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Enhanced sonocatalytic degradation of carbamazepine and salicylic acid using a metal-organic framework

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ABSTRACT

A metal-organic framework (MOF) was used as a sonocatalyst for ultrasonic (US) processes, to improve the degradation of two selected pharmaceutical active compounds (PhACs); carbamazepine (CBM) and salicylic acid (SA). The intrinsic characteristics of the MOF were characterized using a porosimeter (N_2-BET) and scanning electron microscope (SEM). Various experiments were carried out under conditions with different US frequencies (28 and 1000 kHz), US power densities (45–180 W L^{-1}), pH conditions (3.5, 7, and 10.5), and temperatures (293, 303, and 313 K) to investigate the degradation rates of the selected PhACs. Improved removal rates of PhACs were demonstrated within 60 min at 28 kHz (46% for SA; 47% for CBM) and 1000 kHz (60% for SA; 99% for CBM) with an MOF concentration of 45 mg L^{-1} in the US/MOF system, in comparison to 28 kHz (20% for SA; 25% for CBM) and 1000 kHz (37% for SA; 97% for CBM) under the 'US only' process. The removal of CBM was greater than that of SA under all experimental conditions due to the intrinsic properties of the PhACs. The degradation rates of PhACs are related to the quantity of H_2O_2; degradation is thus mostly affected by $OH^{\cdot}$ oxidation, which is generated by the dissociation of water molecules. The advantages of the 'US/MOF system' are as follows: (i) dispersion of MOF by US can improve sites and reactivity with respect to adsorption between the adsorbate (PhACs) and the adsorbent (MOF), and (ii) dispersed MOF acted as additional nuclei for water molecule pyrolysis, leading to the production of more $OH^{\cdot}$. Therefore, based on the synergy indices, which were calculated using the removal rate constants [k_1 ($\min^{-1}$)] of the pseudo-first order kinetic model, the 'US/MOF system' can potentially be used to treat organic pollutants (*e.g.,* PhACs).

1. Introduction

Pharmaceutical active compounds (PhACs), including carbamazepine (CBM) and salicylic acid (SA), are considered to cause severe environmental problems in aqueous systems. Hence, various studies have been carried out on how to manage water pollutants, including pharmaceutical compounds [1,2]. The increase in concentrations of these PhACs in water systems such as rivers, groundwater, and lakes is due to improper disposal of expired or unused drugs, medications, and veterinary medicines [3]. In particular, both CBM and SA (which are the PhACs investigated in this study) have been widely used to control seizures/for psychotherapeutic applications [4], and to treat skin disorders (*e.g.,* scalp, seborrheic disorders, dandruff, calluses, and acne) [5], respectively. Accordingly, these PhACs are commonly detected in water bodies in the United States [6]; for example, CBM and SA have been detected at concentrations of up to 610 ng L^{-1} and 1225 ng L^{-1} in ground water [5,6], respectively, and 318 ng L^{-1} SA has been detected in river water [5]. However, conventional water treatment methods, such as coagulation/sedimentation [7], and membrane processes (*e.g.,* ultrafiltration [8] or forward osmosis [9,10]), are not efficient at removing PhACs [3]. Moreover, the addition of common disinfectants, such as chlorine or ozone, leads to by-products or the transformation of PhACs during the reaction [11,12].

Ultrasonic (US) treatment is one of the most promising advanced oxidation process technologies, which can be used to oxidize complex organic pollutants, including PhACs [11]. The main principle of US is

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based on the three steps of acoustic cavitation: (i) formation, (ii) growth, and (iii) collapse of aqueous cavitation bubbles. High temperatures (*i.e.,* 5000 K) and pressures (*i.e.,* 1000 atm) are reached inside cavitation bubbles for a short period during US processes [13], resulting in the dissociation of water molecules to $H^\cdot$ and $OH^\cdot$. Furthermore, the dissolved O_2 molecules in the aqueous phase can react with $H^\cdot$ and $OH^\cdot$, leading to the formation of $HO_2^\cdot$. H_2O_2 molecules can also be formed by the recombination of two OH· molecules during US [14]. Reactions during US treatment occur in three different reaction zones: (i) the bulk liquid phase, (ii) the gas–liquid transition region, and (iii), the gaseous cavitation bubble region. In other words, there are three regions with different temperatures (approximately (i) 300, (ii) 2000, and (iii) 5000 K, respectively) and concentrations of reactive free radicals, such as $H^\cdot$, $OH^\cdot$, and $HO_2^\cdot$ [15]. Hydrophobic/volatile and hydrophilic/nonvolatile organic pollutants are generally degraded by direct pyrolysis within the gaseous region, and the $OH^\cdot$ reaction within the gas–liquid transition region or bulk liquid phase, respectively [15]. Therefore, the effects of treatment by US processes can be affected by the physico-chemical properties of pollutants such as the values of pK_a, S_H based on Henry's law, and the octanol-water partition coefficient (K_{OW}) [1]. US has been widely researched for water treatment due to its ease of use and environmentally friendly characteristics [16]; however, a major drawback to US is its high energy consumption compared to other mechanisms (*e.g.,* adsorption) [16]. To overcome this drawback of US technology, various sonocatalysts have been researched to improve US cavitation for wastewater treatment, including PhACs removal [1,3,11,14–17].

Various homogeneous or heterogeneous sonocatalysts can be used to enhance the formation of $OH^\cdot$ due to the pyrolysis of water molecules during US processes, because solid sonocatalysts can act as additional nuclei, accelerating the rate of cavitation bubble production and thus improving the degradation rate [18]. Zhao et al. [19] used granular activated carbon (GAC) as a sonocatalyst for US, and improved the degradation rate of perfluorochemicals due to the increased number of $OH^\cdot$ molecules generated by the increased number of cavitation bubbles, as well as physical adsorption onto the surfaces of GAC particles. Similarly, carbon nanotubes have also been used as sonocatalysts due to their unique properties, such as optical activity, electrical conductivity, and mechanical strength [1]. As another example, biochar was applied to a US/adsorbent system due to the strong sorption affinity between biochar and organic compounds [14]. Furthermore, single-metal-based or multiple-metals-doped TiO_2 has been added to sonocatalysts for wastewater treatment, including treatment of organic pollutants, due to its high oxidation capacity, chemical inertness, chemical stability, and nontoxicity [16]. Metal-organic frameworks (MOFs) are a new family of porous and crystalline materials made of coordinated metal ions/clusters and organic linkers [20]. These MOFs have recently attracted attention as possible adsorbents due to their high porosity, flexible structures, intrinsic or modifiable functionality, and excellent performance for adsorption-related applications [20,21]. However, to the best our knowledge, MOFs, which have recently become prominent adsorbents, have not been investigated previously as sonocatalysts for US/adsorbent systems for degrading CBM and SA.

