



Sonocatalytic degrading antibiotics over activated carbon in cow milk

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ARTICLE INFO

Keywords:

Sonocatalysis
Sonochemical process
Pharmaceutical pollutants
Sonocatalysts
Milk purification

ABSTRACT

Herein, an efficient, simple and economical approach to remove antibiotics (ABX), *i.e.* ceftiofur hydrochloride, sulfamonomethoxine sodium (SMM), marbofloxacin and oxytetracycline by sonication with activated carbon (AC) from cow milk has been successfully implemented. The pseudo-first-order kinetics constants for the sonolytic and sonocatalytic degrading SMM are 0.036 and 0.093 min⁻¹, respectively. The synergistic efficiency of removing ABX by using sonocatalysis reached 1.8–4.0. Hydrophobic ABX underwent faster degradation than hydrophilic ABX in sonocatalytic systems. Adding 0.5 mmol L⁻¹ H₂O₂, the optimal concentration, improved the sonocatalytic degradation rates of ABX by 9.1%–28.5%. Surface area and dose of AC play crucial roles in the sonocatalysis of ABX. By sonicating 50 mL of 5.52 μmol L⁻¹ ABX in milk at 500 kHz and 259 W with 20 mg AC for 20–60 min resulted in residual ABX concentrations ranging from 42.6 to 95.1 μg L⁻¹, which meet the relative maximum residue limits set by European Commission.

1. Introduction

Waste milk (or non-saleable milk) could be produced in dairy farms within the withholding period following the administration of cow mastitis and other bacterial infections (Gosselin, Bodmer, Schüpbach-Regula, Steiner, & Meylan, 2022; Prusa, 2020). Antibiotics (ABX) residues in milk can not only cause huge milk wastage, but also diminish the economic efficiency of dairy industries (*e.g.* cheese and fermented milk industries), as well as pose the risk of ABX-resistant genes spreading (Garzon et al., 2020; Gosselin, Bodmer, Schüpbach-Regula, Steiner, & Meylan, 2022; Liu et al., 2022). ABX residuals in milk have been determined at different levels, for instance, 150.4 μg L⁻¹ oxytetracycline (OTC) and 7,688.4 μg L⁻¹ neomycin have been found in raw milk samples in Turkey, and these concentrations are over the maximum residue limits (MRLs) of ABX in milk regulated by Turkish and European Community (Kaya & Filazi, 2010). Therefore, the purification of ABX-spiked waste milk via appropriate techniques is of great importance.

The removal of ABX in milk has also attracted a great deal of attention from researchers in recent decades, for example,

bioremediation (Kumar et al., 2019), adsorption (Ge et al., 2021), heat treatments (Garzon et al., 2020), electrochemical processes (Kitazono, Ihara, Toyoda, & Umetsu, 2017), ozonation (Liu et al., 2022), *etc.*, have been applied for ABX removal from milk. While bioremediation is environmentally friendly, it is also low-efficiency, offers incomplete mineralization of ABX, and ABX are usually recalcitrant and toxic to microorganisms (Ge et al., 2021; Liu, Wu, Cannizzo, Mantegna, & Cravotto, 2022). Adsorption is usually high efficiency, low cost and simple operation, but it only transfers ABX from the aquatic phase to the solid phase instead of the degradation and mineralization (Liu et al., 2022). Heat treatments and electrochemical processes are generally easy to operate, but require high costs and large energy consumption. Ozonolysis is limited by selective reactions between O₃ and ABX molecules, and hampered by its high equipment-maintenance costs, high energy requirements, high pH-dependence and increased ecotoxicity in effluents, *etc.* Moreover, although photocatalysis and its hybrid processes have been extensively used to degrade ABX in water, these processes are unsuitable for milk purification due to the extremely poor transmission of light in milk (Dong et al., 2020; Khataee et al., 2019).

Abbreviations: ABX, antibiotics; ACs, activated carbons; CEF, ceftiofur hydrochloride; CPAC, coconut powder activated carbon; DEs, degradation efficiencies; MAR, marbofloxacin; MRLs, maximum residue limits; OTC, oxytetracycline; PGAC, peat granular activated carbon; PPAC, peat powder activated carbon; SAs, surface areas; SE, synergistic effect; RR_{Cat}, reaction rate per unit catalyst weight; SMM, sulfamonomethoxine sodium; SPE, solid phase extraction; US, ultrasound; WPAC, wood powder activated carbon.

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<https://doi.org/10.1016/j.foodchem.2023.137168>

Received 5 April 2023; Received in revised form 27 July 2023; Accepted 13 August 2023

Available online 22 August 2023

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Unlike the as-mentioned approaches, the sonochemical degradation of ABX in milk has received little attention to date (Bui, Cozzolino, Zisu, & Chandrapala, 2020; Yuan et al., 2020). The propagation of ultrasound (US) could trigger acoustic cavitation, namely, the generation, growth and implosion of cavitation bubbles (Hassandoost et al., 2022; Liu, Wu, Abramova, & Cravotto, 2021). In sonochemical systems, the degradation of organics generally occurs in three reaction zones around cavitation bubbles, *i.e.* inside the cavity, at the gas–liquid interface as well as in the bulk liquid. During the implosion of cavities, reactive oxygen species such as hydroxyl radicals ($\bullet\text{OH}$), can be released by the pyrolysis of water H_2O or O_2 under the extremely high local temperature and pressure. The gas–liquid interface then contains maximum amounts of $\bullet\text{OH}$, thus sonochemical processes could be considered as one of the powerful advanced oxidation processes. Unfortunately, only a tiny percentage ($\sim 10\%$) of $\bullet\text{OH}$ is transferred into the bulk liquid in sonolytic and sonocatalytic systems (Liu, Wu, Abramova, & Cravotto, 2021).

Generally, sonication alone has low ABX-removal efficiency, thus, the enhanced sonocatalytic processes have been developed and used for ABX removal in water subsequently (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Subramani et al., 2019). In sonocatalytic systems, the physicochemical properties of catalysts are crucial and directly linked with the sonocatalytic activities. Currently, a variety of materials including carbon-rich materials, metal compounds and their composites, *etc.*, have been synthesized and used as sonocatalysts for removing ABX in water (Liu, Wu, Abramova, & Cravotto, 2021). Specifically, carbon-based sonocatalysts have been widely used for the removal of organics from water (Gholami, Khataee, Soltani, & Bhatnagar, 2019). For example, activated carbons (AC), which possess high surface areas (SAs) and abundant surface functional groups, can produce more $\bullet\text{OH}$ in sonocatalytic systems (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Liu, Wu, Ge, & Yang, 2019). On the one hand, the shapes and texture of ACs can affect sonocatalytic efficiency as they are closely associated with electron transfer, the generation of cavitation bubbles and $\bullet\text{OH}$ radicals, as well as the adsorption of substrates (Gholami, Khataee, Soltani, & Bhatnagar, 2019). On the other hand, US can not only improve the diffusion of substrates into AC pores, but also refresh or increase the SA of AC (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Liu, Wu, Abramova, & Cravotto, 2021). Furthermore, accelerated degradation of ABX has been reported with the addition of oxidants to sonochemical systems (Khataee et al., 2019; Liu et al., 2021). H_2O_2 is a strong oxidant with a high oxidative potential (1.78 V), which is lower than that of the $\bullet\text{OH}$ radical (2.80 V) and higher than those of hypochlorite (1.49 V), chlorine (1.36 V), and chlorine dioxide (1.27 V) (Hassan & El Nemr, 2017). It has been reported that H_2O_2 can be activated via sonication followed by the enhanced production of $\bullet\text{OH}$ radicals (Liu, Wu, Abramova, & Cravotto, 2021).

