

Synthesising nanocomposite $\text{Co}_2\text{SnO}_4@\text{rGO}$ for peroximonosulphate activation in a hybrid ozonation system to effectively degrade cefalexin from wastewater

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Received 16 September 2022; revised 13 November 2022; accepted 20 November 2022

Abstract:

This study successfully developed $\text{Co}_2\text{SnO}_4@\text{rGO}$ nanocomposites at various composite ratios of Co_2SnO_4 and rGO using the sol-gel method. These nanocomposites were then used as heterogeneous catalysts to activate PMS in the heterogeneous catalytic oxidation of $\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$ as well as the hybrid ozonation system $\text{O}_3/\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$ to degrade cefalexin (CFX). The physical-chemical characteristics of the fabricated catalysts were evaluated through nitrogen adsorption-desorption, SEM images, EDS mapping, and XRD. The catalytic activity of the nanocomposite was investigated in a degradation reaction of CFX from an aqueous solution. Besides this, CFX degradation kinetics were determined by fitting experimental data with a first-order model. The results showed that at the composite ratio of 2- Co_2SnO_4 and 1-rGO for CFX degradation had the highest efficiency reaching 95.07 and 99.07% for $\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$ and $\text{O}_3/\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$ systems, respectively. The degradation of CFX in the $\text{O}_3/\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$ system was higher than that of $\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$. The results were due to a remarkable increase in S_{BET} in 2- $\text{Co}_2\text{SnO}_4@1\text{-rGO}$ compared to both Co_2SnO_4 and rGO, facilitating a catalytic reaction occurring on the catalyst's surface. Moreover, the coupling between O_3 and $\text{Co}_2\text{SnO}_4@\text{rGO}/\text{PMS}$ generated a synergetic effect leading to the generation of more $^{\bullet}\text{SO}_4^-$ and $^{\bullet}\text{OH}$ radicals, which enhanced the CFX degradation rate in the hybrid ozonation system. These primary findings illustrated that the nanocomposite catalyst 2- $\text{Co}_2\text{SnO}_4@1\text{-rGO}$ was feasible for the activation of PMS in hybrid ozonation to effectively degrade antibiotic residues from wastewater.

Keywords: cephalixin, $\text{Co}_2\text{SnO}_4@\text{rGO}$, hybrid ozonation, O_3 , PMS, synthesis.

Classification numbers: 2.2, 5.3

1. Introduction

Today, a large amount of antibiotic residues are being found in natural water bodies such as ponds, lakes, rivers, and effluent after secondary treatment [1]. The discharge from hospital, domestic, livestock, and pharmaceutical wastewater has increased antibiotic residues in these receiving water bodies [2]. The presence of antibiotics in aquatic environments is becoming a major concern around the world due to increases in bacterial resistance towards pharmaceuticals [1]. Penicillin and cephalosporin, a group of β -lactam antibiotics that can break down the synthesis of bacterial cell walls and prevent bacterial growth, have been the most widely used around the world to treat bacterial infections accounting for 50-70% of all antibiotics used [3]. Such high consumption of antibiotics inevitably leads to their release into receiving water bodies [4]. Among the antibiotics from the cephalosporin family, CFX is a systemic antibiotic that is most commonly used to treat

respiratory tract infections, urinary tract infections, and skin and soft tissue infections caused by sensitive bacteria [5, 6]. Besides, CFX possesses a very low biodegradation rate, nearly 10%, with 90% being excreted through urine causing increasing environmental concern of antibiotic resistance [7, 8]. Recent studies have shown that the CFX concentration found in wastewater, surface water, and even sea water ranges from several ng/l to $\mu\text{g/l}$ [9, 10]. The accumulation of CFX in the environment leads to an occurrence of multi-drug resistant pathogens, which have unpredictable impacts on the environment, human health, and other organisms in the ecosystem [11].

Due to the complex chemical structure and antibacterial properties of CFX, conventional wastewater treatments such as physical, chemical, physicochemical, and biological methods are not effective to remove this compound [11, 12]. Meanwhile, advanced oxidation processes using strong oxidant agents such as O_3 , H_2O_2 , and PMS in combination

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with heterogeneous catalysts possess some advantages thanks to generation of free radicals like $^{\bullet}\text{SO}_4^-$, $^{\bullet}\text{OH}$, $^{\bullet}\text{O}_2$, and $^{\bullet}\text{O}_2$. These are very strong oxidation radicals that can oxidize near-persistent organic compounds and antibiotic residues with quick rates and without the formation of by-products. Among these AOPs, advanced sulphate radical ($^{\bullet}\text{SO}_4^-$)-based oxidation processes using heterogeneous catalysts to activate PMS for the generation of $\text{OH}^{\bullet}$, $^{\bullet}\text{SO}_4^-$, and ozonation have been reported effective in the removal of persistent organic compounds. However, using only heterogeneous catalysts/PMS or O_3 to degrade pollutants have several limitations such as high cost, low stability, and slow oxidation rate. Therefore, to remedy these drawbacks, some hybrid ozonation processes have been recently applied such as O_3 /PMS to degrade ibuprofen [13]; O_3 /MnO₂@rGO/PMS for removal of 4-nitrophenol [14]; and O_3 /PMS to treat para-chlorobenzoic acid [15]. The results of these works indicate that all hybrid ozonation systems demonstrate high removal efficiencies of pollutants compared to using oxidation systems alone due to the synergetic effects between O_3 , PMS, and catalysts in the same reactor.

