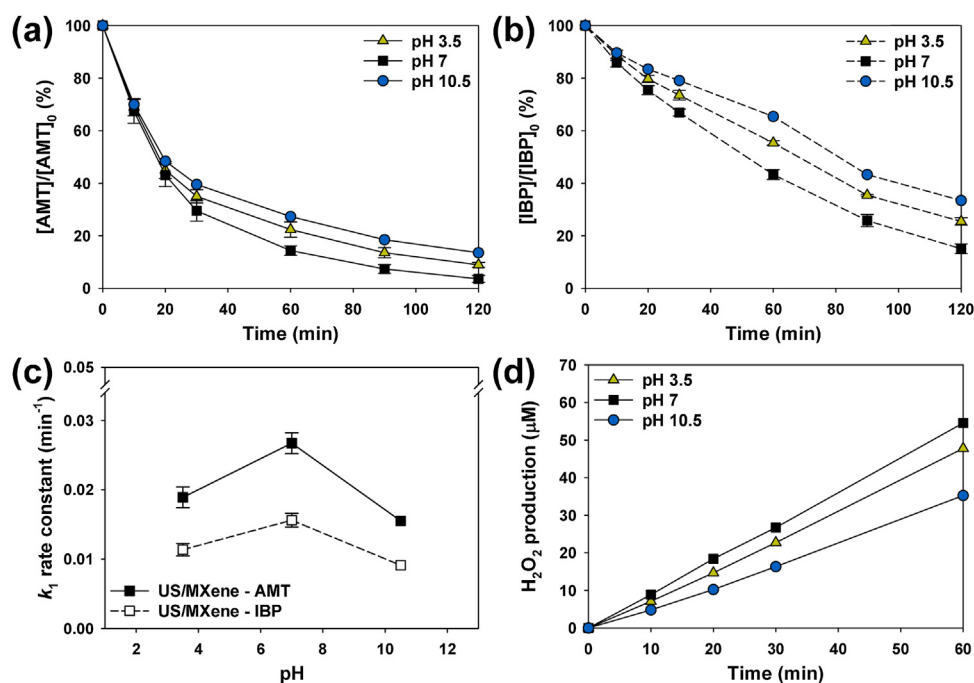


Fig. 1. Influence of pH on sonodegradation performance of (a) AMT and (b) IBP, (c) degradation rate, and (d) H_2O_2 production at different pH levels (US/MXene system, 35 kHz, 50 W L^{-1} , and 293 ± 1 K).

or $1200 \mu\text{S cm}^{-1}$. The initial pH and temperature were set to 7 and 293 K, respectively unless otherwise stated.

2.2. Calculation of synergetic index

The synergetic effect was evaluated by calculation of the synergetic index, according to Eq. (1), which has been described in previous studies (Madhavan et al., 2010) and (Jun et al., 2020a,2020b).

$$\text{Synergetic index} = \frac{k_1 (\text{US/MXene})}{k_1 (\text{US only}) + k_1 (\text{MXene only})} \quad (1)$$

Each of the obtained degradation rate constants of a pseudo-first-order kinetic model was applied to Eq. (1). The US/MXene combined process was considered more efficient compared to the singly conducted processes if the synergetic index value was greater than 1.0.

3. Results and discussion

3.1. Influence of solution pH, temperature, NOM, and ionic strength

The solution pH is an important factor that affects the degradation rate of PhACs. The influence of pH could affect sonodegradation efficiency due to the different oxidation potentials of OH radicals, $\text{p}K_a$ of the selected compounds, and surface charge of MXene. Since the oxidation potential of

OH radicals could change depending on the pH level, the quantity of OH radicals could also change, which might influence the sonodegradation efficiency (Balachandran et al., 2016; Chu et al., 2017). Also, at different pH levels, the $\text{p}K_a$ of the selected PhACs and the pH_{pzc} of MXene could affect the mobility of the PhACs and the surface charge of MXene, thus resulting in different sonodegradation performances (Im et al., 2014, 2013; Zhang et al., 2019).