In one of our previous works, $6.62 \mu\text{mol L}^{-1}$ (2.0 mg L^{-1}) sulfamonomethoxine sodium (SMM) was sonicated in 100 mL of various milk at 500 kHz and 259 W for 130–150 min, where the residual SMM concentrations ($52.9\text{--}96.3 \mu\text{g L}^{-1}$) satisfy the relevant MRL ($100 \mu\text{g L}^{-1}$) (Liu, et al., 2023). Yuan *et al.* have investigated the removal of parathion methyl from bovine milk by using high-intensity US (25 kHz, $3.5\text{--}14.2 \text{ W cm}^{-2}$), noting that power intensity and the initial concentration of parathion methyl are crucial for sonolysis (Yuan et al., 2020). Scudino *et al.* reported high-intensity US treatment (475 W , $5\text{--}7 \text{ kJ mL}^{-1}$) in a thermal way ($85 \text{ }^\circ\text{C}$) led to 100% inactivation of microbial including total and thermos-tolerant coliforms (decreasing of $3.92 \text{ Log CFU mL}^{-1}$) in 25 mL milk (Scudino et al., 2020).

ABX, including amphenicols, penicillins, quinolones, tetracyclines, cephalosporins, macrolides and sulfonamides have frequently been detected in milk (Bitas & Samanidou, 2018). Ceftiofur hydrochloride (CEF, belongs to β -lactam family), SMM (belongs to sulfonamide family), marbofloxacin (MAR, belongs to fluoroquinolone family) and OTC (belongs to tetracycline family) are common ABX that have been used as veterinary for the treatment of cows mastitis, and their residues have been observed in milk (Liu et al., 2022; Subramani et al., 2019; Zhang

et al., 2020). Against the above background, this work aims to evaluate the reaction performances, optimize the sonocatalytic systems and clarify the sonocatalytic degradation mechanisms of CEF, SMM, MAR and OTC over ACs in milk. Four ACs, *i.e.*, coconut powder AC (CPAC), peat granular AC (PGAC), peat powder AC (PPAC) and wood powder AC (WPAC), have been used as sonocatalysts. The synergistic efficiency of sonication with catalysts, and the effects of catalysts nature, ABX properties, *etc.*, have been investigated with and without the addition of scavenger (*n*-butanol) and additive (H_2O_2). Moreover, the comparison of this study with previous methods for removing the model ABX in milk was also provided.

2. Materials and methods

2.1. Materials and chemicals

Pasteurized milk was obtained from the local milk suppliers in Turin (Italy) and kept at approx. $25 \text{ }^\circ\text{C}$. Milk composition was listed in the abovementioned work from our lab (Liu et al., 2023). One of our previous work has proven that the purchased milk were free of the model ABX (Liu et al., 2022). The physicochemical properties of PPAC, PGAC and WPAC were shown in our previous work (Ge et al., 2018; Ge, Wu, Manzoli, Wu, & Cravotto, 2020). CPAC, WPAC, PGAC and PPAC were cleaned in advance to remove the impurities inside. 15–20 g AC was packed into a barrel of a glass syringe, and glass wool was fitted above and below the AC layer to prevent the AC from washing out. 50 mL of deionized water, 25 mL of 30% $\text{NH}_4\text{OH}/\text{EtOH}$ (1/19 v/v) and 50 mL of EtOH were then passed through the column in turn under vacuum-pump suction. The information on ABX and solvents was described in our previous work (Liu, Wu, Cannizzo, et al., 2022; Liu, Wu, Barge, et al., 2022).

2.2. Devices and typical operation

2.2.1. Devices

The device for sonochemical degradation of ABX in milk was shown in Fig. 1, which was described in our previous study (Liu et al., 2023).

A high-frequency (500 kHz) device equipped with an ultrasonic cleaning generator (maximum electrical output power of 318 W, UMC-Premium, Weber Ultrasonics, Germany) was used for ABX degradation. The calorimetrically measured US powers and associated electric powers were also listed in our previous work (Liu, et al., 2023). A centrifuge (Allegra 64R Benchtop Centrifuge, Beckman Coulter, Italy) with a maximum rotation speed of 26,000 rpm was used to separate the supernatants from the milk samples. A HPLC system (Waters Corp., Milford, MA, USA) was used, as described in a previous work, for ABX determination (Liu, Wu, Barge, et al., 2022). A liquid-phase parallel synthesizer (Heidolph Synthesis 1, Germany) was used for the adsorption of ABX by ACs in pasteurized milk. A microprocessor pH meter (Hanna instruments, pH 211) was used to measure the pH values of milk samples before and after sonication. A digital thermometer with a pointed probe (Hanna instruments, HI 98501) was used to monitor the bulk temperature during sonication.

2.2.2. Typical operation

Multiple sets of 50 mL of $5.52 \mu\text{mol L}^{-1}$ ABX-spiked milk with 5–30 mg sonocatalyst (CPAC, WPAC, PGAC, or PPAC) were shaken in a liquid phase parallel synthesizer at 700 rpm for 30–60 min until the adsorption–desorption equilibrium was reached (Table S1 and S2). Subsequently, one of the set mixtures was filtered to obtain a homogeneous medicated milk for sonolytic degradation and, for the sake of comparison, another set mixture was directly used for sonocatalytic degradation. A 1-L Erlenmeyer flask containing 50 mL of ABX spiked milk, without or with sonocatalyst, was set over the serpentine condenser (at approx. 1 cm from the bottom) in the sonication reactor and sonicated at 500 kHz and 259 W in an ambient atmosphere (Fig. 1)

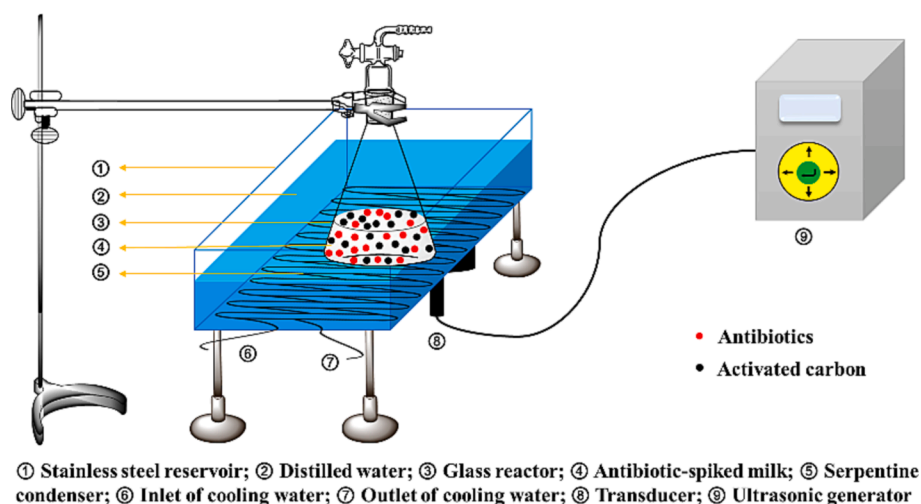


Fig. 1. The device for the sonochemical degradation of ABX in milk.

(Liu, et al., 2023). The bulk temperature was continuously monitored using a digital thermometer and controlled by cooling water during sonication. Milk samples were withdrawn periodically and analyzed via AC-based solid-phase extraction coupled with HPLC (AC-SPE-HPLC) (Liu, Wu, Barge, et al., 2022).

2.3. Analysis and assessment of ABX removal

2.3.1. Determination of ABX in milk and sonocatalysts

ABX in both the milk and sonocatalysts were analyzed using the AC-SPE-HPLC method as described in detail in our previous study (Liu, Wu, Barge, et al., 2022). Firstly, milk samples were filtered through a glass-wool-filled column (free of ACs). Afterward, the residue ABX in the filtrate and sonocatalysts (filter residue) were concentrated and cleaned using the AC-SPE method. Finally, the ABX in the prepared samples was determined using the HPLC system based on peak area.