Recently, cobalt-based catalysts have been developed, popularly used, and proven to be the most effective in heterogeneous catalytic systems to activate PMS, thereby promoting the production of $^{\bullet}\text{SO}_4^-$ radicals due to the high activation efficiency of Co on PMS [16]. For example, M. Stoyanova, et al. (2014) [17] applied CoFe₂O₄ to activate PMS for the mineralization of acid orange 7 while others have used MFe₂O₄/PMS for the removal of di-n-butyl phthalate (DBP) (with the highest activation efficiency in the order CoFe₂O₄ > CuFe₂O₄ > MnFe₂O₄ > ZnFe₂O₄) [18]; CoMn₂O₄ - activated PMS for a Fenton-like reaction to degrade organic dyes [19]; and Fe_{0.8}Co_{0.2}O₄ to remove bisphenol A [20]. Co₂SnO₄ was also used to activate PMS for the degradation of rhodamine B and pentachlorophenol with complete removal of both rhodamine B and pentachlorophenol in a 10 - min reaction [21]. However, cobalt oxide exhibits a disadvantage due to the leakage of metal Co into the water after catalysis, especially under acidic conditions [22]. Therefore, to prevent leakage of Co, a cobalt oxide catalyst can be composited with other metal oxides [23], magnetic molecules [24], biochar [25, 26], or graphite (GO, rGO) [27]. Indeed, compositing metal oxides with graphite is considered effective for the prevention of the abovementioned catalyst drawbacks. Among such nanocomposites, the transition metal cobalt has been the most effectively and widely used. For instance, a composite catalyst of nano-CoFe₂O₄ and graphite (CoFe₂O₄@GO) has

been synthesised to degrade amoxicillin (AMX) from water [28]. The results showed that possessed good magnetic properties and was quickly separated from the aqueous medium after the reaction. CoFe₂O₄@GO also exhibits a rather good catalytic activity in the activation of PMS to produce $^{\bullet}\text{SO}_4^-$. To be specific, at optimal conditions, 99.27, 83.1, and 61.11% of AMX, COD, and TOC were removed after 60 min of reaction, respectively [28]. CoFe₂O₄@GO was also used for the activation of PMS in the degradation of RB5 [29] and RB [30]. A hybrid nanocomposite of reduced graphite oxide rGO and CoFe₂O₄ (CoFe₂O₄/rGO) for the activation of PMS for phenol degradation has also been performed [31]. Indeed, catalytic testing showed that CoFe₂O₄/rGO exhibits much better catalytic activity compared with CoFe₂O₄, indicating that rGO plays an important role in the CoFe₂O₄/rGO hybrid-nanocomposite for the degradation of phenol. In the $^{\bullet}\text{SO}_4^-$ -based heterogeneous catalytic system for the degradation of on organic pollutants, CoFe₂O₄/rGO was synthesised using a surface hydrothermal method to activate PMS to degrade phenol with a high degradation efficiency thanks to its large specific surface and 3D structure that promotes mass transfer and dispersion of the catalytic sites on the surface of the CoFe₂O₄/rGO aerogel [32].

However, rapid oxidation rates cannot be achieved if PMS, PMS activated by catalysts, or ozonation are used separately. Therefore, hybrid processes between O_3 and PMS-activated heterogeneous catalysts are advantageous in the decomposition of difficult-to-biodegrade organic matters due to the creation of synergistic effects that accelerate the decomposition rate of organic pollutants and increase the efficiency of PMS use, which then reduces the dose of PMS necessary for decomposition. The addition of O_3 to a heterogeneous catalytic system has been shown to increase the activation of PMS and generate both $^{\bullet}\text{OH}$ and $^{\bullet}\text{SO}_4^-$ free radicals. However, studies of this hybrid technology in the treatment of difficult-to-biodegrade organic compounds are rare, especially in the treatment of antibiotic residues. Therefore, the aim of this study was to fabricate a nanocomposite catalyst based on a composite of Co₂SnO₄ and rGO, which was used to activate PMS in a hybrid ozonation system for the enhanced degradation of CFX from wastewater. To reach this aim, this study focused on investigating the most suitable conditions for the synthesis of Co₂SnO₄@rGO and using Co₂SnO₄@rGO as a heterogeneous catalyst to activate PMS in a hybrid ozonation system for the degradation of CFX from water medium.

2. Materials and methods

2.1. Chemicals and materials

All chemicals including KMnO_4 , H_2SO_4 , H_2O_2 (30%), HCl , CoCl_2 , SnCl_4 , ethylene glycol, and NaOH were purchased from Kyamata (Japan). NaBH_4 and CFX ($\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$) were obtained from Sigma Aldrich (Germany). Graphite used for the fabrication of rGO was purchased from Merck (Germany). All chemicals were used as received without further purification.

2.2. Preparation of catalyst materials

In this study, the synthesis procedure of the nanocomposite $\text{Co}_2\text{SnO}_4@\text{rGO}$ consisted of two main steps:

(1) Firstly, Co_2SnO_4 NPs and GO were synthesised separately according to the method modified from W.S. Hummers and R.E. Offeman (1958) [33].

