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Rajan Arjan Kalyan Hirani
*Edith Cowan University*

Abdul Hannan
*Edith Cowan University*

Nasir Rafique
*Edith Cowan University*

Lei Shi

Wenjie Tian

See next page for additional authors

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Authors
Rajan Arjan Kalyan Hirani, Abdul Hannan, Nasir Rafique, Lei Shi, Wenjie Tian, Haitao Wang, and Hongqi Sun

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Three-dimensional rGO/CNT/g-C$_3$N$_4$ macro discs as an efficient peroxymonosulfate activator for catalytic degradation of sulfamethoxazole

Rajan Arjan Kalyan Hirani$^a$, Abdul Hannan$^a$, Nasir Rafique$^a$, Lei Shi$^b$, Wenjie Tian$^c$, Haitao Wang$^d$, Hongqi Sun$^{a,e,*}$

$^a$ School of Science, Edith Cowan University, Joondalup, WA 6027, Australia
$^b$ College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China
$^c$ School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia
$^d$ MOE Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin Key Laboratory of Environmental Technology for Complex Trans-Media Pollution, College of Environmental Science and Engineering, Nankai University, Tianjin 300050, China
$^e$ School of Molecular Sciences, The University of Western Australia, Perth WA6009, Australia

**HIGHLIGHTS**

- Novel graphene-based binary and ternary macro discs were fabricated.
- The discs can activate peroxymonosulfate (PMS) for catalytic oxidation.
- The identification of dominant reactive species was conducted.
- PMS activation and sulfamethoxazole degradation pathways were illustrated.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

Over the past few years, advanced oxidation processes (AOPs) have shown promising efficiencies for wastewater remediation. Carbocatalysis, in particular, has been exploited widely thanks to its sustainable and economical properties but has an issue of recovery and reusability of the catalysts. To address this, three-dimensional (3D) binary and ternary graphene-based composites in the form of macro discs were created to activate peroxymonosulfate (PMS) for catalytic oxidation of sulfamethoxazole (SMX). Graphene oxide served as the base, while graphitic carbon nitride (g-C$_3$N$_4$) and/or single-walled carbon nanotubes (SWCNTs) were added. Among the various discs synthesized, rGNTCN discs (ternary composite) were proven to be the most efficient by completely degrading SMX in 60 min owing to their large surface area and nitrogen loading. The catalytic system was further optimized by varying the reaction parameters, and selective radical quenching and electron paramagnetic resonance tests were performed to identify the active radical, revealing the synergistic role of both radical and...
1. Introduction

Antibiotics have been widely used over the years for the treatment of bacterial infections. Recently, some of these drugs have been detected in various wastewater streams such as hospital discharge, municipal waste, wastewater treatment plants and industrial waste where these drugs are produced [57]. Despite their healing power, these antibiotics are being considered a threat in the long run as continuous exposure to these drugs will build up bacterial resistivity in the body which prevents healing and may even lead to the evolution of highly resistive bacteria [13]. Due to their frequent detection in larger quantities and persistent nature, these antibiotics have been classified as emerging contaminants (ECs) [7]. The average concentration of antibiotics in the environment is at the level of a few ng L$^{-1}$ to a few μg L$^{-1}$ [20]. As such, it is urgent to develop sustainable and cost-effective solutions for the remediation of such antibiotics. Over the years, various methods such as sedimentation, adsorption, biodegradation and reverse osmosis have been developed for the removal of pollutants [33,38]. More recently, advanced oxidation processes (AOPs) have been employed for the degradation of organic pollutants from water, air and soil owing to their sustainable nature and promising results [15].

Among various AOPs, sulfate radicals-based AOPs (SR-AOPs) have been widely studied and employed for the remediation of wastewater owing to the nature of producing active radicals such as sulfate (SO\textsuperscript{4}•-) and hydroxyl (•OH) radicals. PMS can be activated via homogenous or heterogeneous pathways for the generation of reactive radicals [2]. However, due to the limitations of homogenous activation such as heavy metal leaching, heterogeneous activation has been preferred. For this matter, various transition metal-based catalysts have been employed over the years such as Co\textsubscript{3}O\textsubscript{4}, Mn\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, CuO, TiO\textsubscript{2}, and RuO\textsubscript{2} because of their low energy requirement and easy electron transfer [1, 31]. Additionally, bimetallic oxides have also shown synergistic enhancement of catalytic activity where one metal acts as the primary activator while the second metal recycles the activating cation through a redox reaction [30]. Nonetheless, despite using metal oxides via heterogeneous activation, metal leaching is inevitable. Additionally, due to high pH dependency and sludge formation, metal-based catalysts have been considered less efficient in terms of environmental sustainability. To overcome these limitations, carbonaceous materials, thanks to their favourable physicochemical properties, such as large surface area, reactivity in a wider pH range and their abundance on the earth’s surface, have been studied and applied in AOPs for PMS activation [17]. More precisely, graphene-based catalysts have demonstrated excellent results in the catalytic oxidation of emerging contaminants without causing any further secondary pollution such as leaching [35].