2.3.2. Adsorption isotherm of the model ABX on CPAC

The adsorption capacities (mg g^{-1}) of the model ABX on CPAC were calculated based on Eq. 1:

$$q_e = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the ABX concentrations before and after adsorption, respectively. m (g) is the mass of CPAC, V (L) is the milk volume.

The investigation of adsorption isotherms is useful for practice applications. Herein, Freundlich and Langmuir isotherms models were used to study the adsorption behavior of the model ABX on CPAC. The Freundlich model is an empirical equation (Wu, Liu, Wu, & Cravotto, 2021):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where K_F (L mg^{-1}) relates to the adsorption capacity and n stands for the adsorption intensity.

The Langmuir isotherm model is usually used to describe adsorption with the homogeneous surface of adsorbents (Wu, Liu, Wu, & Cravotto, 2021):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (3)$$

where C_e (mg L^{-1}) is the equilibrium adsorbate concentration, q_e (mg g^{-1}) is the amount adsorbed per gram adsorbent, q_m (mg g^{-1}) is the maximal adsorption amount of substrate, and K_L (L mg^{-1}) is a constant

corresponding to the adsorption free energy.

2.3.3. Assessment of removing ABX by sonochemical processes

The integrated rate equation for pseudo-first-order (PFO) kinetics and the degradation efficiency (DE) for ABX degradation are described in Eq. 4 and 5 (Liu et al., 2022):

$$\frac{C_t}{C_0} = e^{-k_1 t} \quad (4)$$

$$DE (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (5)$$

where C_0 ($\mu\text{mol L}^{-1}$) represents the initial concentration of ABX, C_t ($\mu\text{mol L}^{-1}$) is the ABX concentration at the given time t (min), and k_1 (min^{-1}) is the PFO constant, which is equal to the slope of the plot of $\ln(C_t/C_0)$ versus t .

All of the experiments were conducted in duplicate. Error bars represent the standard error of duplicate experiments. A lack of error bars on data either indicates that the standard error of the replicates was zero or that the size of the error bar is minor than the label.

3. Results and discussion

The physical effects during acoustic cavitation induced by US, e.g. extremely high local temperatures and pressures, high-velocity micro-jets, etc., favor mass and heat transfer, via microcirculation in bulk liquids, as well as promoting reactions in heterogeneous systems (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Gholami, Khataee, Soltani, & Bhatnagar, 2019). Therefore, synergistic effects may exist between adsorption and sonolysis in sonocatalytic systems. The sonocatalytic systems could be optimized by investigating the effect of sonocatalyst type and dosage. In general, the sonocatalytic degradation kinetics of ABX are closely associated with the physicochemical properties of ABX. Additives including radical scavengers and oxidants can either quench or enhance the sonolytic degradation of ABX, which assists in the understanding of sonocatalytic degradation mechanisms (Liu, Wu, Abramova, & Cravotto, 2021).

3.1. Contribution of various processes to SMM removal from milk

The presence of heterogeneous catalysts in ultrasonic systems can intensify the formation of radicals and cavitation nuclei, followed by improved degradation of ABX (Liu, Wu, Abramova, & Cravotto, 2021; Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). For instance, Gholami et al. have described that the DE s of 0.1 mmol L^{-1} cefazolin in 100 mL

solution reached 32.6%, 6.8% and 97.6% when respective adsorption, sonolysis and sonocatalysis (1 g L⁻¹ Fe-Cu-layered double hydroxides/Biochar) were used at 40 kHz, 300 W and pH 6.5 for 80 min (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020). Mirzaei *et al.* have reported that the *DEs* of 30 mg L⁻¹ ampicillin in a 259 mL solution reached 20%, 5.2% and 87% when respective adsorption (30 min), sonolysis (90 min) and sonocatalysis (90 min, 1 g L⁻¹ Zn(OH)F) were used at 35 kHz, 100 W and pH 7 (Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). Nevertheless, the kinetics and mechanisms for removing ABX in milk via sonochemical processes are still not clear.

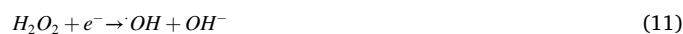
To preliminarily understand the contributions of the various processes for removing ABX in milk, 50 mL of 5.52 μmol L⁻¹ SMM (*i.e.*, 1.67 mg L⁻¹) spiked milk was sonicated at 500 kHz and 259 W, both with and without adding 20 mg of the CPAC sonocatalyst after adsorption, as described in Section 2.2.2. The contributions of adsorption (labeled as CPAC alone), sonolysis (labeled as US alone) and sonocatalysis (labeled as US/CPAC) on removing SMM in milk are shown in Fig. 2.

The adsorption-desorption equilibrium was reached in 30 min (Fig. 2). The adsorption data in Table S1 with the use of CPAC were fitted by Freundlich and Langmuir isotherm models, and the values of q_m , K_L , K_F , and $1/n$ are presented in Table S2. As shown, the adsorption of the model ABX on CPAC in milk follows the Langmuir isotherm model well (R^2 : 0.9948–0.9997). The maximal adsorption amounts of the model ABX by CPAC were calculated in the range of 0.93–1.04 mg g⁻¹. The small adsorption amounts can be attributed to the competitive adsorption between ABX and milk components on CPAC. The low $1/n$ values confirmed CPAC possesses good adsorption properties (Liu, Wu, Ge, & Yang, 2019).

Adding CPAC in the sonolytic system significantly improved the *DE* of SMM under the given conditions. The removal of SMM from milk using sonolysis and sonocatalysis was confirmed following PFO kinetics well with high correlation coefficients (R^2 : 0.9513–0.9985). 10.9%, 66.0% and 93.6% of SMM were removed by CPAC alone, US alone ($3.6 \times 10^{-2} \text{ min}^{-1}$) and US/CPAC ($9.3 \times 10^{-2} \text{ min}^{-1}$) for 30 min, respectively. Based on Eq. 4, the reaction times needed to meet the MRL (t_{MRL}) using sonolysis and sonocatalysis were calculated to be 75 and 29 min, respectively. Meanwhile, the residual SMM concentrations in milk were 150.1 and 95.1 μg L⁻¹ after sonolytic and sonocatalytic degradation, respectively. Fortunately, the residual SMM concentration in milk meets the European Commission MRL (100 μg L⁻¹) after sonocatalysis (Liu *et al.*, 2022).

The low *DE* of SMM under US alone is probably caused by the low production rate and amount of •OH radicals (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020). The improved removal of SMM by sonication alone and US/CPAC could be attributed to the generation high concentration of •OH under high ultrasonic frequency (500 kHz) in milk (Bui, Cozzolino, Zisu, & Chandrapala, 2020). The reasons for the

high *DE* and k_1 under US/CPAC could be: (i) the improved mass transfer by sonication, which created more reaction opportunities between SMM and •OH, as well as diminished the reactions between the •OH and •OH or •H radicals (Reactions 1 and 2 (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Mirzaei, Haghghat, Chen, & Yerushalmi, 2019)); (ii) the sonication-dispersed porous CPAC particles, which lowered the threshold for cavitation-bubble formation and increased the number of nuclei for cavity production, leading to the intensified generation of •OH radicals (Reactions 3 and 4); (iii) the e⁻/h⁺ (conduction band electron/valence band holes) pair generated on the CPAC surface as during acoustic cavitation (Reaction 5), which promoted the formation of •OH directly via h⁺ or indirectly via e⁻ involved radical reactions (Reactions 6–11) (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Soltani *et al.*, 2019); (iv) the sonication-expanded SA of CPAC, which increased the number of active adsorption sites, as well as the continuous cleaning and renewal of the CPAC surface lead to the improved adsorption capacity towards SMM, meaning that more SMM molecules can be oxidized by the •OH formed *in situ* on the CPAC (Soltani *et al.*, 2019); (v) the dispersed AC particles-enhanced microbubbles split off, which intensified the acoustic cavitation and expanded the high temperature and pressure zones (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Gholami, Khataee, Soltani, & Bhatnagar, 2019).