The effect of pH is shown in Fig. 1, which presents the results of MXene-assisted sonodegradation of the target compounds with increasing pH values. Based on the sonodegradation performances, the removal efficiencies of both target compounds were greater at pH 7, followed by pH 3.5 and 10.5. Higher efficiency at the neutral condition could be explained by the production of H_2O_2 , which could represent the amount of produced OH radicals. In Fig. 1d, the amount of produced H_2O_2 was highest at pH 7, followed by pH 3.5 and 10.5, with the trend similar to that of the sonodegradation performances. One research showed that less amount of H_2O_2 was produced at low and high pH due to the scavenging effect of existing ions and fast recombination of OH radicals (Jiang et al., 2002). Considering the research, it can be concluded that more OH radicals were produced and higher removal efficiency was achieved at pH 7 with the US system used in this study. Also, in terms of AMT in particular, since its $\text{p}K_a$ is 9.76, AMT is positively charged at pH 3.5 and pH 7 due to the amine group acting like an electron donor (Guillosoo et al., 2020). Owing to its positively charged characteristic, AMT could be adsorbed on negatively charged MXene having surface functional groups

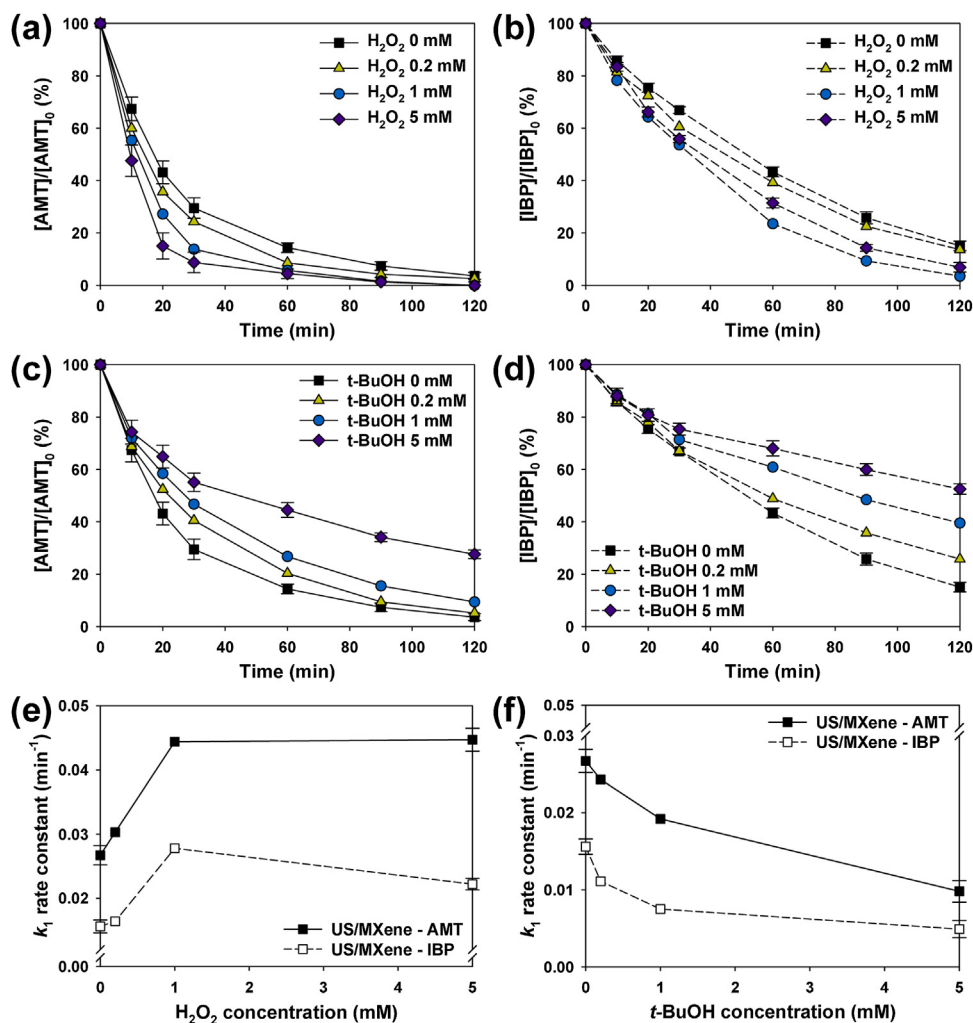


Fig. 2. Influence of OH radical promoter (H_2O_2) on sonodegradation performance of (a) AMT, (b) IBP, and (e) degradation rate, and influence of OH radical scavenger (t-BuOH) on sonodegradation performance of (c) AMT, (d) IBP, and (f) degradation rate at different concentrations of OH radical promoter and scavenger (US/MXene system, 35 kHz, 50 W L^{-1} , pH 7, and $293 \pm 1 \text{ K}$).