Recently, graphene oxide (GO) catalysts have been employed universally as a perfect carbon host for structural and molecular engineering owing to their oxygen moieties which provide a platform for various functionalization options [6]. There are some studies that have been done on the modifications of GO to increase its efficiency in AOPs such as doping with N, B, P, and S as well as metal ions [4]. However, despite showing such a superior efficiency, graphene-based nanocatalysts have shown a major limitation in terms of recovery and reusability due to the nanoparticle size. To overcome this issue, forming a 2-dimensional (2D) to a 3-dimensional (3D) structure has been proposed to be advantageous. With better physicochemical properties compared to their 2D parents, 3D graphene materials have showcased excellent performances in the adsorption/absorption of dyes, oils, pharmaceuticals, and other organic and inorganic pollutants ([14,41, 42]). The interconnected carbon structure in 3D graphene prevents the aggregation occurring in the 2D graphene structure, and in turn, accelerates the mass transfer of the pollutants towards enhanced activity. Over the past few years, 3D graphene-based aerogels and hydrogels have been prepared for the activation of PMS with high degradation efficiencies [16,25,42,49]. A few limitations still exist with these macrostructures due to their fragility, which can cause them to release fragments into the environment. Moreover, the majority of synthesized aerogels are in the form of large bulk monoliths which require further sizing before the application [58,8].

To overcome the above limitations, herein, binary and ternary GO-based macro composites discs were synthesized via a simple hydrothermal procedure followed by one-step ball-milling and green hydraulic pressing. After the synthesis, the physicochemical properties of the as-synthesized discs were studied via various characterization techniques. Compared to other graphene-based catalysts, the macro discs synthesized in this study showed outstanding performances in PMS activation for the oxidation of sulfamethoxazole. The degradation system was optimized by testing various reaction parameters. To identify the existence and role of specific reactive oxygen species (ROSs), selective radical quenching tests and electron paramagnetic resonance (EPR) were conducted. Additionally, the mineralization ability of the degradation system was evaluated by total organic carbon (TOC) while Ultra-high-performance liquid chromatograms (UHPLC) and detailed analysis were used to develop a possible pathway for SMX oxidation.

2. Experimental section

2.1. Chemical and reagents

Pristine graphite flakes (99% Carbon basis and −325 mesh particle), microcrystalline cellulose (MCC), potassium permanganate (KMnO\textsubscript{4}, 99%), concentrated sulphuric acid (H\textsubscript{2}SO\textsubscript{4}, 99.99%), thiourea (≥ 99%), Oxone (PMS, 2KHSO\textsubscript{5}•K\textsubscript{2}SO\textsubscript{4}), sulfamethoxazole (SMX), tert-butanol (TBA), methanol (CH\textsubscript{3}OH), ethanol (CH\textsubscript{3}CH\textsubscript{2}OH), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30%), polyvinyl alcohol (C\textsubscript{2}\textsubscript{2}H\textsubscript{2}O\textsubscript{4}), PVA), glycerol (C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were purchased from Sigma-Aldrich. Single-walled carbon nanotubes (SWCNTs, ≥ 95%) were obtained from XFNano, China. Zirconium grinding balls (1-, 2-, 5-, 10- and 20-mm diameters) were purchased from Nikkato. The Milli-Q water system provided ultrapure water at a temperature of 25 °C and a conductivity of 18.2 MΩ cm for the entirety of the experiments.

2.2. Synthesis of graphene oxide

A modified Hummers method was used for the synthesis of Graphene oxide (GO) via the oxidation of natural graphite flakes [5]. Step-by-step synthesis can be found in our previous works [23].

