The removal of tetracycline with biogenic CeO$_2$ nanoparticles in combination with US/PMS process from aqueous solutions: kinetics and mechanism
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ABSTRACT
Antibiotics have received great attention because of their abuse and potential hazards to the human health and environment. In the current work, peroxymonosulfate (PMS) was added to a cerium oxide (CeO$_2$)/ultrasonic (US) system for tetracycline (TC) degradation. CeO$_2$ nanoparticles (NPs) were synthesized by a simple and cost-effective method using Stevia rebaudiana leaf extract and cerium nitrate as precursors. The as-synthesized CeO$_2$ NPs were characterized by X-ray diffraction, field emission scanning electron microscopy, and Fourier-transform infrared spectroscopy analysis. The effects of catalyst dosage, PMS concentration, US power, initial antibiotic concentration, and pH on TC removal were investigated. The results confirmed the formation of CeO$_2$ NPs with a fluorite structure, spherical shape, and average particle size of 29 nm. The removal efficiency of TC was 92.6% in the optimum oxidation conditions ([TC] = 15 mg/L, [PMS] = 50 mM, [CeO$_2$] = 0.6 g/L, pH = 6, and US = 70 W) and followed the zero-order kinetics. Experiment scavenger demonstrated both sulfate and hydroxyl radicals (SO$_4^-$, *OH) were responsible for degrading antibiotics. Biogenic CeO$_2$ NPs and ultrasound waves-activated PMS is a promising technology for water pollution caused by contaminants such as pharmaceuticals.

Key words | biogenic CeO$_2$ NPs, peroxymonosulfate, sonocatalytic, tetracycline

HIGHLIGHTS
• Biogenic CeO$_2$ nanoparticles were synthesized.
• Tetracycline sonodegradation efficiency was increased using biogenic CeO$_2$ nanoparticles.
• The US/PMS/CeO$_2$ process is powerful for decomposition of pharmaceutical wastewater.
• CeO$_2$ sonocatalyst could be recovered and it presented high activity reusability for five repetitive runs.

INTRODUCTION
Tetracycline (TC; C$_{22}$H$_{24}$N$_2$O$_8$) is the second broad-spectrum antibiotic which is largely used in human and veterinary medicine (Hou et al. 2016). TC used in medical treatment is poorly absorbed by humans or animals (Xing et al. 2013). Around 30–80% of TC is excreted through feces and urine as an active compound into the environment and becomes one of the emerging pollutants in water (Marzbali et al. 2016). TC residual has been detected in influent and effluent of wastewater treatment plants and surface

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water at 0.52 µg/L, 0.17 µg/L, and 0.11 µg/L, respectively (United States) (Eslami et al. 2016). TC, as one of the highly consumed antibiotics, is extensively used for treating infectious diseases from Gram-positive and Gram-negative bacteria for both humans and animals (Jiang et al. 2018; Song Ma & Li 2019).

To eliminate the undesirable TC accumulation in aquatic environments, developing new and reliable treatment processes is necessary (Gao et al. 2012; Daghrir & Drogui 2013). In the case of TC treatment, a variety of techniques, such as adsorption (Gao et al. 2012), electrocatalytic oxidation (Xu et al. 2014), electrocoagulation (Ouaisa et al. 2014), sonochemical processing (Yazdani et al. 2017), photocatalytic degradation (Saadati Keramati & Ghazi 2016), biodegradation (Xiong et al. 2017), and ozonation (Zhu et al. 2012) have been reported. Common treatment processes are not efficient methods because they result in solid waste, thus creating other environmental problems requiring further treatment (Daghrir & Drogui 2013; Priya & Radha 2017).

Advanced oxidation processes (AOPs), based on the production of sulfate and hydroxyl radicals, have been considered for water and wastewater treatment due to their high oxidation power and conversion of antibiotic (Malakootian et al. 2019a, 2019b, 2019c, 2019d, 2020; Nasiri et al. 2019; Tamaddon et al. 2020a, 2020b) and many organic chemical compounds into minerals, water, and carbon dioxide (Pi et al. 2019; Yang et al. 2019). Peroxymonosulfate (PMS = Oxone) is considered to be an environmentally friendly oxidant because it is benign, as are most of the by-products of its reactions (Yang et al. 2018; Ao et al. 2019). The decomposition rate of organic compounds with PMS at the room temperature is low, but it can be enhanced through activation by photolysis (ultraviolet (UV) irradiation) or sonolysis (ultrasonic (US) wave; Equation (1)), or by using transition metals (Equation (2)) or heat (Equation (3)), thereby producing highly reactive SO$_4^-$ and OH radicals (Yin et al. 2018b; Ghanbari Ahmadi & Gohari 2019). The decomposition of TC by PMS is shown in Equations (4) and (5).