The main purposes of this study are: (i) to evaluate the removal rate of CBM and SA under different US conditions (*i.e.,* frequency and power density) and solution conditions (*i.e.,* pH, temperature, and existence of $OH^\cdot$ promoters (H_2O_2) or scavengers [*t*-BuOH)], (ii) to study the effects of MOF on the sonodegradation of CBM and SA in detail, and (iii) to assess the feasibility of MOF in US/adsorbent (MOF) systems based on evaluation of the synergy index. This work was carried out under different US frequencies, US powers, temperatures, pH conditions, and with added H_2O_2 and *t*-BuOH in synthetic wastewater. Furthermore, we carried out kinetic experiments by measuring the $OH^\cdot$ levels and concentrations of the target PhACs (with or without MOF) to explain the degradation mechanisms of CBM and SA, resulting from both (i) increased $OH^\cdot$ due to the addition of MOF as a sonocatalyst and (ii) the dispersion effects of MOF as an adsorbent.

2. Materials and methods

2.1. Chemicals

High-purity CBM ($C_{15}H_{12}N_2O$, > 99%), SA ($C_7H_6O_3$, > 99%), *t*-BuOH ($C_4H_{10}O$, > 99%), H_2O_2 (30% w/v), NaOH (> 98%), HCl (> 99%), and Basolite A100 [$Al(OH)(C_8H_4O_4)$] MOFs were purchased from Sigma-Aldrich (St. Louis, MO, USA). The intrinsic characteristics of the selected PhACs are summarized in Table S1 [22]. The $OH^\cdot$ promoter and scavenger effects were evaluated using H_2O_2 and *t*-BuOH, respectively. HCl and NaOH were used to adjust the initial pH of the model wastewater, including PhACs. KI (> 99%), potassium hydrogen phthalate ($C_8H_5KO_4$, > 99%), and ammonium molybdate tetrahydrate ($H_{24}Mo_7N_6O_{24}{\cdot}4H_2O$ > 99%) were also obtained from Sigma–Aldrich to measure H_2O_2 production. Ultrapure deionized (DI) water was used in all experiments, and all chemicals were used without further purification.

2.2. Apparatus and experimental conditions

All US experiments were carried out in double-jacketed stainless-steel reservoirs [15 cm (W) × 10 cm (D) × 20 cm (H)] connected to a frequency generator and a recirculating chiller to maintain the desired temperature (Fisher Scientific Inc., Pittsburgh, PA, USA) [1]. The initial concentrations of the selected PhACs were adjusted to 20 μM, diluted from each stock solution. The experiments were carried out under different US frequencies (28 and 1000 kHz) and US powers (45, 90, 135, and 180 $W\,L^{-1}$), solution temperatures (293, 303, and 313 K), and solution pH conditions (3.5, 7, and 10.5), and with H_2O_2 as an $OH^\cdot$ promoter (1, 5, and 25 mM) and the $OH^\cdot$ scavenger *t*-BuOH (1, 5, and 25 mM), in model wastewater containing PhACs. The optimal dose of MOF was evaluated based on H_2O_2 production for three different quantities (5, 15, and 45 mg L^{-1}). The adsorption of PhACs by MOF was carried out before and after US so that we could evaluate the synergy index of the US/adsorbent system. We collected samples from all experiments at intervals of 10 min (until 60 min had passed) to elucidate the sonodegradation mechanism, which we evaluated based on the pseudo-first order k_1 (min^{-1}) degradation rate constants. The periodically collected samples were filtered with 0.22 μm glass filters for additional analysis.

2.3. Analysis of target compounds and H_2O_2 concentration

Measurements of the CBM and SA concentrations before and after US treatment were conducted by high-performance liquid chromatography (HPLC; 1200 series; Agilent Technologies, Santa Clara, CA, USA), as described in previous studies [3,17]. The mobile phase was a 50%:50% mixture of DI water:acetonitrile for both CBM and SA, and separation was carried out using a LiChrosorb RP-18 analytical column with a 100-μL sample loop at a flow rate of 1.2 $mL\,min^{-1}$. The detection wavelength was 210 nm for both PhACs. The H_2O_2 concentration, which is indicative of the $OH^\cdot$ content, was measured using the KI dosimetry method with an ultraviolet–visible (UV–vis) spectrophotometer (Agilent Technologies) at 350 nm [23].

2.4. Characterization of MOF

The morphologies and elemental mappings of the MOF were measured using a scanning electron microscope (SEM; SU8220; Hitachi, Tokyo, Japan) and an SEM equipped with energy dispersive spectroscopy (EDX), respectively. Measurements of the surface area and pore size distribution were carried out by assessing N_2 adsorption/desorption isotherms on a Quadrasorb SI-MP porosimeter (Quantachrome, Boynton Beach, FL, USA).

3. Results and discussion

3.1. Characterization of MOF and dose optimization

The microstructures and surface morphologies of the MOF were characterized using SEM-EDX analyses, and Fig. S1a shows SEM images of the MOF with elemental spectra. The measured structures of the MOF were uneven microspheres with rough surfaces and particle size of approximately 5 μm. In addition, elemental mapping of Al, C, and O elements for MOF was carried out, as shown in Fig. S1b. The N_2 adsorption – desorption isotherm for the surface area of the MOF calculated by the Brunauer-Emmett-Teller (BET) equation was 630 $m^2\,g^{-1}$, which is similar to previously reported values [approximately 500 $m^2\,g^{-1}$ of MIL-53 (Al) [24]] and larger than that of commercial γ-Al_2O_3 (195 $m^2\,g^{-1}$) or the mesoporous structure of P-Al_2O_3 (249 $m^2\,g^{-1}$) [25] [Fig. S1c]. The pore size distribution curve of MOF is shown in Fig. S1d, and was centered at 152 Å. Therefore, MOF can be used as efficient adsorbents due to their unique properties, including their high specific surface area [25].