Synthesis of GO: Graphene oxide was prepared from natural graphite powder and exfoliated by common chemical agents according to the modified Hummers method. In the first step of the procedure, 3 g of graphite was placed into a beaker containing 150 ml of 98% sulfuric acid, which was cooled in an ice bath ($3\text{--}5^\circ\text{C}$) and completely agitated. Next, 10.5 g of KMnO_4 was gradually added into the mixture for 20 min with stirring for a further 20 min. The mixture was then cooled to room temperature and stirred for 72 h. Following that, 250 ml distilled water and 5 ml of 30% H_2O_2 were supplemented in the mixture to achieve a yellow solution. The obtained solid was filtered and repeatedly washed with 3% HCl and distilled water. Finally, the obtained graphene oxide was dispersed overnight into distilled water, reduced metal ions, and protons using a dialysis bag and stored in the dark.

Synthesis of Co_2SnO_4 NPs: The magnetic Co_2SnO_4 NPs were synthesised using the sol-gel method. Firstly, 93 g of citric acid was poured in a beaker containing 100 ml of

distilled water and agitated in a magnetic stirrer at 120 rpm under 60°C for 15 min to obtain a clear liquid. In the next step, a mixture of 0.36 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.63 g $\text{SnCl}_4 \cdot 6\text{H}_2\text{O}$, and 40 ml ethylene glycol was added in the above beaker and heated to 80°C until the mixture completely dissolved. Then, the mixture was heated up to 130°C to obtain a gel mixture. The gel mixture was heated up to 150°C for 12 h until it became a completely dry solid. The solid was baked at 300°C for 3 h under oxygen conditions. Finally, the obtained solid was then furnace to 1000°C for a further 2 h and cooled to room temperature ($25 \pm 2^\circ\text{C}$). The obtained black solid were Co_2SnO_4 NPs and were stored in sealed plastic bags to use as a precursor for the synthesis of nanocomposite $\text{Co}_2\text{SnO}_4@\text{rGO}$.

(2) Synthesising nanocomposite $\text{Co}_2\text{SnO}_4@\text{rGO}$: The $\text{Co}_2\text{SnO}_4@\text{rGO}$ at various ratios were prepared using Co_2SnO_4 NPs and GO, which were achieved from the abovementioned procedures. At the beginning of the procedure, a certain amount of GO was dispersed in a beaker containing 20 ml deionised water and sonicated for 60 min. Then, a pre-determined amount of Co_2SnO_4 NPs were also dispersed into the beaker and sonicated for a further 30 min. Afterwards, 10 ml of 0.1 M NaBH_4 was gradually added to the mixture. The mixture was sonicated for a further 30 min. Finally, the achieved precipitate was separated by filtration or centrifugation and cleaned by deionised water and ethanol several times. The precipitate was then vacuumed at 80°C for 6 h. The obtained product was the $\text{Co}_2\text{SnO}_4@\text{rGO}$ nanocomposite at different composite ratios. The products were stored in sealed plastic bags and labelled as 1- $\text{Co}_2\text{SnO}_4@1\text{-rGO}$; 2- $\text{Co}_2\text{SnO}_4@1\text{-rGO}$; 3- $\text{Co}_2\text{SnO}_4@1\text{-rGO}$; 1- $\text{Co}_2\text{SnO}_4@2\text{-rGO}$; and 1- $\text{Co}_2\text{SnO}_4@3\text{-rGO}$ for use in the following experiments. The synthesis procedure of the $\text{Co}_2\text{SnO}_4@\text{rGO}$ nanocomposite is summarized in Fig. 1.

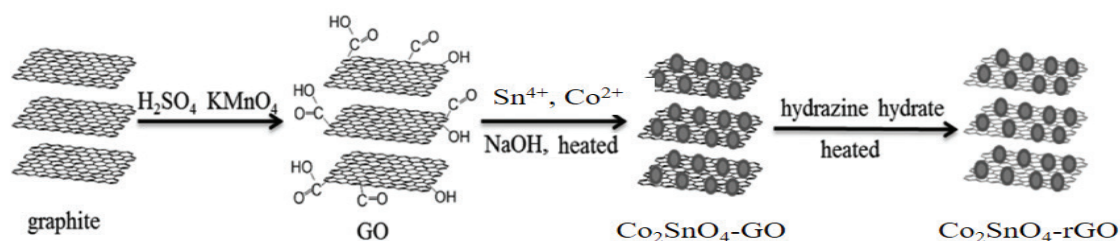


Fig. 1. Schematic description of the synthesis of $\text{Co}_2\text{SnO}_4@\text{rGO}$ nanocomposites.