\[
\begin{align*}
\text{HSO}_5^- + \text{US or UV} & \rightarrow \text{SO}_4^{2-} + \text{OH} \\
\text{HSO}_5^- + \text{metal ion} (\text{M}^n) & \rightarrow \text{M}^{n+1} + \text{SO}_4^{2-} + \text{OH}^n \\
\text{HSO}_5^- + \text{heat} & \rightarrow \text{SO}_4^{2-} + \text{OH} \\
\text{HSO}_5^- + \text{TC} & \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{TC} \\
\text{HSO}_5^- + \text{TC} & \rightarrow \text{SO}_4^{2-} + \text{OH} + \text{TC}^+ 
\end{align*}
\]

Overall, sulfate radical advanced oxidation processes (SR-AOPs) have the following advantages: (1) high performance in a wider range of pH (3–9), (2) higher oxidative potential (2.5–3.1 V), and (3) longer half-life period (30–40 µs) (Gao et al. 2012; Yang et al. 2018). Among AOPs, sonocatalytic systems based on semiconductors typical nano-sonocatalysts (i.e. titanium dioxide (TiO$_2$), zinc oxide (ZnO), cerium oxide (CeO$_2$), etc.) have favorable results in destroying persistent organics (Shen et al. 2020).

Sonocatalytic methods have been studied in various studies using metal oxides under different conditions to eliminate antibiotics (Karimi Fatehifar & Alizadeh 2015). Of those metal oxide catalysts, CeO$_2$ is a suitable activator for PMS (Shen et al. 2020). CeO$_2$ has been widely investigated because of its multiple applications such as in catalysis, as an electrolyte material for solid oxide fuel cells, as a material with a high refractive index, and as an insulating layer on silicon substrates (Wen et al. 2017). CeO$_2$ is abundant, nontoxic, and inexpensive (Saravanakumar Muthupoongodi & Muthuraj 2019; Xing et al. 2019). Therefore, CeO$_2$ can be used in heterogeneous sonocatalysis reactions. Today, the combination of two or three activators is very attractive for wastewater treatment. In this way, the US waves in the presence of CeO$_2$ nanoparticles (NPs) can accelerate PMS activation to produce sulfate radicals.

The current study aims to investigate the ability of the US/PMS/CeO$_2$ sonocatalytic process to remove TC antibiotics from artificial wastewater. In this paper, we demonstrate the effectiveness of the CeO$_2$ NP as a catalyst for TC removal in artificial wastewater. Biosynthesis is a simple method that can be utilized for large-scale production of nanoparticle at low cost. CeO$_2$ nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR) techniques. Reusability of the catalyst and mechanism were also studied. In addition, the effects of pH, catalyst dosage, PMS, TC concentrations, and US power on the removal of TC were studied.

**MATERIAL AND METHODS**

**Materials**

TC hydrochloride [C$_{22}$H$_{25}$N$_2$O$_8$Cl] (AR, 99%) supplied by Sigma-Aldrich Co. (USA) was used to perform sonocatalytic decomposition. The main relevant data for TC are shown in Table 1 (Ao et al. 2019). Oxone (2KHSO$_5$.KHSO$_4$.K$_2$SO$_4$), as the source of PMS, and cerium nitrate (99% pure) were purchased from Sigma-Aldrich Co. (USA). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased.
from Merck, Germany, and used for pH adjustment. Ethanol (EtOH, purity: 99.8%) and tert-butyl alcohol (TBA, purity: > 99.0%), which were used as radical scavenging compounds, were also purchased from Merck. Solutions were prepared daily before the experiments. Distilled water was used throughout the experiment. Preparing *Stevia rebaudiana*  
*S. rebaudiana* leaves were collected from the surrounding areas of Bam, Kerman, Iran, and washed carefully to remove dust particles. Extraction was done by soaking in water. Then, 10 g *S. rebaudiana* leaf powder was dissolved in 100 mL of distilled water and placed on a rotary shaker at 1.6 s⁻¹ for 24 h. The solution was then filtered with Whatman filter paper No. 42. Distilled water was used as a solvent for all described experiments.  