We evaluated the effects of the MOF on the US system with respect to $OH^{\cdot}$ production, because the removal of PhACs by US treatment depends on free $OH^{\cdot}$ production. The H_2O_2 concentration is indicative of $OH^{\cdot}$ production. Hence, we determined the optimum dose of MOF (0, 5, 15, and 45 mg L^{-1}) by measuring the quantities of H_2O_2 produced under the US process [23]. The H_2O_2 production increased continuously as the MOF dose was increased from 0 to 45 mg L^{-1}, as shown in Fig. 1, following the order of $0 < 5 < 15 < 45$ mg L^{-1} under the two frequencies tested (28 and 1000 kHz). The increase in $OH^{\cdot}$ production can be explained in two main ways. First, the formation of cavitation bubbles may have increased due to the existence of rough solid surfaces during US irradiation, leading to an increase in $OH^{\cdot}$ production due to the dissociation of water molecules [17]. Second, the dispersed MOF particles may act as additional nuclei for water molecule pyrolysis during sonication, thus increasing the $OH^{\cdot}$ production as the MOF dose was increased [1]. Therefore, the optimum dose of MOF (45 mg L^{-1}) was selected so that we could further investigate its effect on CBM and SA degradation under various US conditions (*i.e.,* frequency and power) and solution conditions (*i.e.,* pH, temperature, and existence of $OH^{\cdot}$ promoters (H_2O_2) or scavengers [*t*-BuOH]).

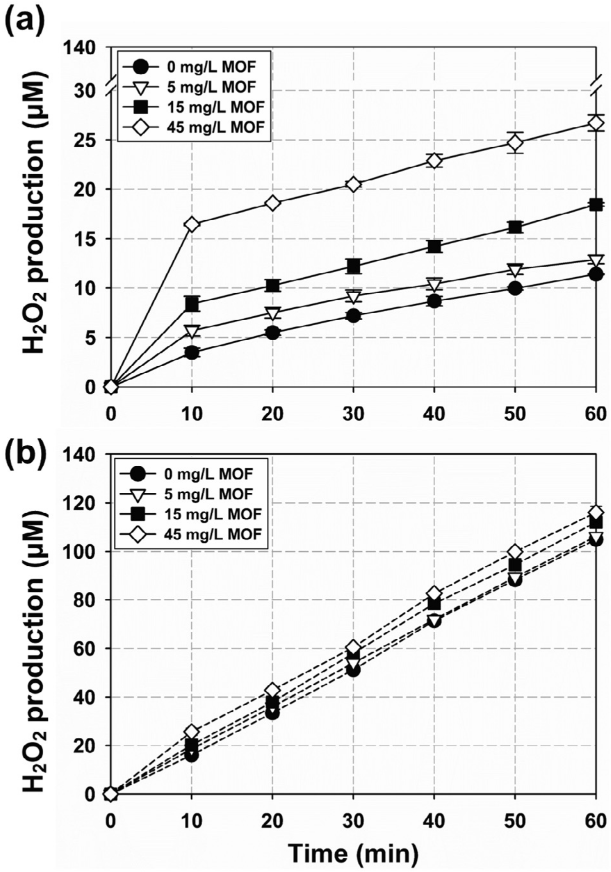

Fig. 1. H_2O_2 production under (a) 28 kHz and (b) 1000 kHz US conditions with increasing contact time in the presence of MOF of 0, 5, 15, and 45 mg L^{-1} at 293 ± 1 K, pH 7, and 180 W L^{-1} ± 3.

3.2. Effect of the US conditions on sonocatalytic degradation of CBM and SA

3.2.1. Frequency of US

The US frequency is known to be an important factor affecting the removal of PhACs [14,23], because US waves are transferred into water molecules to form acoustic cavitation bubbles under high pressures and temperatures, resulting in the production of free $OH^{\cdot}$ [26]. In other words, the major parameters, such as the time taken for the bubble to collapse, quantity of cavitation bubbles, and bubble size, vary with the US frequency [15]. This affects the formation of free $OH^{\cdot}$ molecules due to water molecule dissociation. The removal of CBM and SA was much higher in the high frequency case (1000 kHz) than in the low frequency case (28 kHz), as shown in Fig. 2a and b. There are two adverse effects of using low frequencies (*i.e.,* 28 kHz in this study) rather than high frequencies (*i.e.,* 1000 kHz in this study). First, the relative quantities of cavitation bubbles are lower at low frequencies (28 kHz) and comparatively larger bubbles are formed, so they take longer to collapse [27]. On the other hand, $OH^{\cdot}$ production at high US frequencies results in larger quantities of relatively small cavitation bubbles, so they take less time to collapse [3]. Moreover, at high US frequencies, the produced $OH^{\cdot}$ tended to approach the bulk liquid phase rather than two $OH^{\cdot}$ molecules recombining to produce H_2O_2 [17]. This phenomenon promotes more reactions between target PhACs (*i.e.,* CBM and SA) and free $OH^{\cdot}$, which clearly explains the higher rates of PhACs removal in the higher frequency case (1000 kHz). Fig. 2c shows the quantities of $OH^{\cdot}$ produced at low and high frequencies (28 and 1000 kHz, respectively). These results are in good agreement with those of previous studies, in which higher frequencies were more effective than lower frequencies for PhACs removal [1,3,14,16,17,23].

SA exhibited lower removal ratios than CBM under exactly the same experimental conditions due to its intrinsic properties. The log D_{OW} value, which is the log of the octanol and water distribution coefficient, indicates the change in hydrophobicity with the solution pH (Table S1) [28]. As shown in Table S1, the higher log D_{OW} (2.77) value of CBM indicates that it is more hydrophobic than SA [log D_{OW} = from 1.19 (pH 3) to −1.55 (pH 10.5)]. In other words, higher removal of CBM was attributed to the fact that higher hydrophobic organic compounds are likely to be concentrated at the gas–liquid interface [29]. Thus, the CBM may be more degraded by direct pyrolysis inside the gas bubbles or at the gas–liquid interface. However, reactions of more hydrophilic SA may occur at the gas–liquid interface or in the bulk liquid region, where there are relatively low quantities of free $OH^{\cdot}$ molecules [26]. Therefore, CBM tended to react with more $OH^{\cdot}$ radicals than SA in the US system, resulting in more degradation of CBM than SA, as well as less recombination of 2 $OH^{\cdot}$ to form H_2O_2 [29]. These results are consistent with those of previous studies on different contaminants, such as naproxen and acetaminophen [1], sulfamethoxazole (SMX) and ibuprofen (IBP) [23], azo dyes [30], and 4-chlorophenol removal [31].