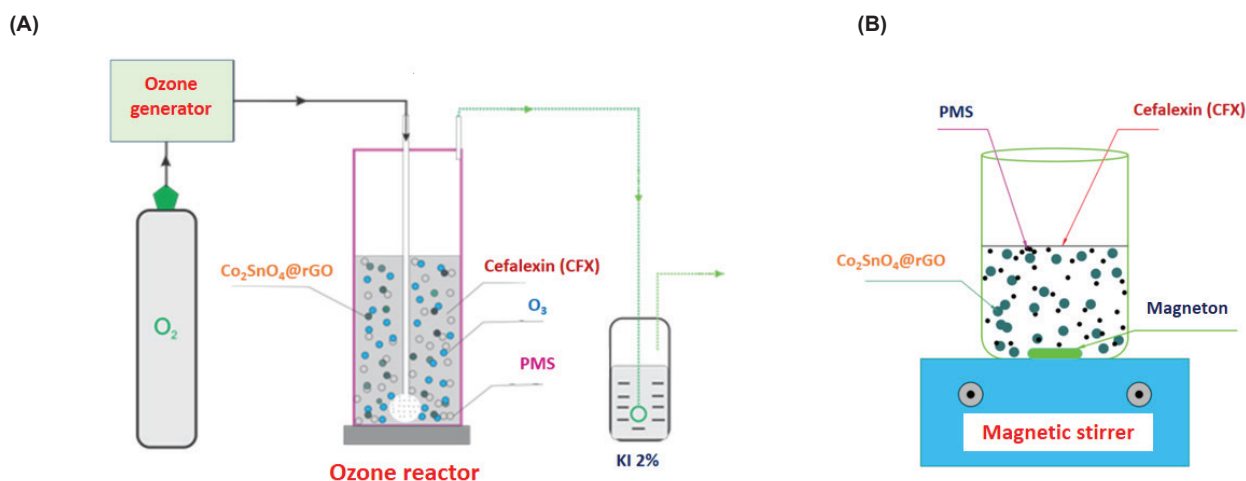


Fig. 2. Scheme of degradation of CFX by O₃/Co₂SnO₄/PMS (A) and Co₂SnO₄/PMS (B).

2.3. Catalytic activity measurement

In this study, CFX was the target pollutant. The CFX degradation experiments were conducted with initial conditions of: CFX concentration of 100 mg/l, pH of 7, catalyst dosage of 0.3 g/l, and PMS dosage of 300 mg/l using Co₂SnO₄@rGO at various composite ratios. All experiments were performed in batch mode. The scheme of CFX degradation by O₃/Co₂SnO₄/PMS and Co₂SnO₄/PMS systems are shown in Fig. 2.

In the O₃/Co₂SnO₄/PMS system, ozone is produced by an ozone generator (NextOzone 20P, Sinh Phu Joint Stock Company, Vietnam). The maximum capacity of O₃ and input O₂ capacity at a flow of 15 ml/min were 5.0 and 3.038 g/h, respectively. The oxygen provided for the O₃ generator was from a pure oxygen container. O₃ is constantly produced and allocated into a tubular borosilicate glass reactor with a height of 450 mm and a diameter of 60 mm through a bubble air stone located at the bottom of the container.

In the Co₂SnO₄/PMS system, the experimental model was set up using a beaker with a volume of 1000 ml containing 500 ml of CFX solution at 100 mg/l and the reaction conditions as abovementioned. The reactor was put on a magnetic stirrer and agitated at 120 rpm.

The reaction kinetics of CFX degradation on the nano-hybrid systems followed a first-order kinetic model (Eq. 1):

$$\ln \frac{C_t}{C_o} = -k_d t$$

where C_t is the left concentration of CFX at time t ; C_o is the initial concentration of CFX, and k_d is the first-order reaction rate constant. By plotting $-\ln(C_t/C_o)$ verse time, k_d and R^2 are determined.

In both reaction systems, the sample was taken out at 40-min intervals to determine the quantity of CFX remaining after reaction.

The CFX removal experiments were triplicated. The results were expressed as average value $\pm$ standard deviation.

2.4. Analysis method

The textural characteristic of materials was analysed using N₂ adsorption-desorption isotherms at 77 K (Quantachrome Instruments version 11.0-NOVA). SEM images were applied to observe the morphology of the catalysts using a Hitachi S-4800 (Japan). The EDX data and mapping data were analysed by X-ray energy-dispersive spectroscopy using the JSM-IT200 (InTouchScop). The phase composition and crystal structure of the nanomaterials at various composite ratios were measured by X-ray diffraction with a scanning speed of 1.25°/min at 2 θ angles between 20 and 80° using a Bruker D8 device with Cu K α emission ($\lambda=0.1540$ nm).

The degree of CFX degradation was measured using UV-Vis (Shimadzu, model Z2000, Japan) at $\lambda=262$ nm. The pH was measured with a pH meter (HANNA, pH HI 2211-02, Romani).

3. Results and discussion

3.1. Characteristics of catalysts

The textural characteristics of the catalysts are presented in Table 1. As can be seen from the data in Table 1, composites of Co₂SnO₄ nanoparticles and rGO led to a remarkable change in the structure of the catalyst. Specifically, at a composite ratio of 2-Co₂SnO₄ and 1-rGO, the S_{BET} of was increased about 17 and 3.9 times compared with Co₂SnO₄ and GO, respectively. Specifically, the S_{BET} of Co₂SnO₄ was 25.43 m²/g, which agreed with previous work reported by M.B. Ali, et al. (2017) [34]. These results illustrate that the existence of rGO effectively improved the surface property of 2-Co₂SnO₄@1-rGO. The growth of S_{BET} after compositing could be because GO possesses a very large specific surface area in its inherent nature and plays the role of support for Co₂SnO₄. According to IUPAC

Table 1. Nitrogen adsorption-desorption isotherm data of materials.