**Synthesis and characterization of CeO₂ NPs**  
CeO₂ NPs were synthesized using cerium nitrate as a salt and prepared plant extract. Briefly, 0.05 M cerium nitrate solution was prepared in deionized water. Then, 50 mL of *S. rebaudiana* leaf extract was added to 50 mL from this solution and stirred for 5 h at 70 °C. Then, the solvent was dried in an oven at 70 °C. Last, the solution was calcined for 5 h at 300, 400, 500, 600, and 700 °C, leaving yellow-colored CeO₂ NPs. The absorption spectra of bio-synthesized CeO₂ NPs were recorded by a UV–Vis spectrophotometer in the spectral range of 200 to 850 nm. FTIR analysis was carried out in the range of 400 cm⁻¹ to 4,000 cm⁻¹ (Perkin Elmer). The surface morphology of the samples (CeO₂ NPs) was observed by using a TESCAN field emission scanning electron microscope (FESEM, Mira3, Czech Republic). FESEM was used to analyze the morphology and particle size of the as-synthesized CeO₂ NPs. XRD analysis using CuKα radiation (λ = 1.54060 Å) was also performed to show the crystallinity and phase composition of the samples (Philips XRD, Model: PW1750, Holland).  

**Sonocatalytic activity of biogenic CeO₂ NPs**  
The sonocatalytic potential of the as-prepared CeO₂ NPs was investigated by degrading TC antibiotics under the US wave. The experiments were performed using the batch flow mode Erlenmeyer flasks (working volume: 500 mL). To measure the US irradiation emitted, a US probe with a titanium tip (Ti-6Al-4 V, 1 cm diameter) on a digital sonicator (IKA®RW 20), which had a constant frequency of 20 kHz and varied power, was placed at the reactor center 3 cm from the bottom. During sonication, the temperature of solution was kept at 25 ± 2 °C thereby circulating cooling water. The reactor contents were mixed using a mechanical mixer. In this test, PMS as an oxidant and CeO₂ as a catalyst was added to the solution. The experimental set-up was covered to avoid the photocatalysis. The residual of TC concentration was analyzed by a spectrophotometer (Shimadzu, Japan) at the wavelength of 261 nm. The removal efficiency and the adsorption capacity of biogenic CeO₂ NPs were calculated using the following equation:

\[
\text{TC removal efficiency (\%) = } \frac{A_0 - A}{A_0} \times 100\% \tag{6}
\]

where \(A_0\) = sample adsorption rate before testing; and \(A\) = sample adsorption rate after the test (Saadati Keramati & Ghazi 2016).

In this work, the effective parameters in the US/PMS/CeO₂ process were studied separately, including pH, PMS concentration, CeO₂ dosage, antibiotic concentration, and US power to determine the optimum conditions. Moreover, the effect of scavenging agents TBA and EtOH and various chemical oxidants on the degradation rate of TC over US/PMS/CeO₂ were evaluated under optimal operating conditions.

The reusability of CeO₂ was examined for up to five catalytic runs at the optimal parameter. After each run, the used catalysts were filtered and separated using centrifuged (100 s⁻¹, 30 min), and then washed with distilled water and dried in an oven at 60 °C for 6 h. Then, the catalyst was reused with a fresh TC aqueous solution for the next run. Herein, a tentative mechanism was proposed for the sonocatalytic system and the generation of reactive oxidizing species.
RESULT AND DISCUSSION

Characterization of CeO$_2$ NPs

The structure of CeO$_2$ was analyzed using XRD and the results are shown in Figure 1. In that figure, the diffraction peaks are at $2\theta = 28.51^\circ$; 33.02$^\circ$; 47.48$^\circ$; 56.34$^\circ$; 59.09$^\circ$; 69.32$^\circ$; 76.52$^\circ$; 78.97$^\circ$; and 88.21$^\circ$. These peaks correspond to the plane: (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0), and (4 2 2) for face center cubic (fcc) structure in XRD standard pattern for CeO$_2$ (JCPDS No. 43-0394) (Liying et al. 2015; Arunachalam Karpagasundaram & Rajaratnam 2018; Nurhasanah Gunawan & Sutanto 2020). The XRD pattern did not show diffraction peaks which were associated with the other phase. This indicated a single phase of CeO$_2$ (Nadjia et al. 2018; Nurhasanah Gunawan & Sutanto 2020). The high and sharp diffraction peaks demonstrated that CeO$_2$ had good crystallinity.