3.2.2. Power density of US

The power density of the US system is an important variable, because most of the power is converted into heat, resulting in the production of $OH^{\cdot}$ and $H^{\cdot}$ radicals due to the dissociation of water molecules [23]. The US degradation of PhACs observed in this study occurred under four different power densities (45, 90, 135, and 180 W

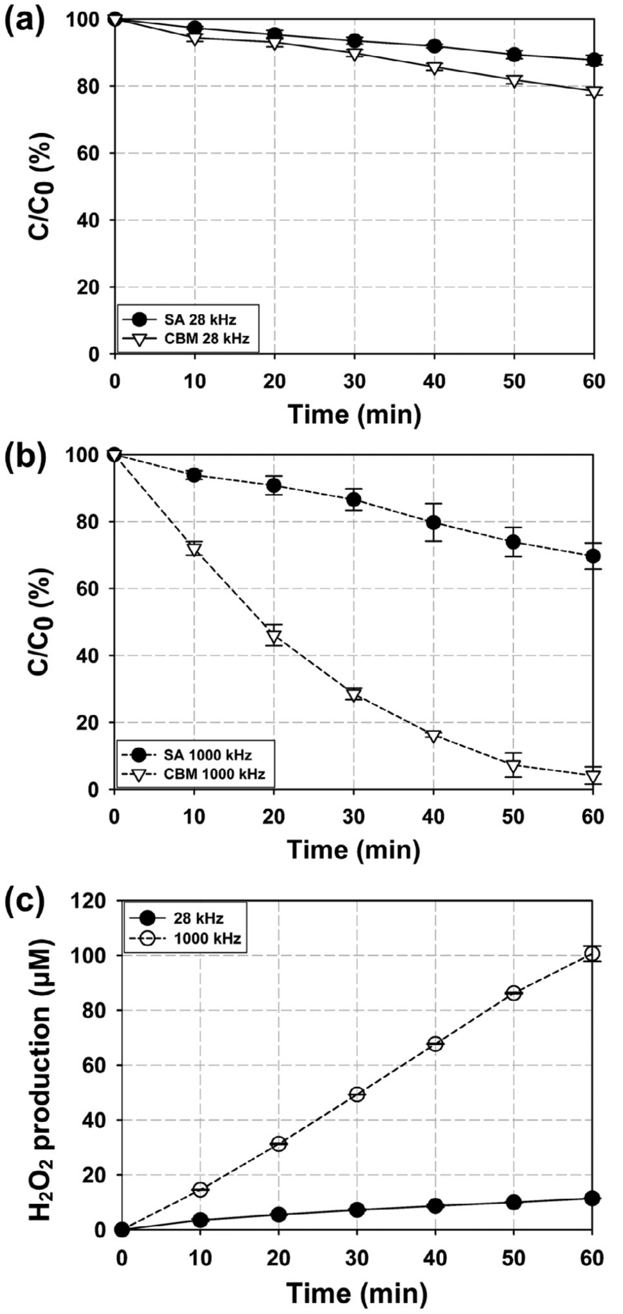

Fig. 2. Effect of frequency at (a) 28 kHz and (b) 1000 kHz on CBM and SA degradation, and (c) H_2O_2 production (293 ± 1 K, pH 7, and 180 W L^{-1} ± 3).

L^{-1}) at 293 K, with lower (28 kHz) and higher (1000 kHz) US frequencies. Figs. S2a/b and S3a/b shows that the degradation of the selected PhACs increased proportionally with the US power density. This can be explained in the following way: (i) an increase in the quantity of cavitation bubbles due to the $OH^{\cdot}$ generated by the dissociation of water molecules in the US system, and (ii) an increase in the collapse time, pressure, and temperature, due to the increase in acoustic energy [26,32]. In other words, the H_2O_2 concentration increased linearly as the power increased from 45 to 180 W L^{-1} in both frequency cases, thus increasing PhACs degradation, as shown in Figs. S2 and S3. Therefore, we can conclude that the degradation of selected PhACs by US observed in this study is preceded by $OH^{\cdot}$ oxidation, which is due to the dissociation of water molecules. These results are consistent with those of previous research that show that degradation rates are directly proportional to US power density (*e.g.,* paracetamol, levodopa [33], amoxicillin [34], and diclofenac [32]).

3.3. Effect of water chemistry on sonocatalytic degradation of CBM and SA

3.3.1. Solution pH

The effect of the pH was investigated with pH values of 3.5, 7, and 10.5, considering the pK_a values of CBM and SA. The degradation rates of the PhACs were strongly dependent on the pH, as shown in Figs. 3 and 4. First, the removal rates of PhACs under acidic conditions (pH 3.5) were higher than under alkali (pH 10.5) and neutral (pH 7) conditions, as shown in the plots for CBM and SA 'with US only' and 'with US/MOF' in Figs. 3 and 4. This phenomenon can be explained by the fact that fast degradation rates occur under acidic conditions (pH 3.5) due to the higher oxidation potential of reactive oxidant species ($OH^{\cdot}$), thus resulting in higher removal rates of both PhACs at (i) pH 3.5 rather than (ii) pH 7 and (iii) 10.5 [28]. In other words, $OH^{\cdot}$ reacted with PhACs more readily, rather than recombining to produce H_2O_2, under acidic conditions (pH 3.5) [14]. Second, the degradation of SA depended on the pH much more than that of CBM, as shown again Figs. 3 and 4. This is due to their pK_a values (indicating acid or basic properties), of 15.96 for CBM and 2.79 (pK_{a1})/13.23 (pK_{a2}) for SA (Table S1). Namely, anionic CBM and SA are the predominant species at pH > pK_a, so they have more hydrophilic characteristics than their molecular states (at pH < pK_a), as shown by Eqs. (1) and (2).

$$C_{15}H_{12}N_2\mathrm{O}(\mathrm{CBM}) < pk_a(=15.96) < C_{15}H_{11}N_2O^- + \mathrm{H}^+ \tag{1}$$

$$C_7H_6O_3(\mathrm{SA}) < pk_{a1}(=2.79) < C_7H_5\mathrm{O}_3^- + \mathrm{H}^+ < pk_{a2}(=13.23) < C_7H_4\mathrm{O}_3^{2-} + \mathrm{H}^+ \tag{2}$$

Third, the degradation of SA depended on the pH more than that of CBM in the case 'with MOF only,' as shown in Figs. 3 and 4. This is because the pH_{pzc} value of MOF (A100) is known to be pH 9.1 [35], so there is electrostatic attraction or repulsion between SA and MOF when the pH is less or more than pH 9.1, respectively. However, CBM only exists in molecular states for pH values from 3.5 to 10.5, which is the pH range used in this study. Thus, there were no opportunities for electrical interactions with the MOF. Furthermore, the adsorption results were attributed to both hydrophobic interactions and $\pi-\pi$ interactions, and this is the reason for the adsorption of CBM by the MOF, regardless of electrical attraction [17].