	Unit	Co ₂ SnO ₄	GO	2-Co ₂ SnO ₄ @1-rGO
S _{BET}	m ² /g	25.43	112.9	435.432
V _{pore}	cm ³ /g	0.087	0.412	0.383
D _{pore}	nm	0.07	0.94	0.127

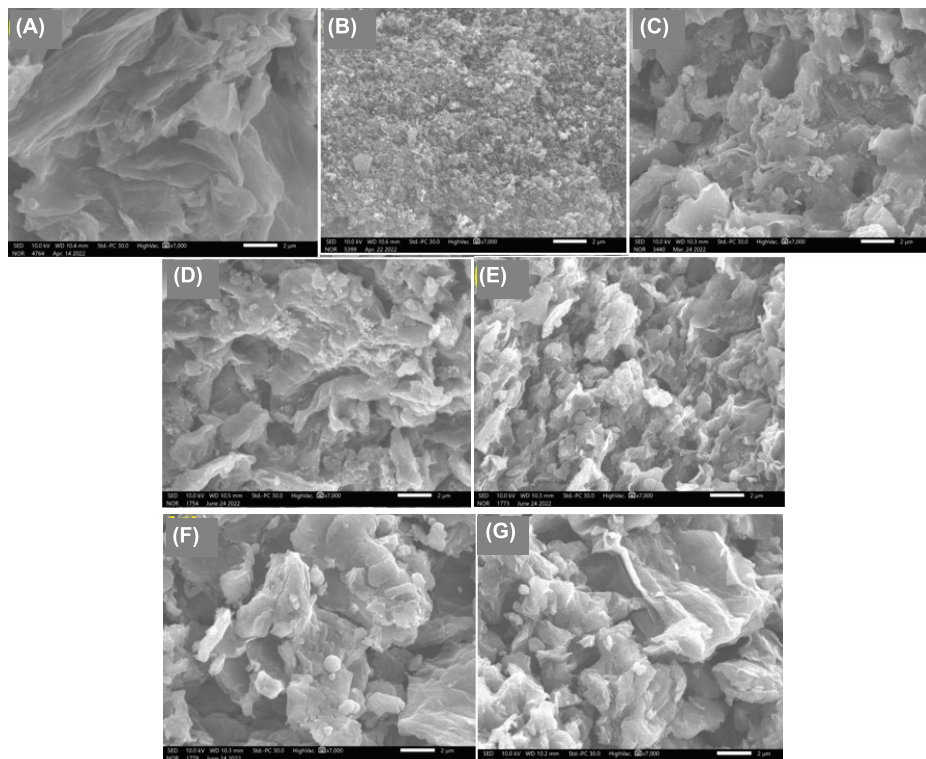


Fig. 3. SEM images of Co₂SnO₄@rGO at various modification ratios. (A) GO, (B) Co₂SnO₄, (C) 1-Co₂SnO₄@1-rGO, (D) 2-Co₂SnO₄@1-rGO, (E) 3-Co₂SnO₄@1-rGO, (F) 1-Co₂SnO₄@2-rGO, (G) 1-Co₂SnO₄@3-rGO.

classification, the 2-Co₂SnO₄@1-rGO nanohybrid had a type-IV isotherm with an H3 hysteresis loop, showing its mesoporous nature. The S_{BET} of 2-Co₂SnO₄@1-rGO was calculated to be 335.432 m²/g. A similar result was obtained by A.H. Mady, et al. (2019) [27] when compositing γ -MnO₂@ZnFe₂O₄ with rGO with an S_{BET} of 376.88 m²/g. The high surface area provides more adsorption/reaction sites for the activation of PMS during the catalytic reaction, leading to higher catalytic activity.

The morphologies of Co₂SnO₄@rGO at various composite ratios were observed using SEM. The results are demonstrated in Fig. 3. From Fig. 3A, the SEM image of GO showed a regular lamellar structure with drapes of GO. Meanwhile, Fig. 2B displays a typical SEM image of Co₂SnO₄, which indicates particles in an aggregated form with a formation of spherical and cubic nanoparticles. Besides, it is clear that most of the NPs had uniform crystallite size.

Figs. 3C-3F, G indicate the morphology of Co₂SnO₄@rGO at various composite ratios. The SEM results showed that Co₂SnO₄@rGO possessed a heterogamous structure with rough surface and Co₂SnO₄ nanoparticles appeared on the surface of nanocomposite. Besides, the transparent silk yarn lamella structure of graphene is more obvious when the GO dosage was increased (Figs. 3E, 3F). Especially, the spherical Co₂SnO₄ particles were more homogeneously loaded on the surface and edges of rGO (Fig. 3D) and the particle size is smaller than those in Fig. 3B, which suggests that agglomeration has been weakened due to the effective fixation and dispersion of rGO on the surface of the Co₂SnO₄ particles. Therefore, it was concluded that the optimum loading ratio of Co₂SnO₄ and rGO was 2:1.

The EDX spectrum of the GO, Co₂SnO₄ NPs, and Co₂SnO₄@rGO at various composite ratios (Fig. 4) essentially show the presence of Co, Sn, C, and O elements indicating good purity of the as-prepared materials. Besides, mapping data also showed a distribution of the constituent elements of Co₂SnO₄@rGO (Fig. 4H). When increasing the composite ratio of Co₂SnO₄, the amounts of Co and Sn elements of Co₂SnO₄@rGO also grew (Figs. 4C-4E). Especially at a composite ratio of 2-Co₂SnO₄ and 1-rGO (Fig. 4D), the amount of Co was the highest. However, when rGO was increased, almost no Co or Sn elements were found in Co₂SnO₄@rGO. The transition metal Co has been proven to effectively activate PMS in catalytic reactions for the degradation of persistent organic compounds. Thus, the Co₂SnO₄@rGO catalyst at a composite ratio of 2-Co₂SnO₄ and 1-rGO was the optimal ratio and used for the rest of this study.