The SEM image showed that CeO$_2$ consisted of particles in the sphere-like form. It showed that particles were interconnected with each other to form aggregates (Figure 2). The appearance of the aggregates was similar to CeO$_2$ NPs which are synthesized using a precipitation method (Sane et al. 2018).

A histogram of the diameter size distribution of the as-synthesized CeO$_2$ NP is illustrated in Figure 3. Most particles have a diameter in the range of 1–50 nm (in the defined range for nanoparticles). Most of the as-generated particles were smaller than 300 nm, indicating the high surface area along with more reactive sites for generating 'OH radicals to catalytically decompose TC.

FTIR spectra of the synthesized CeO$_2$ NPs are shown in Figure 4. FTIR spectroscopy was used to identify the functional group and also atomic and molecule vibration. The functional group is one of the many factors that affect adsorption efficiency. The FTIR spectrum showed several absorption peaks in the interval of the wavelength of 400 cm$^{-1}$ to 4,000 cm$^{-1}$. The absorption peak at 3,480.29 cm$^{-1}$ confirmed the presence of CeO$_2$ NPs. The absorption range of 3,800–3,000 cm$^{-1}$ corresponded to the O–H stretching frequency. As CeO$_2$ readily traps atmospheric CO$_2$, its corresponding peaks were observed at 2,426 cm$^{-1}$ and 1,385 cm$^{-1}$. The absorption band at 1,542 cm$^{-1}$ and 1,342 cm$^{-1}$ was related to OH-adopted water molecule. An absorption peak at 492 cm$^{-1}$ associated with the vibration of Ce–O indicated the formation of pure CeO$_2$ phase as observed by XRD analysis (Liying et al. 2015). The Ce–O stretching frequency was expected below 400 cm$^{-1}$, but in this study, it was observed at 452 cm$^{-1}$, indicating the formation of CeO$_2$.

Similar observations were reported by Goharshadi et al. where the Ce–O stretching band appeared at 450 cm$^{-1}$ (Goharshadi Samiee & Nancarrow 2011).

Effect of operating parameters on the sonocatalytic degradation of TC

Effect of pH solution

In the sonocatalytic system, the rate of decomposition depended on the pH because the antibiotic uptake capacity on a catalyst is an important factor. The increase in the number of molecules absorbed on the catalyst was due to the increase in the decomposition of the molecule (Zargar Pourreza & Samadifar 2016; Wang et al. 2020). In this study, in order to investigate the effect of pH on sonocatalytic decomposition (condition experiment: 0.6 g/L CeO$_2$ NP dosage, 50 mM PMS concentration, 15 mg/L TC concentration, and US power = 50 W), pH ranges acidic (3), neutral (6), and alkaline (9) were adjusted by adding appropriate amounts of NaOH and HCl (0.1 M). TC degradation performance at different pH is shown in Figure 5(a). The efficiency of TC decomposition at pH values of 3, 6, and 9...
after 120 min reaction was achieved as 77.4, 82.1, and 85.7%, respectively. The pKa value of TC was 3.3, and thus, at pH < 3.3, its molecules were negatively charged, and at pH > 3.3, its molecules were positively charged (Zhu et al. 2022). The pH value dependency can be explained based on the metal oxide zero point charge (pHzpc). The pHzpc of CeO2 was 6.8. For pH values lower than pHzpc, the surface became positively charged; for pH values higher than pHzpc, the CeO2 surface was negatively charged (Zargar Pourreza & Samadifar 2019).

Regarding these conditions, therefore, TC removal can occur effectively when pKaTC < pH < pHzpc can be ascribed to a negatively charged catalyst surface, and is more available for the adsorption of the cationic form of TC molecules (Zhang et al. 2013). Heterogeneous AOPs can be operated in a broad pH range, but always have better performance in neutral conditions (Nurhasanah Gunawan & Sutanto 2020). This has been previously reported in other studies. According to the results, pH 6.0 was selected as the optimal pH for subsequent experiments due to the similarity to the neutral environment, which allowed the process to be used in a real-time destruction process without pre-pH adjustment.