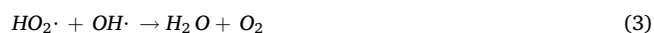
including -O, -F, and/or -OH (Jeon et al., 2020). Since MXene is more negatively charged at higher pH, shown in Fig. S1, AMT could be more adsorbed on MXene at pH 7 than pH 3 due to higher electrostatic interaction; similar result is shown in the research conducted by Kim et al. (Kim et al., 2021).

The influence of temperature on the degradation rate of the PhACs is shown in Fig. S2. In Fig. S2c, the degradation rates of AMT and IBP slightly increased up to 303 K and decreased at 313 K. The result shows the above-mentioned positive and negative effects of temperature, and it is consistent with the result of H₂O₂ production in Fig. S2d, which indirectly represents the concentrations of the OH radical at different temperatures. The tendency for H₂O₂ production is well matched by the degradation rate constants of both PhACs, so it can be concluded that, in this study, the quantity of H₂O₂ is an important factor in US degradation. The influence of HA is shown in Fig. S3, which indicates that the removal rates of both PhACs increased when HA was added. This result is in agreement with the results of the research conducted by a previous study, which showed higher degradation rates after adding HA as a representative of NOM (Park et al. 2011). They demonstrated that HA could trap H radicals with background ions, thereby preventing OH radicals from recombination with the H radicals, although they noted that more detailed studies are needed to confirm this phenomenon. The influence of ionic strength is shown in Fig. S4, which presents the result of the sonodegradation with MXene with adjusted conductivity levels of the solution. According to Fig. S4, there was no significant effect observed by addition of NaCl to increase conductivity. This result is in good agreement with the result of a research conducted by Minero et al. on the influence of inorganic anions on sonodegradation of acid blue 40 (Minero et al. 2008). They conducted the experiments using ultrasonication with several inorganic compounds, including NaHCO₃, Na₂CO₃, and NaCl, and concluded that the addition of NaCl has practically no influence on sonodegradation. They confirmed that there is only a marginal effect of ionic strength when NaCl is used. Detailed influence of temperature, NOM, and ionic strength on degradation is demonstrated in SI (Section 2).

3.2. Influence of the promoter (H₂O₂) and scavenger (t-BuOH)

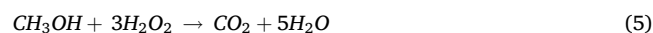
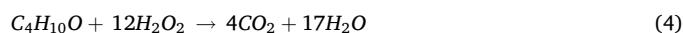
The production of OH radicals was found to be vital factor for US degradation, which is in good agreement with other researches (Chu et al., 2017; Im et al., 2015; Jun et al., 2020a,2020b). H₂O₂ and t-BuOH are widely known as an OH radical promoter and scavenger, respectively, and they were essential to investigate how influential was the role of OH radicals in the experiments. To confirm the effect of the quantity of OH radicals, H₂O₂ and t-BuOH, ranging from 0 to 5 mM, were used for sonodegradation of the PhACs.

In Fig. 2a, b, and e, the effects of the OH radical promoter on the sonodegradation are shown. At a concentration of up to 1 mM of H₂O₂, the rate constants (*k*₁) of both PhACs clearly increased, and until a concentration of 5 mM was reached, these rate constants tended to remain constant or decrease. Although H₂O₂ is a well-known OH radical promoter, the possible reason for this result could be because it can also have scavenging effects at high concentrations, as shown in Eqs. (2) and (3) (Adewuyi, 2001). OH radicals could react with hydrogen peroxide to be converted to hydroperoxyl radicals and, eventually, water molecules. Since HO₂[·] is considered a less reactive radical than an OH radical due to lower oxidation potential, the rate constant at 5 mM of H₂O₂ is likely to be decreased than expected. Thus, this phenomenon could strengthen the conclusion that OH radical is the main mechanism for the PhACs degradation in this study.