Figure 5 depicts typical XRD patterns of GO, Co₂SnO₄ NPs, and Co₂SnO₄@rGO at various composite ratios synthesised by the sol-gel method. Clearly, the GO pattern has a typical peak at 9.7° corresponding to the (001) crystal plane. However, this characteristic peak was smaller in the Co₂SnO₄@rGO X-ray diffraction and a small diffraction peak appeared at 19°, which suggested that GO was

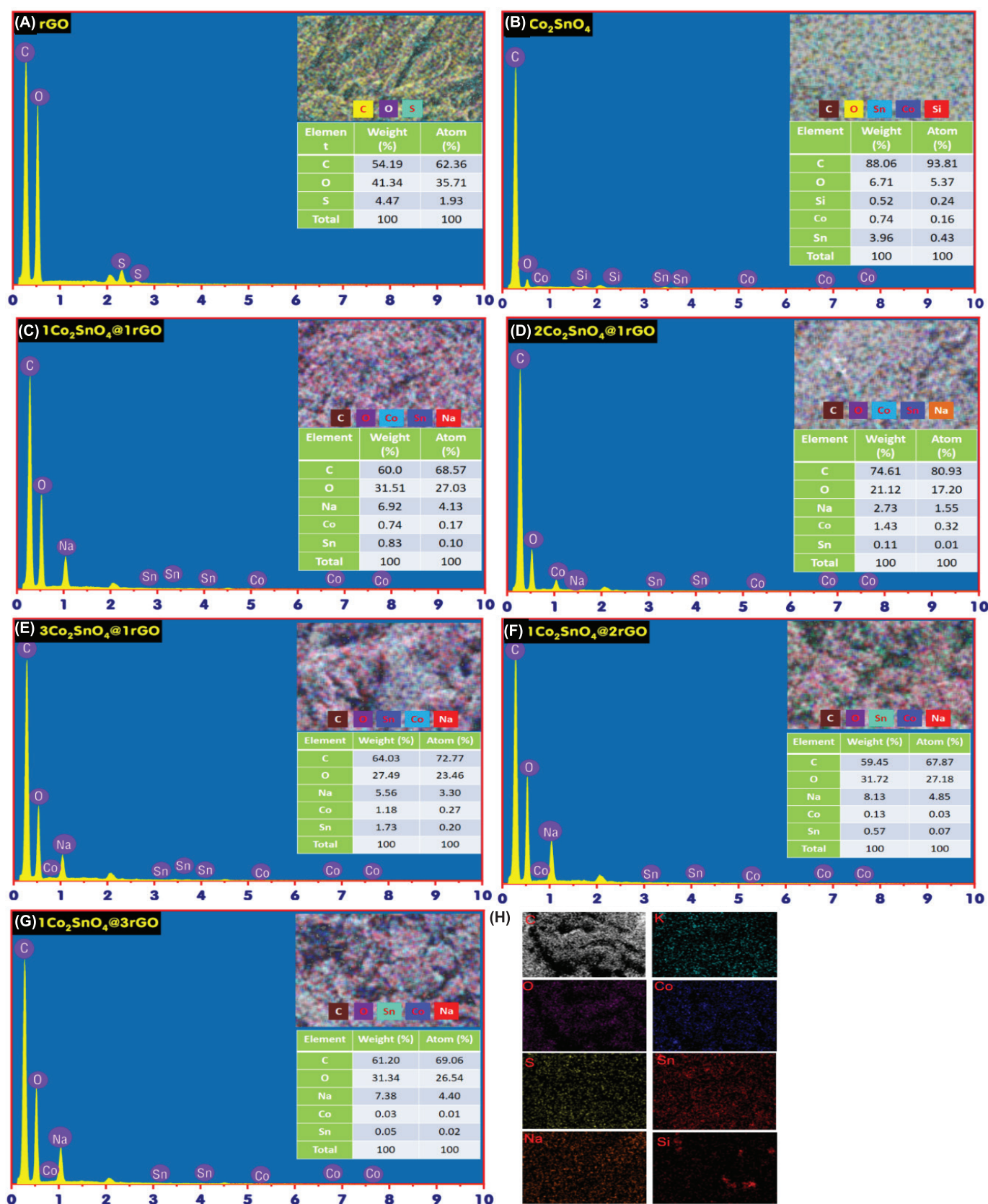


Fig. 4. EDX spectra of Co₂SnO₄@rGO at various modification ratios. (A) rGO, (B) Co₂SnO₄, (C) 1-Co₂SnO₄@1-rGO, (D) 2-Co₂SnO₄@1-rGO, (E) 3-Co₂SnO₄@1-rGO, (F) 1-Co₂SnO₄@2-rGO, (G) 1-Co₂SnO₄@3-rGO, (H) Mapping of Co₂SnO₄@rGO.