2.3. Preparation of rGNTCN composite

g-C\textsubscript{3}N\textsubscript{4} was prepared by our previously reported method [7]. For the synthesis of the ternary composite material, the as-prepared GO (0.2 g) was sonicated in ultrapure water (40 mL) for 15 min. Subsequently, SWCNTs (0.006 g) and g-C\textsubscript{3}N\textsubscript{4} (0.006 g) were dispersed in ultrapure water (20 mL). The latter solution was then added to GO dispersion under continuous stirring and the resulting solution was transferred into a stainless-steel autoclave and heated in an oven at 180 °C for 24 h. After natural cooling, the resulting aerogel was dialysed with ultrapure water for 12 h with periodic replacement of water after every hour followed by freeze drying for 36 h. The as-prepared composite was denoted as
rGNTCN. For comparison, binary composite rGNT was synthesized via a similar route without the addition of g-C$_3$N$_4$ and binary composite rGCN without the addition of SWCNTs.

2.4. Preparation of rGNTCN discs

rGNTCN discs were prepared by a simple ball-milling and mechanical pressing method as shown in Fig. 1. More precisely, the as-prepared ternary composite rGNTCN (1 wt%), microcrystalline cellulose (MCC, 10 g), PVA (0.1 g) and glycerol (0.15 g) were ground and mixed in a planetary ball mill using zirconium grinding balls for 150 min at 260 rpm. The milled powders were then moved to an automatic sieve shaker (Retsch, AS 200 Control) to acquire uniformly fine powders. These powders were then placed into a triturate mould and subjected to hydraulic pressurization at a 5-tonne load setting for 1 min to obtain green-pressed GO macro discs. The obtained discs were then dried and strengthened by annealing them at 100 $^\circ$C in a tubular furnace in a nitrogen atmosphere for 2 h. Binary composite rGNT and rGCN discs were prepared with a similar method.

2.5. Materials characterization

The surface and elemental chemistry of the prepared catalysts were evaluated using various characterization techniques as reported in Text S1 of the supplementary information.

2.6. Catalytic activity evaluation

A batch reactor was used to investigate the catalytic performance of the synthesized cubes. Sulfamethoxazole (SMX), a common antibiotic was chosen as the primary contaminant in this experimental set-up. Detailed experimental procedures for the degradation experiments are described in Text S2 of supplementary information.

3. Results and discussions

3.1. Characterization of graphene-based discs

The phase change and crystallinity of the samples were characterized by XRD analysis as depicted in Fig. 2a. The characteristic peaks located at $2\theta = 11.5^\circ$ and $2\theta = 28.1^\circ$ respectively correspond to (1 0 0) and (0 0 2) planes of g-C$_3$N$_4$. Further, CNT exhibited its characteristic peak at $2\theta = 24.8^\circ$ which corresponds to the (0 0 2) plane. In rGNT binary material, it can be observed that the peak slightly shifted from 24.8$^\circ$ to 24.0$^\circ$ and was slightly broadened. This could be attributed to the introduction of oxygen-containing functional groups from the rGO which disrupted the C-C network. Additionally, when g-C$_3$N$_4$ is added to rGO instead of CNTs, the peak position remains the same with a slight increase in the degree of crystallinity. This could suggest that some nitrogen-containing functional groups have been attached to the rGO [18]. In the ternary rGNTCN, the peak intensity is slightly lower than GCN due to the introduction of CNTs.

The chemistry of functional groups in the catalyst plays a critical role in determining the degradation efficiency. Fig. 2b shows the FT-IR spectra of the synthesised catalysts. In pristine g-C$_3$N$_4$, several vibrations were noted between 750 and 1750 cm$^{-1}$. The stretching of aromatic C–N bands were attributed to the vibrational band at 1190 cm$^{-1}$, while the peaks observed at 1570 and 1700 cm$^{-1}$ corresponded to C–N stretching. Additionally, the weak vibration observed at 800 cm$^{-1}$ was attributed to the breathing vibrations of triazine ring units. Further, the wideband between 2800 and 3500 cm$^{-1}$ was identified as the vibrations of uncondensed amino groups (–NH$_2$/–NH) [46,47]. In CNTs, a small vibration band at 1580 cm$^{-1}$ corresponds to the C–C bonds. All three rGNT, rGNC and rGNTCN depicted band stretching of C=O, C–C and C–O at 1045, 1580 and 1750 cm$^{-1}$, respectively, suggesting the presence of carbonyl and other oxygenated functional groups [27]. When g-C$_3$N$_4$ was added, the C=O bond was eliminated and a new C–N bond emerged at 1230 cm$^{-1}$, while the peaks at 1580 and 1750 cm$^{-1}$ could be ascribed to the C=C/C=N and C=O/C=N overlapping respectively [19,45].