In Fig. 2c, d, and f, the effects of t-BuOH, at concentrations ranging from 0 to 5 mM, on the sonodegradation of the PhACs are shown. With

increasing concentration up to 5 mM of t-BuOH, the rate constants of the degradation of both compounds decreased accordingly during ultrasonication. This result could be attributed to the reaction of t-BuOH with H₂O₂, competing with the PhACs. Eq. (4) shows the conversion of t-BuOH to carbon dioxide and water molecules. Since t-BuOH can react with H₂O₂ instead of the PhACs, there would be less chance for the PhACs to be degraded by OH radicals and H₂O₂, thus having decreased rate constant. Similar result can be achieved by using methanol (MeOH), shown in Eq. (5) (Im et al., 2014). Im et al. explained the phenomena that the decreased rate constant of PhACs is attributed to the addition of t-BuOH and MeOH, indicating the sonodegradation of PhACs is OH radical-dependent. This result is in good agreement with other studies using t-BuOH and MeOH as OH radical scavengers (Im et al., 2014, 2013; Jun et al., 2019b).



The presence of the OH radical promoter and scavenger could affect the produced OH radicals and eventually affect the degradation of the PhACs. It can also be concluded that the quantity of OH radicals during sonodegradation of PhACs is an important factor. These results are in good agreement with those of some previous studies (Al-Hamadani et al., 2017b; Chu et al., 2017; Im et al., 2015; Jun et al., 2020a,2020b, Jun et al., 2019b).

3.3. Evaluation of synergetic indices

To investigate the synergetic effect of using MXene during ultrasonication, the experiments were conducted in a US only process, MXene only process, and US/MXene combined process to obtain the rate constants for each process. Synergetic indices, summarized in Table 1, were calculated with the rate constants of the three experimental processes, and the degradation performances are shown in Fig. 3. The US/MXene process was observed to be the most effective of the three processes. It is described that the synergetic indices of the US/MXene process for both compounds were above 1 (1.45 and 1.13 for AMT and IBP, respectively). This result shows that there was a synergetic effect of the US/MXene combined system for the both compounds, and the effect was more pronounced on the result of AMT in particular. This synergetic effect could be attributed to the enhanced adsorption by MXene, since MXene, as a nanomaterial, can become well dispersed and acquire a more negative surface by being sonicated (Jun et al., 2020a,2020b). During ultrasonication, the hydrodynamic diameter of MXene decreases by preventing aggregation, which could lead to enhancement of its adsorption capacity. Also, the zeta potential of sonicated MXene is more negative than that of pristine MXene, which could support electrostatic interaction with positively charged compounds (Jun et al., 2020b; Kim et al., 2021). Overall, it can be concluded that a US/MXene process has a synergetic effect that is attributable to enhanced adsorption by sonicated MXene.

Table 1
Degradation rate (*k*₁), coefficient of determination (*R*²) and synergetic index of PhACs in US only, MXene only, and US/MXene process within 120 min at 293 ± 1 K and pH 7.

Processes	AMT		IBP	
	<i>k</i> ₁ (min ⁻¹)	<i>R</i> ²	<i>k</i> ₁ (min ⁻¹)	<i>R</i> ²
US only	0.0177	0.984	0.0138	0.998
MXene only	0.0007	0.418	0.00001	0.565
US/MXene	0.0267	0.986	0.0156	0.996
Synergetic index	1.451		1.130	