Non-volatile organic compounds are commonly degraded outside cavitation bubbles. However, volatile molecules are degraded by thermal reactions inside the cavitation bubbles [26]. In this case, CBM and SA are both non-volatile organic compounds due to their low values for Henry's constant (K_H; 1.1×10^{-10} and 1.4×10^{-8} atm m^3 mol^{-1}, respectively), as shown in Table S1. Hence, it is difficult to degrade these PhACs inside the cavities [1]. Thus, PhAC degradation is induced by reactions with $OH^{\cdot}$ outside the cavitation bubble. In the case of pH > pK_a, anionic PhACs mainly react with the bulk liquid (which has a lower concentration of $OH^{\cdot}$ molecules) due to their hydrophilic characteristics [34]. This leads to increased degradation of SA under acidic conditions (pH 3.5). SA organic compounds have highly variable log D_{OW} values [1.19 (pH 3.5) to −1.55 (pH 10.5)] compared to CBM (2.77); therefore, the degradation of SA was more dependent on the pH of the solution.

3.3.2. Solution temperature

Fig. 5 shows the degradation rates (k_1) of CBM and SA under temperatures ranging from 293 to 313 K during the US processes. The removal rates of both PhACs (CBM and SA) were higher when they were treated at higher frequencies. Moreover, much more CBM degraded than SA during US reactions, regardless of the temperature, as already discussed in Section 3.2.1. The degradation rates of both PhACs varied with the temperature (293, 303, and 313 K). As shown in Fig. 5, the degradation rates of both PhACs tended to increase as the temperature increased from 293 to 313 K when they were treated at 1000 kHz.

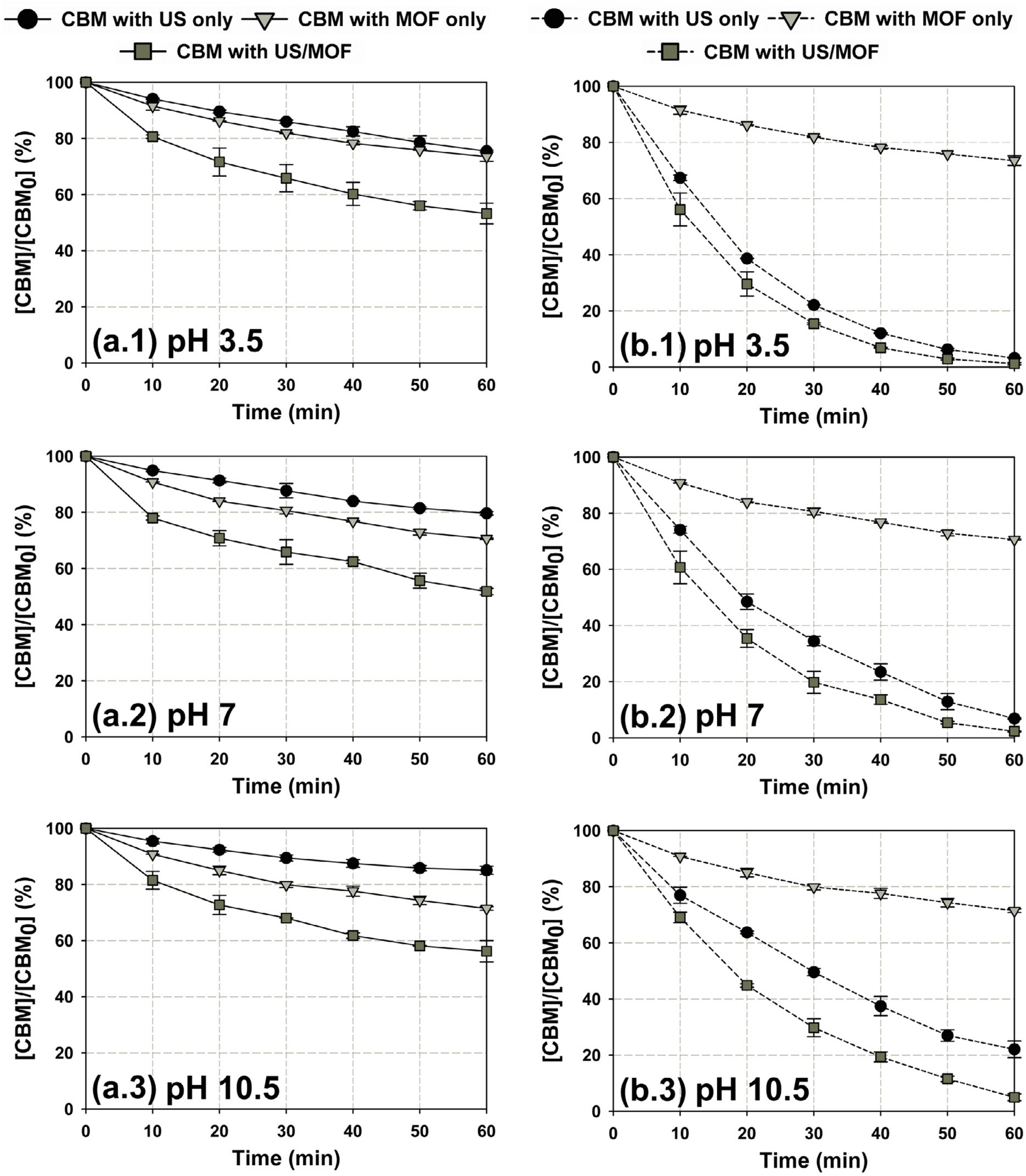

Fig. 3. Effect of pH on the degradation of CBM at (a) 28 and (b) 1000 kHz in the presence or absence of MOF at 293 ± 1 K.