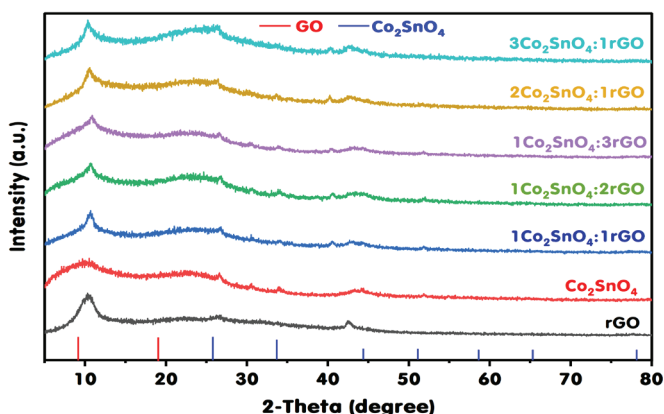


Fig. 5. XRD of catalysts at various modification ratios. (A) rGO, (B) Co_2SnO_4 , (C) $1\text{Co}_2\text{SnO}_4@1\text{rGO}$, (D) $2\text{Co}_2\text{SnO}_4@1\text{rGO}$, (E) $3\text{Co}_2\text{SnO}_4@1\text{rGO}$, (F) $1\text{Co}_2\text{SnO}_4@2\text{rGO}$, (G) $1\text{Co}_2\text{SnO}_4@3\text{rGO}$.

successfully reduced to reduced graphene oxide [35] in the synthesis procedure. The observed diffraction peaks at 26.131° , 34.321° , 35.911° , 44.711° , 51.761° , 57.111° , 66.491° and 78.111° are indexed and well matched to cubic Co_2SnO_4 with the space group $\text{Fd}3\text{m}$ (JCPDS No. 29-0514). The sharp intensity peaks denote the high crystallinity of Co_2SnO_4 . It is worth noticing the presence of small diffraction peaks due to SnO_2 and $\text{CoSn}(\text{OH})_6$.

The diffraction peaks of $\text{Co}_2\text{SnO}_4@r\text{GO}$ at different composite ratios are consistent with that of Co_2SnO_4 indicating that Co_2SnO_4 was basically deposited on the surface of the graphene layer and its crystal form was unchanged during the synthesis. However, the characteristic peak of $\text{Co}_2\text{SnO}_4@r\text{GO}$ at the ratio of 2- Co_2SnO_4 :1-rGO is slightly wider and clearer in comparison with other ratios.

3.2. Catalytic performance of $\text{Co}_2\text{SnO}_4@r\text{GO}$ in the $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ and $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ systems

To assess the catalytic activity of $\text{Co}_2\text{SnO}_4@r\text{GO}$ at various composite ratios for PMS activation in $\text{Co}_2\text{SnO}_4@r\text{GO}$, $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$, and $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ systems, degradation experiments of CFX were conducted. The experiment to evaluate catalytic performance of the fabricated heterogeneous catalysts to activate PMS in the $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ and $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ systems were conducted with varying composite ratios of $\text{Co}_2\text{SnO}_4:r\text{GO}$, specifically, 1:1, 2:1, 3:1, 1:2, and 1:3 at an initial CFX concentration of 100 mg/l, PMS dosage of 300 mg/l, catalyst dosage of 0.3 g/l, and at a pH of 7. The results are presented in Fig. 6.

What stands out from the data in Figs. 6A, B is that the CFX degradation efficiencies were varied when the compositing ratios were changed. CFX degradation was completely achieved after 40 min of reaction time. The CFX degradation curves for both $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ and $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ systems followed the same trend.

The removal efficiency of CFX reached a peak at a composite ratio of 2- Co_2SnO_4 and 1-rGO in both system (95.07% for $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ and 99.07% for $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$).

The degradation of CFX was the lowest in both systems at a composite ratio of 1- Co_2SnO_4 and 1-rGO reaching 23.2 and 82.0%, respectively, for $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ and $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$. When increasing the amount of rGO, the degradation of CFX increased. The degradation efficiency of CFX in the $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ system was higher than that of $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$, showing a synergetic effect in the hybrid ozonation system for the removal of CFX from wastewater. The results showed that the composite ratio had a significant effect on CFX degradation efficiency in both treatment systems in this study.

Previous works have also suggested that the degradation of CFX by advanced $\text{SO}_4^{\cdot-}$ -based oxidation systems using heterogeneous catalysts for the activation of PMS follows a first-order model [28, 34]. Thus, in this work, the experimental degradation data of CFX at various composite ratios were fit with a first-order model and the obtained results are presented in Table 2. As expected, the R^2 values of the fit were very high. Besides, all k_d values agreed well with degradation results of CFX at various composite ratios between Co_2SnO_4 and rGO as discussed earlier. Among the composite ratios tested, 1- Co_2SnO_4 and 1-rGO was the most effective for degrading CFX. The k_d values were determined to be 0.007, 0.076, 0.033, 0.026, and 0.043 min^{-1} and 0.047, 0.112, 0.560, 0.047, 0.049 min^{-1} corresponded with composite ratios of $1\text{Co}_2\text{SnO}_4@1\text{rGO}$, $2\text{Co}_2\text{SnO}_4@1\text{rGO}$, $3\text{Co}_2\text{SnO}_4@1\text{rGO}$, $1\text{Co}_2\text{SnO}_4@2\text{rGO}$, and $1\text{Co}_2\text{SnO}_4@3\text{rGO}$ for $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ and