**Effect of initial PMS concentration**

To obtain the optimal concentration of PMS on the removal efficiency, the PMS concentrations of 2, 10, 20, 50, and 80 mM (condition experiment: 0.6 g/L CeO2, 15 mg/L TC, time = 120 min, US power = 50 W) were investigated. As shown in Figure 5(b), the efficiency of TC removal increased rapidly with increasing the concentration of PMS from 2 to 50 mM. After 120 min of contact time, the TC removal efficiency was about 83% when the PMS concentration was 50 mM. However, by increasing the concentrations of PMS from 50 to 80 mM, the removal efficiency decreased. Excessive chemical oxidant dosage has been reported to have an unfavorable effect on the performance of AOPs. The maximum removal efficiency was obtained at the PMS concentration of 50 mM. Increasing the removal efficiency by increasing the concentration of PMS was due to the fact that, by increasing the concentration of PMS in the solution, the sulfate radical that plays a major role in the decomposition of antibiotics and other pollutants also increased (Cao et al. 2013; Li et al. 2019). In some studies, increasing the sulfate radical beyond a certain concentration does not affect the removal efficiency, which has been attributed to the recombination of sulfate radicals. In other words, when concentration exceeds a certain limit, the PMS removes the radical hydroxyl (by recombining them) and produces low reactivity radicals (Wang & Wang 2012; Luo et al. 2019).

**Effects of CeO2 NP dosage**

In this study, the sonocatalytic degradation of TC at different doses of CeO2 NPs between 0.2 and 0.8 g/L was investigated. Figure 5(c) shows that by increasing the CeO2 NPs to 0.6 g/L, the removal efficiency of TC increased and, in quantities greater than 0.6 g/L, the removal efficiency decreased. An increase in the rate of antibiotic degradation may be due to
an increase in the number of active sites available on the surface of CeO$_2$, which could expedite reactions to produce more free radicals, resulting in an increase in the number of antibiotic molecules absorbed at the catalyst level (Yi et al. 2012; Guan et al. 2013). At a concentration greater than 0.6 g/L of catalyst, the rate of antibiotic degradation decreased due to density, reduction of penetration depth, and scattering of efficiency radiation. Also, the lower degradation efficiency for higher CeO$_2$ dosage (0.6 g/L) can be explained by insufficient consumption of PMS due to the agglomeration of catalysts (Shen et al. 2020). Hence, the optimum catalyst dosage was selected as 0.6 g/L for TC degradation. To prevent unnecessary catalyst loss, it is important to avoid adding more than the optimal amount of catalyst for sonocatalytic analysis (Tizhoosh et al. 2020). The stabilization of the removal efficiency of pollutants with a further increase in CeO$_2$ catalyst may also be because the Ce$^{2+}$ plays the role of scavenger for sulfate radicals at high concentrations. Pouretedal et al. (Pouretedal & Kadkhodaie 2010) found that the CeO$_2$ activated sunlight irradiation was effective at 1 g/L with 90.6% methylene blue (20 mg/L) removal after 125 min.

**Effect of initial TC concentration**

The effect of the initial concentration of TC (15–70 mg/L) on the efficiency of the process is shown in Figure 5(d). With increasing the TC concentration, the removal efficiency of this process declined. Generally, the rate of degradation decreased with increasing initial TC concentration. The removal efficiency obtained was 85, 72, 68, and 59% for 15, 30, 50, and 70 mg/L TC, respectively,
after 120 min of treatment. Three factors reduced the efficiency of degradation by increasing the antibiotic concentration: (1) the increase in the number of antibiotic molecules adsorbed on the surface of the catalyst led to a decrease in the number of active sites that generated hydroxyl and sulfate radicals (Yi et al. 2018); (2) the production rate of free reactive species in the system was constant, therefore, they would not be able to degrade all the pollutant (Ghanbari Ahmadi & Gohari 2019); and (3) intense competition was formed between primary compounds and by-products to react with oxidizing species at higher concentrations of pollutants (Isari et al. 2020).

**Effect of US power**

The effect of intensity of US irradiation using the US/PMS/CeO₂ system on TC degradation rate as another affecting operational factor was evaluated at 30, 50, and 70 W in optimal conditions. The results are presented in Figure 5(e). An increasing trend in antibiotic degradation was observed with enhancement in intensity of the US. When the US power was increased from 30 to 70 W, the decontamination percentage accelerated substantially from 74.1 to 92.6%. As shown in the literature, improvement in the intensity of ultrasound can effectively increase the amount of US energy transferred to the system and result in enhancing the collapse of cavitation bubbles and forming more reactive oxidizing radicals (Hou Zhang & Xue 2012). On the other hand, this result can be described by the fact that the improvement of the US intensity increases the catalytic activities and available catalyst surface area due to cleansing the catalyst surface from aggregated particles by microstreaming of US irradiation (Nasserì et al. 2017). According to the maximum removal percentage, 70 W of US power was used as their optimum intensity for further experiments.