Furthermore, synergistic efficiency (*SE*) is a suitable index for evaluating the applicability of combined processes. Herein, it has been defined as the degradation rates of the combined process divided by the sum of degradation rates regarding each independent process under optimal conditions, as shown in Eq. (6) (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020):

$$SE = \frac{k_{\text{Sonocatalysis}}}{k_{\text{Adsorption}} + k_{\text{Sonolysis}}} \quad (6)$$

where $k_{\text{sonocatalysis}}$, $k_{\text{Adsorption}}$ and $k_{\text{Sonolysis}}$ are the degradation rates in the sonocatalysis, adsorption, and sonolysis of ABX under the given conditions, respectively. In general, synergism occurs between the adsorption and sonolysis processes in sonocatalytic systems when the *SE* value is over 1.0.

In this study, the *SE* value was calculated to be 2.58, demonstrating the existence of synergistic effects between CPAC and US in this US/CPAC process. A high *SE* value (15.8) has also been reported by Hassandoost *et al.* during the sonocatalytic degradation of OTC in water (Hassandoost *et al.*, 2022).

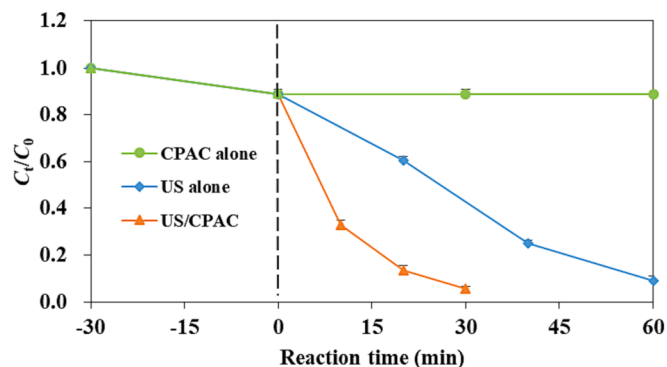


Fig. 2. The contributions of various processes to the removal of SMM from milk (conditions: 5.518 μmol L⁻¹ (initial SMM concentration before adsorption); 50 mL; 20 mg CPAC; 500 kHz; 259 W; room temperature).

3.2. Sonocatalytic degradation of SMM using various ACs in milk

In general, the performance of sonocatalytic degrading organics is associated with the physicochemical properties of the catalysts (Haddadi et al., 2023; Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). For example, Gholami *et al.* have stated that carbon-based materials, including AC, Granular AC, biochar, *etc.*, possess different characteristics when used as sonocatalysts for organics removal (Gholami, Khataee, Soltani, & Bhatnagar, 2019). To scan the optimal carbon-based catalyst, 50 mL of 5.518 $\mu\text{mol L}^{-1}$ SMM spiked milk was sonicated at 500 kHz and 259 W, with the addition of 20 mg PPAC, PGAC, WPAC or CPAC. The results of sonocatalytic removing SMM from milk are shown in Fig. 3.

The efficiencies of sonocatalytic degrading SMM in milk with the use of various ACs are ordered as follows: CPAC > WPAC > PPAC > PGAC (Fig. 3a). The sonocatalytic degradation of SMM using various ACs is well described by PFO kinetics (R^2 : 0.9695–0.9985), and the k_1 values are 1.8×10^{-2} , 4.7×10^{-2} , 6.2×10^{-2} and $9.3 \times 10^{-2} \text{ min}^{-1}$ for the US/PGAC, US/PPAC, US/WPAC and US/CPAC processes, respectively, resulting in the relevant *DEs* of 42.8%, 75.9%, 82.4% and 93.7% by sonication for 30 min. Under the given conditions, the residual amounts of SMM in milk after degradation and the t_{MRL} values were 953.5, 379.8, 271.3, 95.1 $\mu\text{g L}^{-1}$ and 150, 57, 44, 29 min with the use of PGAC, PPAC, WPAC and CPAC, respectively.

Generally, specific catalyst properties can be evaluated using the reaction rate per unit catalyst weight (RR_{Cat} , $\mu\text{mol min}^{-1} \text{ g}^{-1}$). To a certain degree, higher RR_{Cat} values indicate higher catalytic efficiency. The RR_{Cat} can be calculated using Eq. 7 (Yamazaki, Matsumoto, Ishikawa, & Sato, 2023):

$$RR_{Cat} = \frac{\mu\text{mol of ABX removed } (\mu\text{mol}) / \text{reaction time (min)}}{\text{Weight of catalyst (g)}} \quad (7)$$

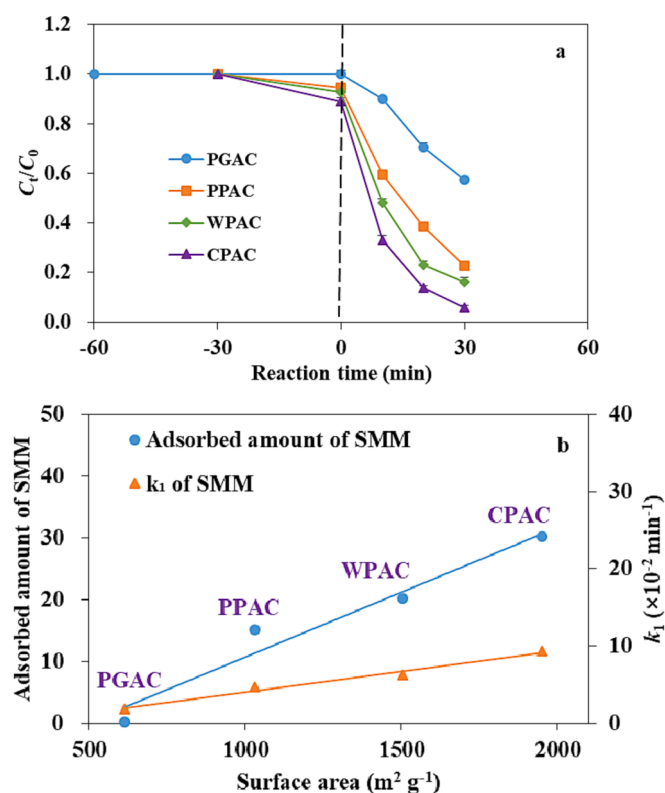


Fig. 3. The effect of AC type on the rates of SMM sonocatalytic degradation in milk (a), and the dependence of SMM adsorption amount and k_1 values on SA of AC in batch mode (b) (conditions: 5.518 $\mu\text{mol L}^{-1}$ (initial SMM concentration before adsorption); 50 mL; 20 mg sonocatalyst; 500 kHz; 259 W; 30 min; room temperature).

Based on Eq. 7, the RR_{Cat} values for sonication with PGAC, PPAC, WPAC and CPAC were calculated to be 0.20, 0.33, 0.35 and 0.38 $\mu\text{mol min}^{-1} \text{ g}^{-1}$, respectively, suggesting that CPAC possesses the highest catalytic efficiency among the various ACs.