However, in the case of 28 kHz, the degradation rate decreased with increasing temperature, then increased slightly at 313 K. Thus, the optimal temperature for degrading CBM and SA was identified as 293 K at 28 kHz and 313 K at 1000 kHz, respectively. These results can be explained by the following.

The effect of temperature on US reactions is quite complex, because the cavitation phenomenon produces highly reactive OH˙ at high pressures and temperatures [1]. Three different temperature effects have been reported during US. First, the increase in the solution temperature has a negative effect on the cavitation energy, which causes the collapse pressure to decrease [31]. Second, an increase in the solution temperature has a positive effect, accelerating the number of cavitation bubbles due to the decreased threshold limit of cavitation [31]. Furthermore, organic compounds move towards the gas–liquid interface, where both the OH˙ concentration and temperature are higher, thus increasing the PhAC degradation rate [32]. Finally, the optimal temperature for US can be determined by considering both the characteristics of organic pollutants and the kinetics between OH˙ and each organic pollutant [36]. Vichare et al. [37] reported that vapor cavities have lower energies than gaseous cavities when they collapse during US. Therefore, the results of this study can be explained by the fact that, when the temperature increases beyond the optimal point, the vapor pressure increases, thus decreasing the collapse pressure and reducing the net energy between the OH˙ and PhACs in the US system [28]. Furthermore, H_2O_2 production (as shown in Fig. 5c), which offers an indirect method for measuring OH˙ concentrations, strongly influences the degradation efficiency of PhACs at both lower (28 kHz) and higher frequencies (1000 kHz) under different temperature conditions.

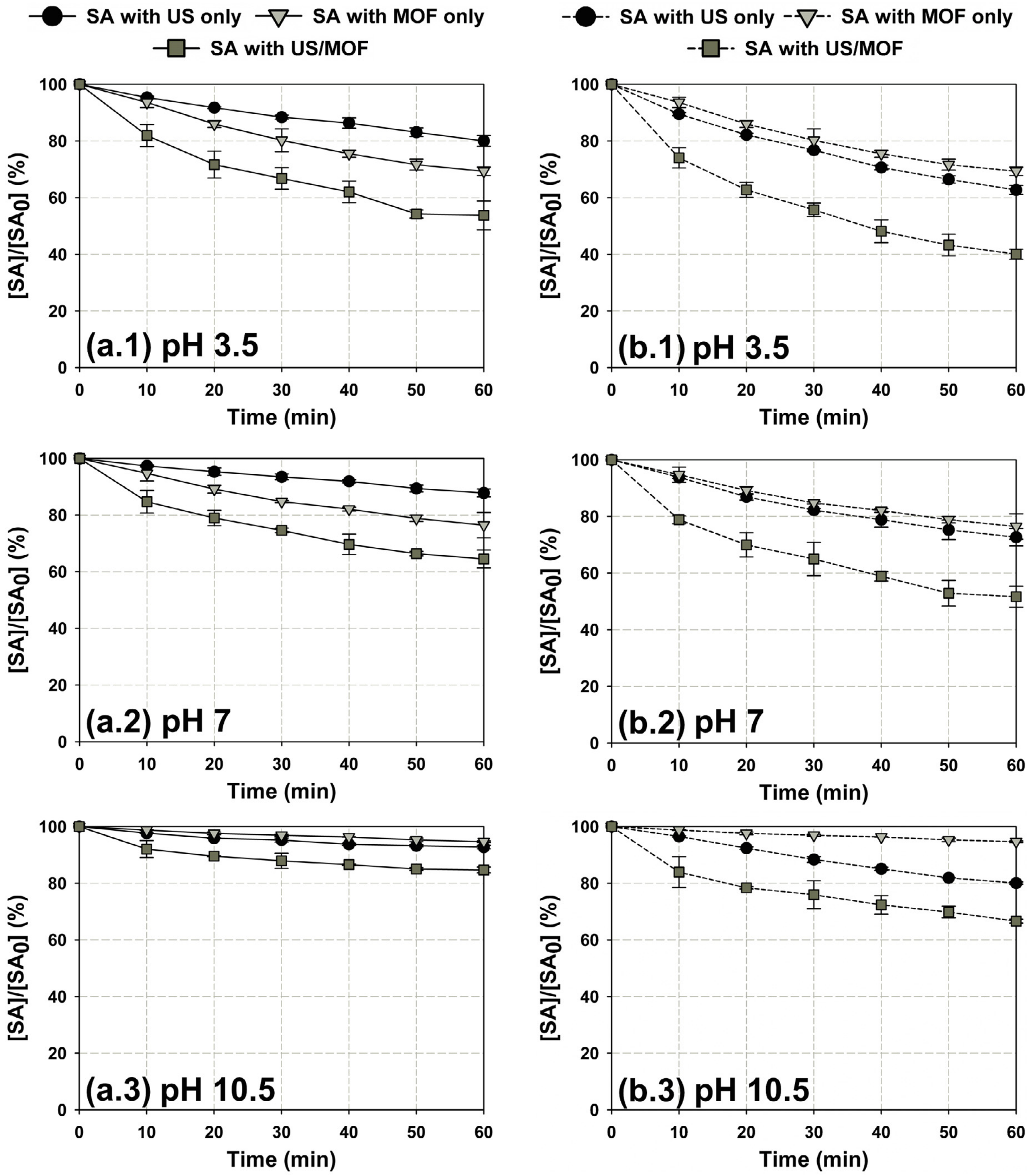

Fig. 4. Effect of pH on the degradation of SA at (a) 28 and (b) 1000 kHz in the presence or absence of MOF at 293 ± 1 K.

Therefore, in this study, the degradation rate of PhACs was mainly determined by the OH˙ concentration.