Some studies show that increasing the US power beyond the optimal amount reduces the removal efficiency. It can be deduced that at high US power, a portion of US power would be consumed and converted into heat because of the scattering effect (Malakotian et al. 2019).

**Effect of radical scavengers**

In order to investigate free radicals on TC degradation using the US/PMS/CeO₂ process, tests in the presence of TBA and EtOH scavengers were performed. Results with the quenching agents are shown in Figure 6. Two quencher agents, including TBA and EtOH, were used at a concentration of 100 mM. The scavenging rate constants for EtOH varied from 1.2 to 2.8 × 10⁹ M⁻¹ s⁻¹ for OH and from 1.6 to 7.7 × 10⁷ M⁻¹ s⁻¹ for SO₄²⁻. For TBA, the rate constant was approximately 1,000-fold greater for OH (5.8 to 7.6 × 10⁸ M⁻¹ s⁻¹) than that for SO₄²⁻ (4 to 9.1 × 10⁵ M⁻¹ s⁻¹) (Yin et al. 2018a).

The ratio of scavenging rates of oxidant radicals by EtOH and TBA varied between 1.5 and ~3.5 for OH radicals and between ~18 and 200 for SO₄²⁻ radicals. TBA was used as a specific scavenger of holes and ‘OH, while EtOH was applied to quench ‘OH and dioxygen (O₂) (Li et al. 2019; Yan et al. 2019). From these results, holes, ‘OH, SO₄²⁻, and O₂ species, were contributed during TC degradation in the US/PMS/CeO₂ system. TC degradation in the presence of TBA and EtOH was reported as 68% and 46%, respectively. TC degradation was much higher in the presence of TBA than for EtOH. Therefore, in the sonolytic US/PMS/CeO₂ system, the sulfate, and hydroxyl radicals were the oxidizing and destroying agents of TC. PMS can also produce sulfate radicals during the direct sonolysis reaction, which allows TC to absorb free radical species to produce intermediate products and complete the mineralization.

**Comparison of the efficiency of alternative processes for TC degradation**

In order to verify the efficiency of the process of US/PMS/CeO₂ against US alone, PMS alone, CeO₂ alone, PMS/US, and CeO₂/US, the CeO₂/PMS processes were tested for tetracycline antibiotic removal under similar conditions (Figure 7). The results showed that the use of the US alone, PMS alone, and CeO₂ alone had a slight effect on TC removal, which could be related to the absence of hydroxyl and sulfate radical production. The results showed that US waves alone could remove only 12.5% of antibiotics because of the low production of the hydroxyl radicals. Some studies show that increasing the US power beyond the optimal amount reduces the removal efficiency. It can be deduced that at high US power, a portion of US power would be consumed and converted into heat because of the scattering effect (Malakotian et al. 2019).
radical (·OH). The application of PMS alone (50 mM) induced about 21% antibiotic removal as the result of direct oxidation by PMS. In the CeO₂-only process (0.6 g/L), about 30.12% antibiotic removal was obtained due to adsorption on the catalyst surface. The combined process of US waves with catalysts (US/CeO₂) had low efficiency (58%) due to its low ability to produce reactive radicals. The US/PMS process had the removal efficiency of 40.11%, which was due to the breaking of the O–O band in PMS and producing radicals by US waves (Equations (7)–(9)) (Feizi et al. 2019). When PMS was combined with CeO₂, it was able to remove 25% of the antibiotic. In fact, Ce²⁺ was the main activator of PMS for sulfate radical production. The highest removal efficiency was associated with the US/PMS/CeO₂ system with a removal efficiency of 92.6%. This high performance of the US/PMS/CeO₂ system can be explained by: (1) the simultaneous existence of both catalytic oxidation and adsorption in the system, (2) the presence of several PMS activators (i.e. US and Ce²⁺), which could lead to the efficient decomposition of PMS molecules and generation of more reactive species (hydroxyl and sulfate radicals), and (3) the synergistic effect among the techniques applied for PMS activation (Ghanbari Ahmadi & Gohari 2019). In relation to the high adsorption capacity and the excellent catalytic potential of the as-synthesized catalyst in coupling the US into PMS activation, the US/PMS/CeO₂ process was selected as the best method for the subsequent experiments of TC degradation.