To further clarify the role of AC properties in US/AC processes, the dependence of SMM adsorption amount (AA_{SMM} , nmol), in batch mode, and k_1 values on the SAs of the various ACs (S_A , $\text{m}^2 \text{ g}^{-1}$) were fitted and are presented in Fig. 3b. As shown, the AA_{SMM} and k_1 values linearly correlated to the SA of AC (Eq. 8 and 9).

$$AA_{SMM} = 0.021S_A - 10.356, \quad R^2 = 0.954 \quad (8)$$

$$k_1 = 0.0053S_A - 1.3068, \quad R^2 = 0.9798 \quad (9)$$

The high R^2 values in Eq. 8 and 9 indicate that SA is a key factor and that adsorption plays a crucial role in sonocatalytic degradation. Al-Ahmed *et al.* have also reported that high-SA AuNPs@MCC (gold nanoparticles containing microcrystalline cellulose) exhibited greater sonocatalytic activity than low-SA PdNPs@MCC (palladium nanoparticles containing microcrystalline cellulose) for degrading paracetamol and sulfamethazine in water (Al-Ahmed et al., 2023). Furthermore, the order of the various ACs, in terms of their sonocatalytic efficiency, is consistent with their SAs, which can be attributed to the higher number of active sites and intensified SMM oxidation by $\cdot\text{OH}$ (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). Overall, CPAC was selected as the optimal sonocatalyst among the various ACs for SMM removal in milk.

3.3. Optimization of sonocatalyst dosage

Generally, the sonocatalytic degrading organics in heterogeneous systems is enhanced with increasing catalyst dosage due to the improved formation of reactive oxygen species and the adsorption of substrates onto catalysts (Liu, Wu, Abramova, & Cravotto, 2021; Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). For instance, Gholami *et al.* have reported that *DEs* increased, from 57.1% to 98.1%, when the Fe-Cu-LDH/BC dose was increased, from 0.5 to 1.5 g L^{-1} , during the sonocatalysis of 0.1 mmol L^{-1} cefazolin sodium in 100 mL of aqueous solution at 40 kHz, 300 W and pH 6.5 for 80 min (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020). Haddadi *et al.* also stated that the *DE* values increased from 79.3% to 100%, when the catalyst dosage was increased from 0.25 to 1.00 g L^{-1} during the sonocatalysis of 10 mg L^{-1} OTC in 100 mL of aqueous solution at 36 kHz and 150 W for 120 min (Haddadi et al., 2023). To optimize the catalyst dose, 50 mL of 5.52 $\mu\text{mol L}^{-1}$ ABX (*i.e.* 3.09 mg L^{-1} CEF, 1.67 mg L^{-1} SMM, 2.0 mg L^{-1} MAR and 2.54 mg L^{-1} OTC)-spiked milk was sonicated at 500 kHz and 259 W, with 5–30 mg CPAC. The results are shown in Fig. 4.

As displayed in Fig. 4a, the k_1 values of the model ABX degradation increased linearly with increasing CPAC dose (d_{CPAC}). And the relationships between k_1 values and CPAC doses were fit and shown in Eqs. (10)–(13):

$$k_{1,CEF} = 0.22d_{CPAC} + 10.53, \quad R^2 = 0.9992 \quad (10)$$

$$k_{1,SMM} = 0.31d_{CPAC} + 4.56, \quad R^2 = 0.9228 \quad (11)$$

$$k_{1,MAR} = 0.19d_{CPAC} + 4.46, \quad R^2 = 0.9697 \quad (12)$$

$$k_{1,OTC} = 0.18d_{CPAC} + 2.70, \quad R^2 = 0.9256 \quad (13)$$

Eq. (11) possesses the largest slope of the four equations above, indicating that the dosage of CPAC has a more obvious enhancement on sonocatalytic degrading SMM than that of the other ABX. High R^2 values (0.9447–0.9985) prove that the sonocatalytic degradation of ABX can be well described by PFO kinetics (Table S3). The k_1 values for the sonocatalytic degradation of CEF, SMM, MAR and OTC lie in the following respective ranges: 1.16×10^{-1} – $1.72 \times 10^{-1} \text{ min}^{-1}$, 0.66×10^{-1} –

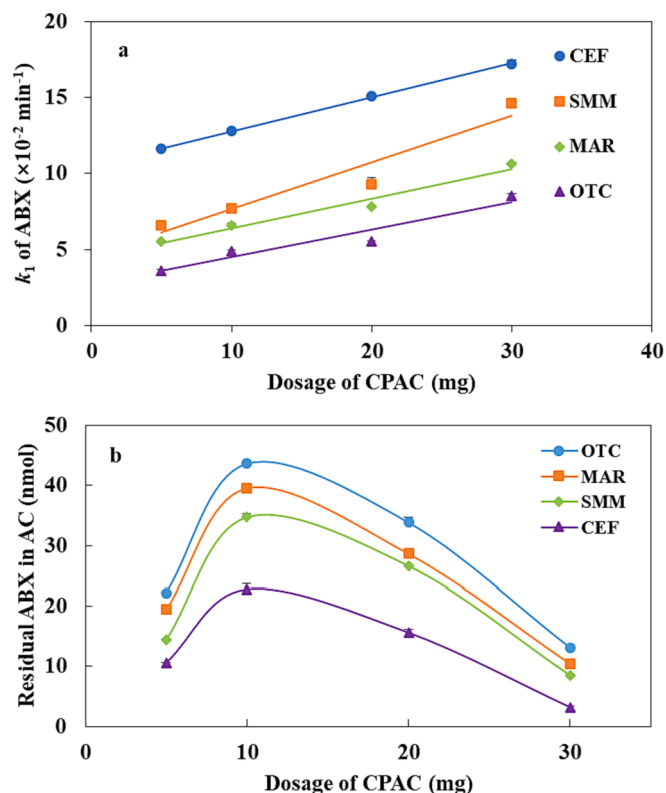


Fig. 4. Effect of CPAC dose on the k_1 values of ABX degradation (a), and the residual ABX in CPAC after sonocatalysis (b) (conditions: $5.52 \mu\text{mol L}^{-1}$ (initial ABX concentration before adsorption); 50 mL; 500 kHz; 259 W; room temperature).

$1.46 \times 10^{-1} \text{ min}^{-1}$, 0.55×10^{-1} – $1.06 \times 10^{-1} \text{ min}^{-1}$ and 3.6×10^{-2} – $8.5 \times 10^{-2} \text{ min}^{-1}$, with various doses of CPAC. Similarly, Mirzaei *et al.* have also described that the k_1 values increased, from 6.1×10^{-4} to $1.99 \times 10^{-2} \text{ min}^{-1}$, when the sonocatalyst dosage of ZF1 (F/Zn = 2:1) was increased from 0 to 1.5 g L^{-1} during the sonocatalysis of 30 mg L^{-1} ampicillin in 250 mL of aqueous solution at 35 kHz, 100 W and pH 7 for 90 min (Mirzaei, Haghghat, Chen, & Yerushalmi, 2019).

By increasing the dosage of CPAC from 5 to 30 mg, the respective reaction rate per unit catalyst weight, *i.e.* RR_{Cat} values, reduced from 2.42 to $0.38 \mu\text{mol min}^{-1} \text{ g}^{-1}$ for CEF, from 1.55 to $0.25 \mu\text{mol min}^{-1} \text{ g}^{-1}$ for SMM, from 1.11 to $0.17 \mu\text{mol min}^{-1} \text{ g}^{-1}$ for MAR and from 0.78 to $0.13 \mu\text{mol min}^{-1} \text{ g}^{-1}$ for OTC, meanwhile, the respective t_{MRL} values decreased from 29 to 19 min for CEF, from 41 to 18 min for SMM, from 58 to 30 min for MAR and from 87 to 37 min for OTC (Table S3). Briefly, the sonocatalytic efficiencies of model ABX are ordered as follows: CEF > SMM > MAR > OTC. Meanwhile, the RR_{Cat} values with the various CPAC doses are ordered as follows: 5 mg > 10 mg > 20 mg > 30 mg. It is clear that the use of CPAC at a dose of 5 mg exhibits the highest sonocatalytic efficiency, although an extended reaction time was also observed. By contrast, the t_{MRLs} can be shortened by using 30 mg CPAC.