3.3.3. Existence of OH˙ promoter (H_2O_2) and scavenger (t-BuOH) in the solution

To investigate the effects of OH˙ promoters (H_2O_2) on the degradation rate, CBM and SA were treated using different H_2O_2 concentrations, ranging from 0 to 25 mM, as described in Fig. S4. The removal rates of both PhACs increased with increasing H_2O_2 concentrations up to 5 mM, then decreased as the concentration increased further, to 25 mM. This means that 5 mM of H_2O_2 is the optimal concentration, judging by the PhACs removal performance. H_2O_2 is found in bulk solution rather than cavitation bubbles due to its lower volatility (7.04×10^{-9} atm m^3 mol^{-1}) and high water solubility (1×10^6 mg L^{-1}) [14]. The lower removal rate at 25 mM H_2O_2 can be explained by OH˙ scavenging effects, as shown in Eqs. (3) and (4).

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \quad (3)$$

$$HO_2\cdot + OH\cdot \rightarrow O_2 + H_2O \quad (4)$$

In other words, the OH˙ scavenging effect was increased, rather than the quantity of H_2O_2 itself [Eq. (3)] as HO_2˙ [Eq. (4)], because HO_2˙ has a lower oxidation potential than OH˙ [26], thus decreasing the degradation rates of both PhACs. The effect of H_2O_2 on the degradation of target compounds in US systems has also been reported previously (*e.g.,* Adewuyi [38] and Im et al. [14]), and the results of this study were in good agreement with those of the previous studies.

OH˙ is the main compound that degrades the selected PhACs under the conditions described previously, including the various US

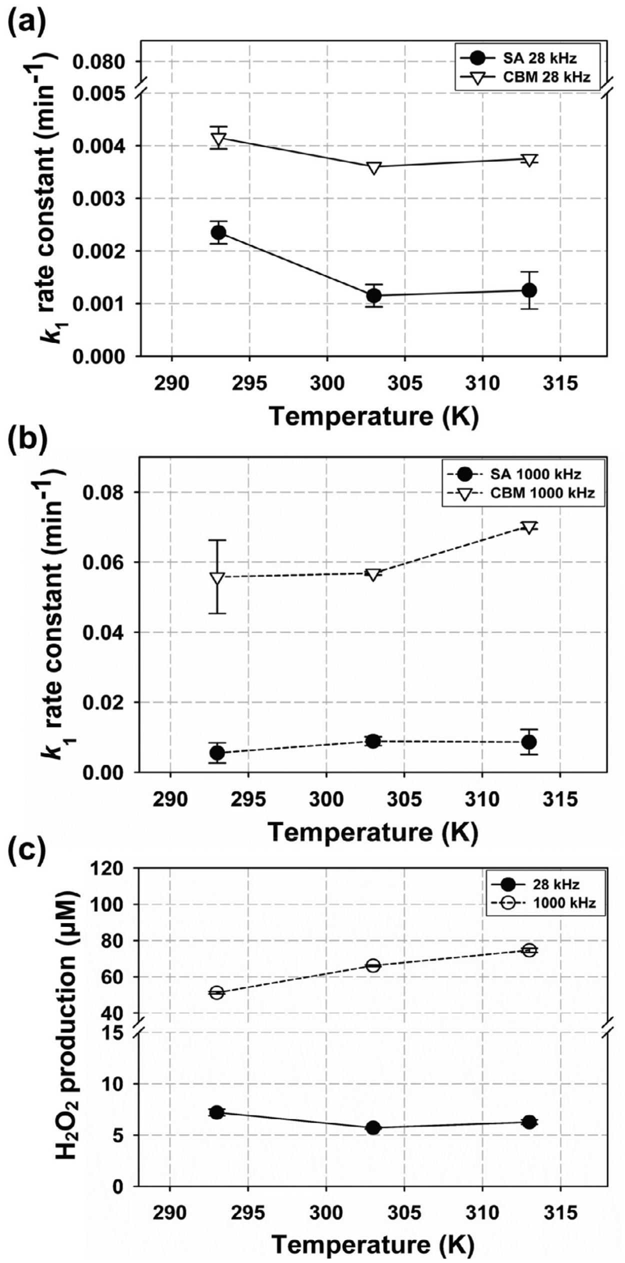

Fig. 5. Degradation rates of CBM and SA at (a) 28 and (b) 1000 kHz increasing with solution temperature at pH 7 and (c) H_2O_2 production at 30 min.

frequencies and power densities tested, and the solution conditions (*i.e.,* pH, and temperature), in Sections 3.2–3.3. The degradation of PhACs with *t*-BuOH, which is a widely known OH˙ scavenger [39], was carried out to demonstrate that the degradation mechanism of PhACs observed in this study depends on the OH˙ concentration. The degradation rates of the PhACs in the presence of OH˙ scavengers (*t*-BuOH) clearly decreased, as shown in Fig. S5. The figure shows that the presence of OH˙ scavengers (*t*-BuOH) decreases the degradation rates at both frequencies tested, regardless of the target compounds. These results provide additional evidence that the degradation of CBM and SA is mainly caused by OH˙ radicals, similar to previous studies [14,23].

3.4. Estimation of the synergetic index of MOF as a sonocatalyst

We summarized the PhAC degradation results, including the effects of the US frequency (28 and 1000 kHz), pH (3.5, 7, 10.5), and MOF as a sonocatalyst for US systems, by evaluating the synergism (Table 1). Table 1 shows the synergy indices for the removal of CBM and SA under different US and pH conditions in the presence and absence of MOF. The synergy indices of each process were evaluated based on the difference between the degradation rate constant of the combined effects (‘US/MOF’) and the sum of the individual effects (‘US only’ and ‘MOF only’) according to Eq. (5), which is reproduced from a previous study [40]:

$$\text{Synergy index} = \frac{k_1(US/MOF)}{k_1(US\ \ only) + k_1(MOF\ \ only)} \tag{5}$$

where (i) k_1 is the pseudo-first order degradation rate, (ii) ‘US only’ and ‘MOF only’ is the single effect without MOF and US, respectively, and (iii) ‘US/MOF’ is the US effect when MOF are used. In other words, a synergy index greater than 1 indicates that the combined system (*i.e.,* ‘US/MOF’) is better than the sum of the individual systems (*i.e.,* ‘US only’ and ‘MOF only’).