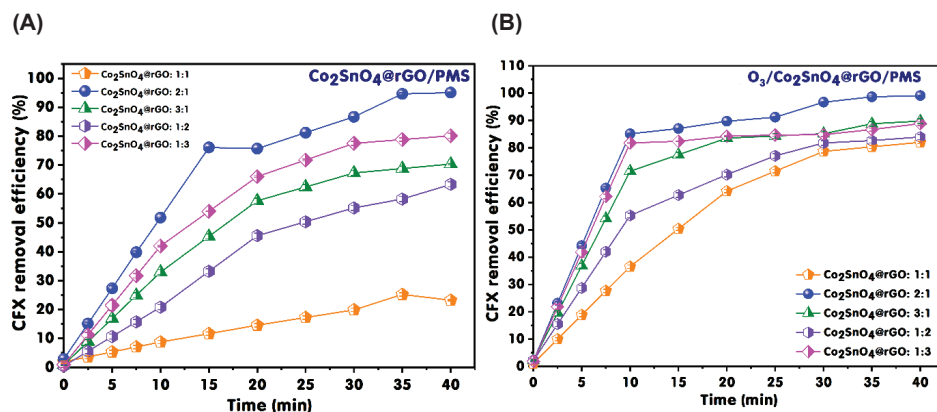


Fig. 6. Time evolution of CFX degradation by $\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ (A) and $\text{O}_3/\text{Co}_2\text{SnO}_4@r\text{GO}/\text{PMS}$ (B) at various modification ratios between Co_2SnO_4 and rGO.

Table 2. Degradation kinetic of CFX by Co₂SnO₄@rGO/PMS and O₃/Co₂SnO₄@rGO/PMS.

Reaction conditions		Co ₂ SnO ₄ @rGO/PMS		O ₃ /Co ₂ SnO ₄ @rGO/PMS	
		<i>k_d</i> (min ⁻¹)	R ²	<i>k_d</i> (min ⁻¹)	R ²
Modification (Co ₂ SnO ₄ @rGO)	1:1	0.007	0.9788	0.047	0.9852
	2:1	0.076	0.9736	0.112	0.9649
	3:1	0.033	0.9656	0.560	0.8984
	1:2	0.026	0.9882	0.047	0.9599
	1:3	0.043	0.9733	0.049	0.7308

O₃/Co₂SnO₄@rGO/PMS, respectively. The *k_d* value reached a peak at a composite ratio of 2-Co₂SnO₄ and 1-rGO for both reaction systems. The *k_d* values in the O₃/Co₂SnO₄@rGO/PMS system were higher than those in Co₂SnO₄@rGO/PMS at all composite ratios. The results showed that in the addition of O₃ into the Co₂SnO₄@rGO/PMS system promoted the degradation rate of CFX thanks to the synergetic effect of O₃ and Co₂SnO₄@rGO/PMS. Besides, the composition of rGO with Co₂SnO₄ nanoparticles remarkably increased the S_{BET} of the nanocomposite, specifically from 112.9 and 25.43 m²/g, respectively, for rGO and Co₂SnO₄ to 435.432 m²/g for 2-Co₂SnO₄@1-rGO. This result proved that the Co₂SnO₄ NPs were successfully loaded onto the surface of rGO. Such a high S_{BET} from the 2-Co₂SnO₄@1-rGO nanocomposite provided more adsorption/catalysis sites for activating PMS during the catalytic process, leading to higher catalytic activities for the degradation of CFX in both systems. Similar results were obtained by previous works. For example, D. Ge, et al. (2016) [36] indicated that the degradation of methyl orange in a O₃/Fe²⁺/PS reactor increased because inlet ozone concentration enhanced the synergistic effect between ozone and persulphate, thus leading to a higher degradation rate of MO. O₃ was also proved to be enhancement of degradation rate of 4-nitrophenol in the O₃/MnO₂/rGO/PMS system thanks to the synergistic effect between catalytic ozonation and the coupling of PMS activation to generate more *SO₄⁻ and *OH radicals, leading to enhancement of pollutants degradation rate [14].

4. Conclusions

In this study, a heterogeneous catalyst derived from a composite of Co₂SnO₄ NPs and rGO at various composite ratios was successfully developed using the sol-gel method. The Co₂SnO₄NPs@rGO at different composite ratios were used to activate PMS in both Co₂SnO₄@rGO/PMS and O₃/Co₂SnO₄@rGO/PMS for the degradation of CFX. The degradation efficiencies of CFX in both systems followed the same trend. However, the removal efficiencies of CFX in hybrid ozonation were higher than those in Co₂SnO₄@rGO/PMS. The degradation of CFX was maximised at a composite ratio of 2-Co₂SnO₄ and 1-rGO. The material characteristics data showed that S_{BET} of the catalyst was

remarkably improved at a composite ratio of 2-Co₂SnO₄ and 1-rGO, which facilitated more active sites on the catalyst to degrade CFX. Besides, the presence of Co in 2-Co₂SnO₄@1-rGO was the highest, leading to an enhancement of PMS activation to produce more *SO₄⁻. Notably, the combination of O₃ in the Co₂SnO₄@rGO/PMS reactor formed a synergetic effect to increase the generation of *OH radicals, leading to the promotion of CFX degradation rate to reach the standards of QCVN 40:2011/BTNMT (Column A).

CRedit author statement

Van Long Nguyen: Conceptualisation, Methodology, Software; Minh Thanh Le: Visualisation, Investigation, Data curation; Lan Huong Nguyen: Supervision, Writing - Original draft preparation, Writing - Reviewing and Editing.

ACKNOWLEDGEMENTS

The study was supported by Youth Incubator for Science and Technology Program, managed by Youth Development Science and Technology Center - Ho Chi Minh Communist Youth Union and Department of Science and Technology of Ho Chi Minh City under contract number 34/2021/HD-KHCNT-VU.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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