The low RR_{Cat} values observed when using high CPAC doses can be explained by US attenuation, the limitation of ABX interphase diffusion and CPAC-particle aggregation (Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). However, the faster ABX degradation observed with higher CPAC doses has been attributed to the increase in absolute active adsorption sites on the CPAC surface and the rapid formation of $\cdot\text{OH}$ (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Mirzaei, Haghghat, Chen, & Yerushalmi, 2019). The higher RR_{Cat} values at smaller CPAC doses are rational since the unobstructed propagation of US provides more energy, which can split CPAC into smaller sizes, increasing the SA and adsorption capacity towards ABX, as well as intensifying cavitation

events and effects (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Hassaan & El Nemr, 2017).

To further clarify the role of adsorption in US/CPAC processes and determine the optimal dosage of CPAC, the relationship between CPAC dose and residual ABX amount in CPAC was plotted and is displayed in Fig. 4b. As shown, the residual amounts of ABX (nmol) in CPAC increased when the CPAC dosage was reduced from 30 to 10 mg, but the values decreased when the dose was further reduced from 10 to 5 mg. The proposed reasons for this include: i) the beneficial effect that US has on increasing SA of CPAC surface area being limited by CPAC dose (not exceeding 10 mg), meaning that the effective SAs of CPAC at 5 and 10 mg may be larger than those at 20 and 30 mg; ii) the degradation rates of ABX *in situ* on the CPAC surface at high doses being higher than the rates of CPAC-surface renewal via adsorption (Gholami, Khataee, Soltani, & Bhatnagar, 2019). The highest ABX residual amounts in CPAC suggest that the active sites on CPAC were maximally utilized at the dosage of 10 mg under these sonication conditions. The results above, once again, demonstrate that the sonocatalytic degradation of ABX mainly occurs on the CPAC surface, where the adsorbed ABX is rapidly oxidized by $\cdot\text{OH}$ formed *in situ*, with the free active site then being quickly filled by ABX adsorption from the bulk milk.

3.4. Comparison of various ABX for sonocatalysis in milk

In general, the inconsistent physicochemical properties and reactivity of the organics in question mean that their kinetics and mechanisms of sonolytic degradation are different (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Liu, Wu, Abramova, & Cravotto, 2021). For instance, Al-Ahmed *et al.* have reported different k_1 and DEs values for the sonocatalysis of paracetamol ($31.7 \pm 1.5 \times 10^{-3} \text{ min}^{-1}$ and 99%) and sulfamethazine ($52.5 \pm 4.1 \times 10^{-3} \text{ min}^{-1}$ and 98%) within 90 min in water under the same reaction conditions (Al-Ahmed *et al.*, 2023). To compare the sonocatalysis of the model ABX in milk, 50 mL of $5.52 \mu\text{mol L}^{-1}$ CEF-, SMM-, MAR- and OTC-spiked milk were sonicated at 500 kHz and 259 W with 20 mg CPAC. The results are shown in Fig. 5.

The removal rates of ABX follow the order: CEF > SMM > MAR > OTC. High R^2 values (0.9529–0.9985) demonstrate that the degradation of ABX is controlled by PFO kinetics (Fig. 5). The k_1 values of PFO kinetics were calculated to be 1.51×10^{-1} , 9.30×10^{-2} , 7.80×10^{-2} and $5.50 \times 10^{-2} \text{ min}^{-1}$ for CEF, SMM, MAR and OTC, respectively. The DEs and residual concentrations of CEF, SMM, MAR and OTC in milk were 96.6%, 93.6%, 97.6%, 96.2%, and 94.1, 95.1, 42.6 and $85.5 \mu\text{g L}^{-1}$ (meeting the relevant MRLs: $100 \mu\text{g L}^{-1}$ for CEF, SMM, and OTC, and $75 \mu\text{g L}^{-1}$ for MAR), under sonocatalysis for 20, 30, 45 and 60 min, respectively (Liu *et al.*, 2022). In addition, the t_{MRLs} , SE and RR_{Cat} values for the sonocatalysis of CEF, SMM, MAR and

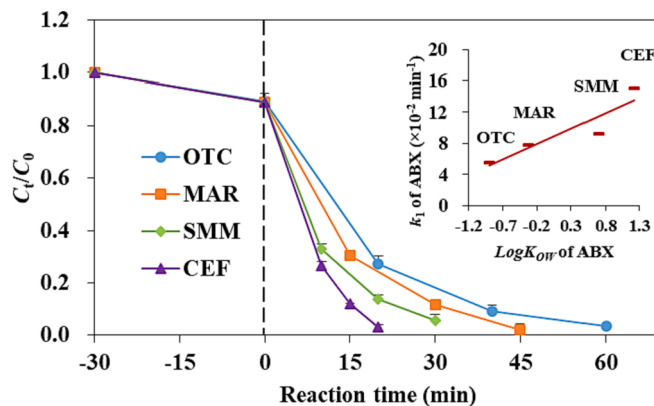


Fig. 5. The sonocatalytic degradation of ABX in milk and the dependence of k_1 of PFO kinetics on $\text{Log}K_{OW}$ (octanol–water partition coefficient) of the model ABX (conditions: $5.52 \mu\text{mol L}^{-1}$ (initial ABX concentration before adsorption); 50 mL; 20 mg CPAC; 500 kHz; 259 W; room temperature).

OTC were calculated to be 22, 29, 41, 57 min; 4.0, 2.6, 2.4, 1.8; and 0.59, 0.38, 0.27 and 0.20 $\mu\text{mol min}^{-1} \text{g}^{-1}$, respectively. Thus, synergistic effects between sonication and adsorption by catalysts clearly existed during sonocatalytic degrading ABX. And the sonocatalytic efficiency of ABX removal using CPAC can be ordered as follows: CEF > SMM > MAR > OTC.

These results may be attributed to the different physicochemical properties of the model ABX. It has been reported that the transfer processes and sonolysis of organics are mainly controlled by their hydrophobicity (Al-Hamadani et al., 2017; Liu, Wu, Abramova, & Cravotto, 2021). The $\text{Log}K_{OW}$ values of CEF, SMM, MAR and OTC range from -0.90 to 1.22 , thus making it necessary to clarify the inherent relationship between degradation rates and the $\text{Log}K_{OW}$ values of the model ABX. The dependence of k_1 values for the PFO kinetics of ABX removal on the ABX $\text{Log}K_{OW}$ values is shown in Fig. 5. As shown, the k_1 of ABX was linearly correlated to the $\text{Log}K_{OW}$ values. Similarly, Wu et al. have also reported that the sonolytic degradation of volatile chloroform with larger $\text{Log}K_{OW}$ value is faster than that of phenol and fumaric acid with smaller $\text{Log}K_{OW}$ value in aqueous solutions (Wu, Cravotto, Adrians, Ondruschka, & Li, 2015). ABX with higher $\text{Log}K_{OW}$ values, CEF and SMM, are readily transferred to the gas–liquid interfaces of sonication-induced cavities where there is an abundance of *in-situ* generated $\cdot\text{OH}$ radicals. By contrast, ABX with lower $\text{Log}K_{OW}$ values, MAR and OTC, are less readily transferred to the microbubble interface. Thus, the k_1 values for hydrophobic CEF and SMM are higher than those for hydrophilic MAR and OTC.

$\cdot\text{OH}$ is a crucial oxidative species in the sonocatalytic process, and it more efficiently removes organic substrates than superoxide anion radicals ($\text{O}_2^{\cdot-}$), valence band holes (h^+), etc. in water (Gholami, Khataee, Soltani, & Bhatnagar, 2019; Liu, Wu, Abramova, & Cravotto, 2021). Scavenger *n*-butanol has widely been used to remove $\cdot\text{OH}$ and thus clarify the role of $\cdot\text{OH}$ in aqueous solutions and complex matrices, e.g. milk and landfill leachate (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Liu, Wu, Cannizzo, Mantegna, & Cravotto, 2022). Herein, 0.23 mL *n*-butanol (50 mmol L^{-1}) was added to milk during sonocatalytic degrading the model ABX. The inhibition efficiencies by *n*-butanol on the k_1 values of ABX degradation are displayed in Fig. 6.