According to Table 1, the synergy indices ranged from and 1.031 to 1.671 for CBM and 1.020 to 3.667 for SA in the ‘US/MOF system’, representing a noteworthy synergistic effect. These results can be explained as follows: (i) The dispersion of MOF by US increased the reactivity and number of sites for adsorption between the adsorbent and adsorbate, and (ii) the particles dispersed by US acted as additional nuclei for the pyrolysis of water molecules, leading to the production of more OH˙. Fig. 6 shows a proposed schematic diagram of the PhACs degradation mechanisms when US with or without MOF processes are used. Thus, the ‘US/MOF system’ can be concluded to be more efficient than the sum of the ‘adsorption (MOF) system alone’ and ‘US processes system alone’ processes.

4. Conclusions

In this study, we systemically investigated the removal of selected PhACs (CBM and SA) in the presence and absence of MOF at different US frequencies, US powers, temperatures, and pH conditions, and according to the existence of H_2O_2 and *t*-BuOH in synthetic wastewater. We characterized the sonocatalytic effects of MOF by BET and SEM, which we used to evaluate their physical properties and surface morphologies, respectively. The degradation trends for CBM and SA followed a pseudo first-order kinetic reaction in all cases, and the optimal condition for degrading PhACs was observed at 1000 kHz with 45 mg L^{-1} MOF (‘US/MOF’) for 60 min of US. The degradation of both CBM and SA was improved by the inclusion of MOF. The enhanced results were achieved due to (i) an increase in the reactivity and number of sites for adsorption between the adsorbent (*i.e.,* MOF) and adsorbates (*i.e.,* CBM and SA) due to the dispersion of MOF by US, and (ii) the increase in quantity of OH˙ due to the particle dispersion induced by the US, which acted as additional nuclei for the pyrolysis of water molecules. Therefore, MOF are a promising sonocatalyst for use in US systems and can be applied to treat PhACs in aqueous solution.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2019.04.019.

Table 1
Evaluation of the constants for pseudo-first order (k_1) degrading rate, coefficient of determination (R^2), and value for synergistic index for 'US only', 'MOF only', and 'US/MOF' results within 10 or 60 min at 28/1000 kHz, 293 ± 1 K, pH 3.5/7/10.5, and 180 W L^{-1} ± 3.

Within 10 min	PhACs	CBM				SA			
	Frequency	28 kHz		1000 kHz		28 kHz		1000 kHz	
pH		k_1	R^2	k_1	R^2	k_1	R^2	k_1	R^2
pH 3.5	US only	0.006	–	0.040	–	0.005	–	0.011	–
	MOF only	0.009	–	0.009	–	0.007	–	0.007	–
	US/MOF	0.022	–	0.058	–	0.020	–	0.030	–
	Synergy index	**1.433**		**1.200**		**1.754**		**1.701**	
pH 7	US only	0.005	–	0.030	–	0.003	–	0.006	–
	MOF only	0.010	–	0.010	–	0.005	–	0.005	–
	US/MOF	0.025	–	0.050	–	0.017	–	0.024	–
	Synergy index	**1.671**		**1.264**		**2.062**		**2.017**	
pH 10.5	US only	0.005	–	0.026	–	0.002	–	0.004	–
	MOF only	0.010	–	0.010	–	0.001	–	0.001	–
	US/MOF	0.021	–	0.037	–	0.008	–	0.018	–
	Synergy index	**1.424**		**1.031**		**2.371**		**3.667**	
Within 60 min	**PhACs**	**CBM**				**SA**			
pH 3.5	US only	0.005	0.996	0.058	0.995	0.004	0.995	0.008	0.990
	MOF only	0.005	0.966	0.005	0.966	0.006	0.985	0.006	0.985
	US/MOF	0.010	0.948	0.074	0.993	0.010	0.952	0.015	0.958
	Synergy index	**1.042**		**1.173**		**1.020**		**1.043**	
pH 7	US only	0.004	0.989	0.044	0.983	0.002	0.997	0.005	0.984
	MOF only	0.006	0.970	0.006	0.970	0.005	0.986	0.005	0.986
	US/MOF	0.010	0.942	0.061	0.983	0.007	0.937	0.011	0.944
	Synergy index	**1.053**		**1.234**		**1.045**		**1.071**	
pH 10.5	US only	0.003	0.956	0.026	0.996	0.001	0.942	0.004	0.994
	MOF only	0.005	0.964	0.005	0.964	0.001	0.988	0.001	0.988
	US/MOF	0.009	0.938	0.048	0.980	0.003	0.846	0.006	0.898
	Synergy index	**1.136**		**1.552**		**1.190**		**1.229**	

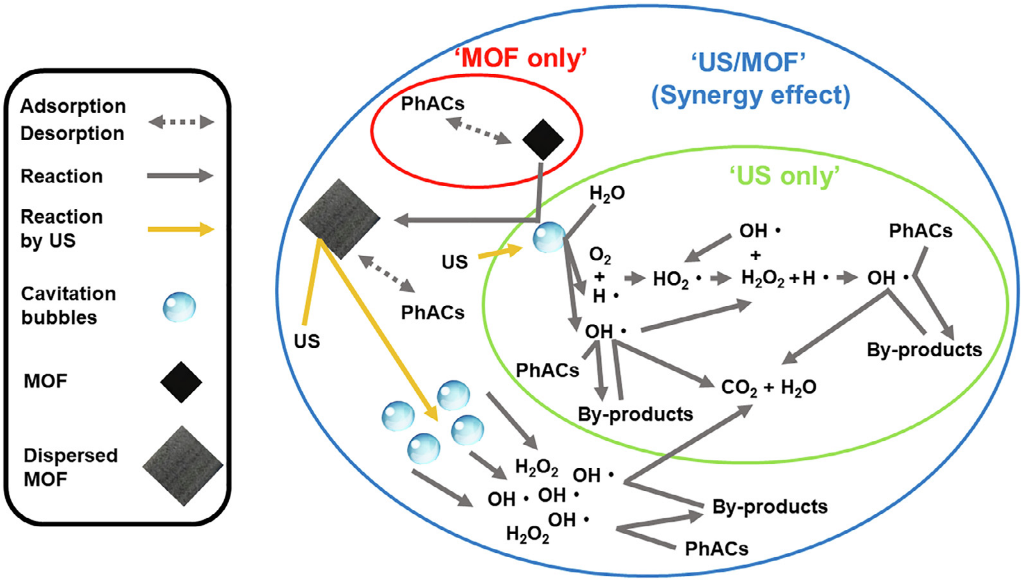

Fig. 6. Proposed schematic diagram related to degradation mechanisms of CBM and SA by US and US/MOF processes.

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