\[
\text{HSO}_5 + \text{US} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} \tag{7}
\]

\[
\text{H}_2\text{O} + \rightarrow \cdot \text{OH} + \text{H}^* \tag{8}
\]

\[
\text{HSO}_5 + \text{H}^* \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} \tag{9}
\]

**Effect of reusability of CeO₂ for sonocatalytic degradation**

Recycling tests were performed to evaluate the reusability potential of an as-prepared catalyst (biogenic CeO₂) in the US/PMS/CeO₂ system for five consecutive cycles without any chemical/physical modification. For supported heterogeneous catalysts, reusability is of fundamental importance in practical applications. Figure 8 shows the effects of the reusability of CeO₂ NPs in the sonocatalytic process of TC degradation. As shown in Figure 8, CeO₂ exhibited a similar catalytic activity during five cycles and more than 86% of TC was removed after five cycles. The study showed that the rate of sonocatalytic analysis of CeO₂ in the first stage was higher than that in the subsequent stages, which can cause a decrease in activity due to the accumulation and deposition of antibiotics around CeO₂ (Fadzeelah et al. 2019). Today, one of the strategies for industrial wastewater treatment is to focus on developing environmentally friendly technology. Reusing CeO₂ is a good and suitable suggestion for treating sustainable wastewater because it has been
demonstrated that the catalyst can be reused after the sonocatalytic treatment process.

### Degradation kinetics

The effect of experimental operating variables on the TC degradation by the US/PMS/CeO₂ process was performed in a batch environment. Different types of kinetic models for the US/PMS/CeO₂ process were studied (Table 2). The best fit was considered for the model with the highest value of linear regression coefficient (R²). The experimental results indicated that the TC degradation using the US/PMS/CeO₂ process followed the zero-order kinetic model. To evaluate the removal coefficient, Equation (10) was used for the zero-order model:

\[ C_t = C_0 - k_{obs} t \]  

(10)

where \( C_0, C_t \), and \( k_{obs} \) represent the initial TC concentration (mg/L), TC concentration (mg/L) at a specific reaction time, and constant reaction rate (mg/L.min), respectively (Nasseri et al. 2017).

### Comparison of PMS with persulfate and hydrogen peroxide

PMS (HSO₅⁻), hydrogen peroxide (HP), and persulfate (PS, S₂O₈²⁻) have been widely used for degrading and treating several organic pollutants and contaminated water. In this step, the performance of the US/CeO₂ system in TC degradation was evaluated in the presence of 50 mM of various chemical oxidants. The experiments were conducted under optimum conditions over 120-min reaction time. The process efficiency was calculated and compared as follows:

US/PMS/CeO₂ > US/PS/CeO₂ > US/HP/CeO₂

The removal efficiency of antibiotics by process US/PMS/CeO₂, US/PS/CeO₂, and US/HP/CeO₂ was 92.6, 89.1, and 83%, respectively. This significant increase can be expressed by a significant increase in the production rate of reactive species in the system and, consequently, the further degradation of contaminant molecules. Here, additional free radicals can be formed by: (1) decomposition of oxidants by US irradiations (Equation (11)) and (2) reaction between transition metal ions (Ce²⁺) on CeO₂ NPs and oxidants (Equation (12)) (Wang & Wang 2018; Kakavandi et al. 2019).

\[ \text{HSO}_5^- / S_2 O_8^{2-} / H_2O_2 + \text{US wave} \rightarrow SO_4^{2-} / ^*OH \]  

(11)

\[ \text{HSO}_5^- / S_2 O_8^{2-} / H_2O_2 + \text{Ce}^{2+} \rightarrow SO_4^{2-} / ^*OH \]  

(12)

Therefore, it is obvious that H₂O₂ and PS cannot be activated completely on the CeO₂ surface.

Activating PS and H₂O₂ by CeO₂ may occur during the high dosage of PS and H₂O₂ and prolonged reaction times. The symmetrical structure of H₂O₂ and PS can be a logical reason for this resistance to activation. In fact, it is more difficult to separate the O–O bond in PS and H₂O₂ than PMS (Feizi et al. 2019).