The sonocatalytic degradation of ABX was inhibited by *n*-butanol to different degrees (Fig. 6). The inhibition efficiencies by *n*-butanol are ordered as follows: OTC (65%) > MAR (51%) > SMM (39%) > CEF (28%), which linearly correspond to the $\text{Log}K_{OW}$ values of ABX (Eq. (14)), illustrating that $\cdot\text{OH}$ radicals dominate the degradation of ABX. Similar results have been reported by Soltani et al. and Gholami et al. during the sonocatalytic degradation of tetracycline and cefazolin sodium in water, respectively (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Soltani et al., 2019).

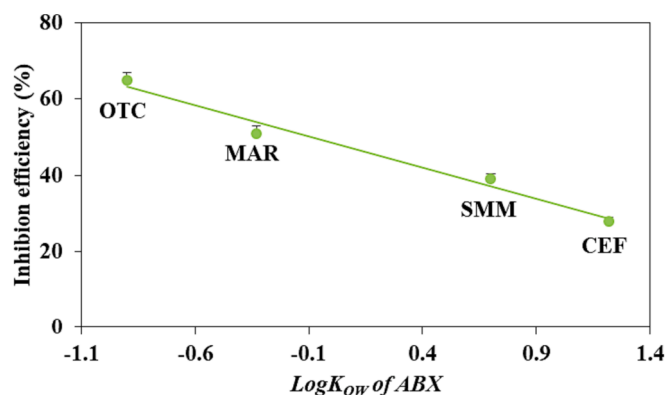


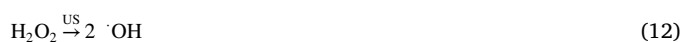
Fig. 6. The inhibition efficiency of *n*-butanol on the sonocatalytic degradation rates of ABX (conditions: $5.52 \mu\text{mol L}^{-1}$ (initial ABX concentration before adsorption); 50 mL; 20 mg CPAC; 500 kHz; 259 W; 0.23 mL *n*-butanol; room temperature).

$$\text{Inhibition efficiency (\%)} = -16.36\text{Log}K_{OW} + 48.57, R^2 = 0.9794 \quad (14)$$

Scavenger *n*-butanol is relatively hydrophobic ($\text{Log}K_{OW}$: 0.88) compared to the model ABX, meaning that, once it is added to sonocatalytic systems, it locates near the gas–liquid interface and rapidly reacts with the *in-situ* generated $\cdot\text{OH}$. However, the reaction rate of *n*-butanol with $\cdot\text{OH}$ ($5.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) is much lower than those of CEF ($9.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), SMM ($9.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), MAR ($9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and OTC ($7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), meaning that the reaction rates of *n*-butanol with $\cdot\text{OH}$ should not control the sonocatalytic degradation of the model ABX (Liu et al., 2023). Hydrophobic CEF and SMM mainly react with $\cdot\text{OH}$ near the microbubble interface, where the $\cdot\text{OH}$ content is still somewhat higher than that in the bulk milk, even after the addition of *n*-butanol. However, less MAR and OTC are transferred to the active sites due to their higher hydrophilicity. Therefore, higher MAR and OTC sonocatalysis inhibition by *n*-butanol was observed than for the other two ABX (Liu et al., 2022).

3.5. Role of H_2O_2 addition on sonocatalysis of ABX in milk

The oxidant H_2O_2 can intensify the generation of $\cdot\text{OH}$ via radical reactions (Reactions 10–13), and thus accelerate the sonocatalytic degradation of organics (Al-Ahmed et al., 2023; Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020; Khataee et al., 2019).



Gholami et al. have described that *DEs* improved, from 49.2% to 70.3%, with the addition of $0.3 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ during the sonolytic degradation of 0.2 mmol L^{-1} cefazolin in 100 mL aqueous solution using 0.5 g L^{-1} of the catalyst Fe-Cu layered double hydroxide/biochar nanocomposite at 40 kHz, 300 W and pH 6.5 for 80 min (Gholami, Dinpazhoh, Khataee, Hassani, & Bhatnagar, 2020). Khataee et al. have also reported that *DEs* increased, from 90.4% to 93.1%, with the addition of $20 \text{ mg L}^{-1} \text{H}_2\text{O}_2$ during the sonocatalytic degradation of 20 mg L^{-1} moxifloxacin in 100 mL aqueous solution with 1 g L^{-1} of the catalyst NiFe layered double hydroxide/reduced graphene oxide (NiFe-LDH/rGO) at 36 kHz, 150 W and pH 8 for 60 min (Khataee et al., 2019). To evaluate the effect of adding H_2O_2 on the sonocatalysis of the model ABX, 50 mL of $5.52 \mu\text{mol L}^{-1}$ ABX-spiked milk was sonicated at 500 kHz and 259 W with $0.25\text{--}1.0 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ and 20 mg CPAC. The results are illustrated in Fig. 7.

The 0.5 mmol L^{-1} was the optimal H_2O_2 dose for the sonocatalysis of all the model ABX, and the k_1 value of CEF was the highest (Fig. 7a). With adding $0.25\text{--}1.00 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ in sonocatalytic systems (US/CPAC/ H_2O_2), the k_1 values were calculated in the ranges of $1.71 \times 10^{-1} \text{--}1.94 \times 10^{-1} \text{ min}^{-1}$ for CEF, $1.04 \times 10^{-1} \text{--}1.15 \times 10^{-1} \text{ min}^{-1}$ for SMM, $8.4 \times 10^{-2} \text{--}8.8 \times 10^{-2} \text{ min}^{-1}$ for MAR, and $5.7 \times 10^{-2} \text{--}6.0 \times 10^{-2} \text{ min}^{-1}$ for OTC, leading to the relevant *DEs* ranging from 99.5% to 99.8%, from 96.3% to 96.9%, from 98.4% to 98.7%, and from 96.9% to 97.1% for CEF, SMM, MAR, and OTC under the given conditions for 20, 30, 45 and 60 min, respectively (Table S4). Moreover, the residual ABX concentrations in milk after degradation by US/CPAC/ H_2O_2 were in the ranges $5.3\text{--}15.0 \mu\text{g L}^{-1}$, $45.6\text{--}54.2 \mu\text{g L}^{-1}$, $23.5\text{--}28.2 \mu\text{g L}^{-1}$ and $66.5\text{--}79.0 \mu\text{g L}^{-1}$ for CEF, SMM, MAR and OTC, respectively, which meet the relative MRLs. The t_{MRLs} values were also calculated to be in the ranges 17–19 min, 23–26 min, 36–38 min and 52–55 min for CEF, SMM, MAR and OTC, respectively. Moreover, there are negligible changes in RR_{Cat} values.