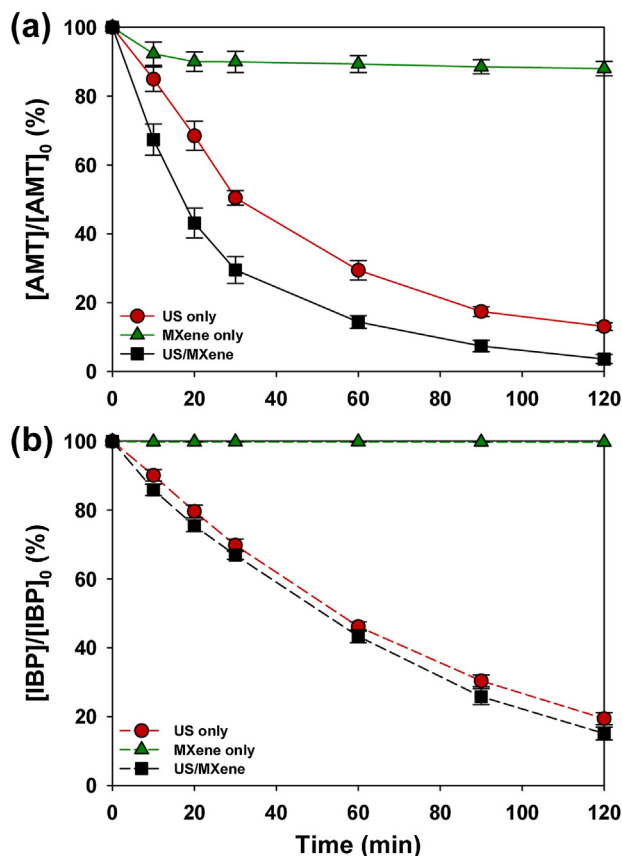


Fig. 3. Degradation performance during MXene only, US only, and US/MXene combined process for (a) AMT and (b) IBP (35 kHz, 50 W L⁻¹, pH 7, and 293 ± 1 K).

3.4. Mineralization of PhACs

TOC measurement was conducted to evaluate the degree of mineralization of the PhACs in a US only process and a US/MXene combined process. The result of TOC measurement is shown in Fig. S5, from which it can be seen that the result of mineralization of the US only process turned out to be low (6 % and 10 % for IBP and AMT, respectively). This result is not consistent with the degradation performances discussed above, which could be due to the by-product of the sonochemical oxidation of the PhACs. The difference between the removal rates of AMT and IBP could be attributed to their log K_{ow} , shown in Table S1. Since AMT is more hydrophobic than IBP, based on their log K_{ow} at pH 7, there might be a higher chance of AMT degradation in a gas-liquid interface than IBP (Naddeo et al., 2010, 2009). However, in the US/MXene combined process, the removal rates of IBP and AMT increased up to 15 % and 23 %, respectively, which are more than double the values in the US only process. This result could be attributed to the removal of the PhACs from the solution due to adsorption by MXene. Therefore, it can be concluded that the mineralization of the PhACs is not significant and MXene plays a vital role in the removal of the target compounds from solutions.

4. Conclusions

This study investigated the removal of two selected PhACs (AMT and IBP) by ultrasonication with MXene. It was observed that the degradation performances were affected by the quantity of H₂O₂ produced by ultrasonication under the experimental parameters of pH and temperature. The removal rates were higher at the conditions that caused more H₂O₂ production, and the importance of OH radicals was also confirmed

with experiments conducted in the presence of OH radical promoters and scavengers. Additionally, the effect of NOM and ionic strength was also evaluated, and confirmed to be relatively insignificant. For the effect of NOM in particular, the removal rates slightly increased by addition of more HA; this result can be attributed to less recombination of OH radicals, but more research is needed to confirm this effect. To confirm the synergetic effect of using MXene during US, the synergetic indices were calculated, and the result showed that using MXene with US could yield better removal rates for both PhACs than using MXene and US separately. This could be due to enhanced adsorption performance of MXene during sonication, which leads to a smaller hydrodynamic diameter and lower zeta potential. Lastly, mineralization of the PhACs in a US only and US/MXene process was evaluated, and the result demonstrated that the mineralization of AMT was more favored than that of IBP due to their different hydrophobicity, and the US/MXene process achieved better removal rates than the US only process due to the adsorption capacity of MXene. Since the MXene, used in this study, is consisted of transition metals and carbon, there might be a possibility of leaching of the metals or soluble exfoliated nanosheets. The potential leaching has not been confirmed and it is necessary to be investigated as future research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.hazl.2021.100028>.

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