### Probable mechanism for sonodegradation of TC using synthesized CeO₂ NPs

The sonocatalytic reaction mechanism of biosynthesized CeO₂ NPs is shown in Equations (13)–(24). When the surface of the CeO₂ NPs irradiate US waves, the electron (e⁻) from the valence band of CeO₂ moves to the conduction band leaving a hole (h⁺) in the valence band. The holes (h⁺) act as an oxidizing agent and oxidize the pollutant directly, or they may react with water to provide hydroxyl radicals. The electron (e⁻) in the conduction band performs as a reducing agent to reduce the oxygen adsorbed on the surface of the CeO₂ sonocatalyst (Pourteadal & Kadkhodaei 2010; Niu et al. 2020). Furthermore, after irradiation, the antibiotic becomes excited and the excited antibiotic injects an electron into the conduction band of CeO₂ and is scavenged by pre-adsorbed oxygen to form active oxygen radicals. These generated active radicals drive the sono degradation process. The CeO₂ NPs play an important role as an electron carrier. Such assisted sonocatalytic processes provide an attractive path for treating antibiotics under US wave (Fadzeelah et al. 2019). The reasonable mechanism for the sonocatalytic degradation of TC antibiotics is schematically

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**Table 2** | The equations and constants of kinetic models of TC degradation using the US/PMS/CeO₂ process at optimum conditions

| Kinetic models | R²     | kₘₐₓ (mg/L.min) | Line equations          |
|---------------|--------|----------------|-------------------------|
| Zero-order    | 0.9866 | –0.073         | \( y = -0.073x + 9.4665 \) |
| First-order   | 0.9711 | 0.0188         | \( y = 0.0188x + 0.1845 \) |
| Second-order  | 0.9315 | 0.0017         | \( y = 0.0017x + 0.0365 \) |
shown in Figure 9.

\[
\text{CeO}_2 + \text{hv}(\text{US}) \rightarrow \text{CeO}_2(\text{e}_\text{CB} + \text{h}_\text{VB}^+) \quad (13)
\]

\[
\text{H}_2\text{O} + \text{CeO}_2(h_\text{VB}^+) \rightarrow \text{OH}^- + \text{H}^+ \quad (14)
\]

\[
\text{OH}^- + \text{CeO}_2(h_\text{VB}^+) \rightarrow \cdot \text{OH} \quad (15)
\]

\[
e^- + \text{O}_2 \rightarrow \cdot \text{O}_2^- \quad (16)
\]

\[
\cdot \text{O}_2^- + \text{H}^+ \rightarrow \cdot \text{OOH} \quad (17)
\]

\[
\text{TC} + \text{hv}(\text{US}) \rightarrow \text{TC}^+ \quad (18)
\]

\[
\text{TC}^+ + \text{CeO}_2 \rightarrow \text{TC} + \text{CeO}_2(\text{e}^-) \quad (19)
\]

\[
\text{CeO}_2(\text{e}_\text{CB}) + \text{O}_2 \rightarrow \text{CeO}_2 + \text{O}_2^- \quad (20)
\]

\[
\text{CeO}_2(\text{e}_\text{CB}) + \cdot \text{O}_2^- + \text{H}^+ \rightarrow \text{CeO}_2 + \text{H}_2\text{O}_2 \quad (21)
\]

\[
\text{CeO}_2(\text{e}_\text{CB}) + \text{H}_2\text{O}_2 \rightarrow \text{CeO}_2 + \cdot \text{OH} + \text{OH}^- \quad (22)
\]

\[
\text{H}^+ + \text{TC} \rightarrow \text{degradation products} \quad (23)
\]

\[
\text{TC}^+ + \text{O}_2 \text{or} \cdot \text{OH} \text{or} \cdot \text{O}_2^- \rightarrow \text{degradation products} \quad (24)
\]

**CONCLUSION**

The results obtained in this study indicated that the AOP using PMS and biogenic CeO$_2$ NPs under US waves was a feasible treatment method for TC elimination from the aqueous phase. It is found that the percentage of TC removal increased with a decreased initial TC concentration, and at the higher oxidant and catalyst concentration than its optimum value. The removal efficiency of TC was 92.6% under the optimum oxidation conditions (PMS = 50 mM, TC concentration = 15 mg/L, CeO$_2$ dosage = 0.6 g/L, US power = 70 W, and 120 min time). Biogenic CeO$_2$ was synthesized, suggesting that excellent activity and reusability characteristics were found during the antibiotic decomposition process. Scavenger tests showed that sulfate and hydroxyl radicals were equally responsible for antibiotic degradation. The TC degradation under the US/PMS/CeO$_2$ system followed the zero-order reaction kinetics under optimum conditions.

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**CONFLICT OF INTEREST**

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this article.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.
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