The different enhancements in efficiency caused by H_2O_2 are probably linked to the variety in ABX-molecule properties. To prove this hypothesis, the relationship between $\text{Log}K_{OW}$ and the enhanced efficiency of k_1 values in the degradation of model ABX using $0.5 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ was plotted and is shown in Fig. 7b. As shown, the enhanced

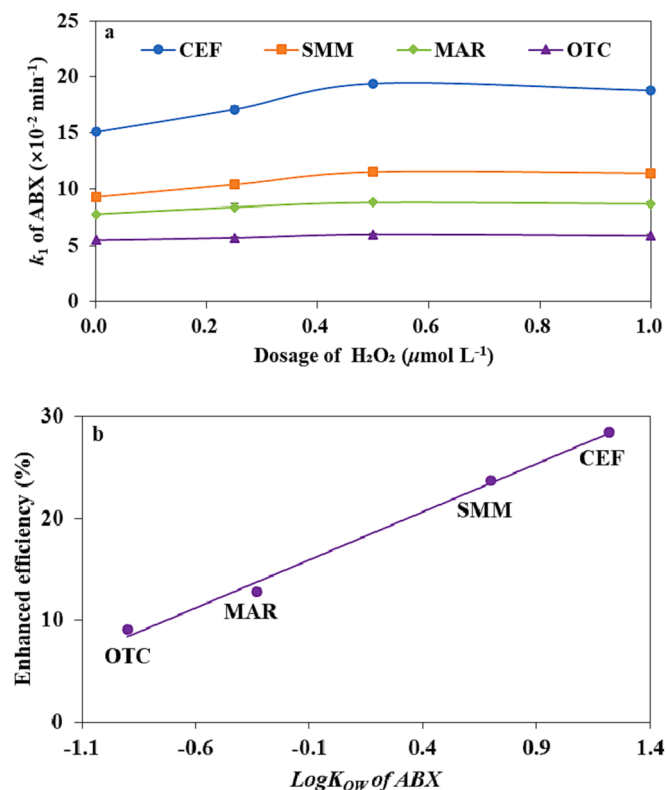


Fig. 7. Effect of H_2O_2 dose on the k_1 values of PFO kinetics for ABX removal using sonocatalysis (a), and effect of $\text{Log}K_{OW}$ on the enhanced efficiency of k_1 values for ABX removal using sonocatalysis (b) (conditions: $5.52 \mu\text{mol L}^{-1}$ (initial ABX concentration in milk before adsorption); 50 mL; 20 mg CPAC; 500 kHz; 259 W; room temperature).

efficiency linearly increased with the increase in model-ABX $\text{Log}K_{OW}$ values (Eq. (15)); the enhanced efficiencies are 28.5%, 23.7%, 12.8% and 9.1% for CEF, SMM, MAR and OTC, respectively.

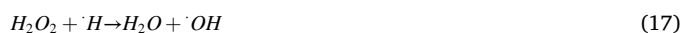
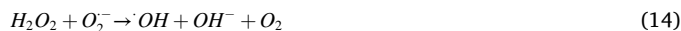
$$\text{Enhanced efficiency}(\%) = 9.417\text{Log}K_{OW} + 16.901, R^2 = 0.9940 \quad (15)$$

This result demonstrates that the enhanced efficiency of adding H_2O_2 on the degradation of model ABX is $\text{Log}K_{OW}$ dependent. Furthermore, the calculated RR_{Cat} and t_{MRLs} values are 0.20, 0.27, 0.40, $0.61 \mu\text{mol min}^{-1} \text{g}^{-1}$ and 52, 36, 23, 17 min for OTC, MAR, SMM and CEF, respectively, in the US/CPAC/ H_2O_2 system, with H_2O_2 being added at 0.5 mM.

To further clarify the role of H_2O_2 , the influence of H_2O_2 on the k_1 of SMM removal using H_2O_2 alone, sonolysis (US/ H_2O_2) and sonocatalysis (US/CPAC/ H_2O_2) were investigated with H_2O_2 being added at $0.25\text{--}1.0 \text{ mmol L}^{-1}$. The results are presented in Fig. S1. As shown, the optimal dosage of H_2O_2 in US/ H_2O_2 or US/CPAC/ H_2O_2 systems was demonstrated to be 0.5 mmol L^{-1} . The negligible degradation of SMM (4.8%–10.3%) exhibits after 60 min treatment by H_2O_2 alone, while DES of SMM reached the ranges of 89.9%–97.6% and 96.3%–96.9% after 60 min and 30 min treatment by using US/ H_2O_2 and US/CPAC/ H_2O_2 processes, respectively. The k_1 values were calculated to be in the ranges $0.2 \times 10^{-2} \text{--} 0.4 \times 10^{-2} \text{ min}^{-1}$, $3.8 \times 10^{-2} \text{--} 4.2 \times 10^{-2} \text{ min}^{-1}$, and $1.04 \times 10^{-1} \text{--} 1.15 \times 10^{-1} \text{ min}^{-1}$ for H_2O_2 alone, US/ H_2O_2 and US/CPAC/ H_2O_2 processes, respectively. By using various US/ H_2O_2 or US/CPAC/ H_2O_2 processes, the residual concentration of SMM in milk met the MRLs (Table S4). The synergistic efficiencies were calculated in the scopes 1.06–1.17 for US/ H_2O_2 and 1.12–1.24 for US/CPAC/ H_2O_2 processes, indicating the slight synergy effects.

The enhanced degradation of SMM by adding H_2O_2 can be attributed to the promoted formation of $\cdot\text{OH}$ via Reactions 14–17, while the slight change by increasing H_2O_2 dosage from 0.5 to 1.0 mmol L^{-1} may arise

from the partly consume of $\cdot\text{OH}$ by H_2O_2 (Reaction 18) (Gholami et al., 2020; Hassandoost et al., 2022; Liu et al., 2022). These results, once again, proven that $\cdot\text{OH}$ oxidation is the main way for sonocatalytic degrading SMM.



Sonication was reported can lead to the enhanced thermal stability of milk, and a positive change in the physicochemical properties of nutrients, e.g., proteins and fat, in milk (Bui, Cozzolino, Zisu, & Chandrapala, 2020; Shokri, Javanmardi, Mohammadi, & Khaneghah, 2022). In our previous work, negligible changes in milk nutrients and no antibacterial activity were observed after sonication for 60 min, where possible pathways for model ABX degradation were also proposed (Liu et al., 2023). Additionally, the comparison of this study with previous methods including hydrodynamic cavitation combined with ozonation, adsorption, heating with high temperature for a long time, treatment with high pH and electrochemical oxidation for removing the model ABX in milk were also provided and discussed in Table S5 and Section S1.

4. Conclusions

The sonocatalytic degradation of CEF, SMM, MAR and OTC in milk over ACs has been successfully performed in this study. There is an obvious synergism between adsorption and sonication during sonocatalysis. Sonocatalytic degradation of ABX in milk can be well-described by the PFO kinetics. Hydrophobic CEF and SMM were more easily degraded than hydrophilic MAR and OTC. The model ABX were mainly oxidized by $\cdot\text{OH}$ formed *in-situ* at the active sites on ACs. Adding H_2O_2 accelerated ABX removal and $0.5 \text{ mmol L}^{-1} \text{H}_2\text{O}_2$ was the optimal dose. Adsorption was crucial in sonocatalysis and could be enhanced by sonication. Large AC surface area either accelerated model-ABX removal or promoted the sonocatalytic efficiency of CPAC. After sonication with ACs, the residual ABX in milk meets the residue tolerance levels set by the European Commission. Compared with the previous methods, US/CPAC could efficiently degradation of the model ABX in milk within 1 h without adding additional oxidants and excess sonocatalyst.

CRedit authorship contribution statement

Pengyun Liu: Investigation, Data curation, Writing – original draft. **Zhilin Wu:** Investigation, Methodology, Supervision, Validation, Writing – original draft. **Judy Lee:** Conceptualization, Writing – review & editing. **Giancarlo Cravotto:** Conceptualization, Supervision, Validation, Writing – original draft, Writing – review & editing.

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.

Data availability

No data was used for the research described in the article.

Acknowledgments

This research was supported by both Fondazione CRT “Sviluppo di

tecnologie integrate per l'eliminazione dei residui di antibiotici dal latte vaccino" and the China Scholarship Council (CSC). Liu P. acknowledges the support of the CSC (grant No. 201909505008).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2023.137168>.

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