Fig. 2c shows the optical photograph of rGNTCN discs. The discs had...
a diameter of 5 mm and a width of 2 mm. The mass of each disc was calculated based on the average mass of 10, 25 and 50 discs as shown in Table S1 and was evaluated as approximately 5 mg. SEM imaging was used to analyse the morphologies of all samples, as depicted in Fig. 2d-h. The SEM images of binary composite rGNT and rGCN reveal that the guest (CNTs and g-C$_3$N$_4$) formed an interactive layer on the host (rGO). The rGO sheets were uniformly decorated by the guests indicating the successful synthesis of these binary composites. Further, when both guests were added simultaneously to form a ternary composite, a fully wrapped sandwich-like material was formed as seen in Fig. 2h. The CNTs were evenly layered between 2D rGO sheets and by a very thin layer of g-C$_3$N$_4$ possibly due to the low amount of guest loadings.

The high-resolution TEM and elemental mapping were further used to evaluate the structural morphology and elemental composition. Fig. 2i-j depicts the successful synthesis of a closely stacked ternary composite. HRTEM image shows the three precursors based on their contrast intensities. The darker region is identified as g-C$_3$N$_4$ because of the presence of the nitrogen functional groups, while the lighter region is identified as rGO due to the thin 2D carbon-carbon network [7]. The SWCNT was identified by its characteristic length. Further, elemental
maps as depicted in Fig. 2k-n show the even distribution of C, N and O atoms in the structure.

The surface and textural properties of the prepared catalysts were analyzed by 

\[ \text{N}_2 \] adsorption-desorption curves as shown in Fig. 51. The BET surface areas of rGNT, rGCN and rGNTCN were recorded as 149.6, 151.2 and 170.5 m\(^2\)/g respectively. All three samples exhibited type-IV isotherms suggesting a substantial amount of reactive sites and their mesoporous nature.

### 3.2. Catalytic evaluation of SMX

The chemical decomposition and adsorption of SMX were performed in a simple batch reactor and the removal profiles are reported in Fig. 3. Initially, binary composites were employed in the degradation reaction in the presence of PMS, and in 60 min approximately 88% and 80% degradation efficiency was achieved with rGCN and rGNT respectively. While maintaining similar reaction conditions, ternary rGNTCN discs were employed in the system for the activation of PMS and catalytic oxidation of SMX. It was noted that complete degradation of SMX was achieved within 60 min suggesting that it was a superior catalyst compared to the binary catalysts. This superiority could be attributed to the synergistic role of the surface area and nitrogen functional groups.

Further, to evaluate the effect of the size and shape of catalytic disc, three different batches of degradation systems, involving the catalysts in the form of powder, multiple 5 mm discs and a single 28 mm disc, were performed. Fig. S2 shows the SMX degradation efficiencies under different catalyst forms. For consistency, all three forms of the catalysts performed. Fig. S2 shows the different catalyst forms. For consistency, all three forms of the catalysts performed.

Nonetheless, apart from the highly acidic conditions, SMX degradation efficiency was quite stable over a wide range of pH suggesting its self-decomposition at higher pH due to its instability making higher pH slightly desirable for activation [16]. Alternatively, the generated sulfate radicals could also be transformed into hydroxyl radicals leading to a slightly enhanced performance in basic conditions (Liu et al., 2019). Nonetheless, apart from the highly acidic conditions, SMX degradation efficiency was quite stable over a wide range of pH suggesting its

### 3.2.1. Impact of reaction parameters

Fig. 4 shows the influence of various reaction parameters on the catalytic reaction. Fig. 4a-b depicts the effect of the initial dosage of catalytic discs on SMX oxidation. The number of discs varied from 0 to 150 discs/L (equivalent to 0 – 0.075 g/L catalyst loading). It can be noted that as the loading increased, the rate of reaction increased, and the corresponding rate constants increased from 0.002 to 0.150 min\(^{-1}\). Such an increase in SMX degradation efficiency could be explained by the increased number of active sites enhancing the electron transfer from the catalysts’ surface for the generation of reactive radicals.

To verify that the removal of SMX was not due to physical separation, an adsorption experiment was conducted for 60 min without the addition of any oxidant. It was observed that the physical adsorption could only remove 18% SMX from the system over the reaction period which could be attributed to the high surface area of the as-synthesized catalyst [11]. An interesting phenomenon was noted from the SMX degradation curve. A rapid degradation curve was observed during the first 10 min, followed by a gradual degradation until 60 min. This can be attributed to the reaction taking place on the surface of the discs during the initial 10 min. As the reaction progresses, the solution gradually diffuses into the core of the disc, leading to a slower degradation after the first 10 min.

The influence of the active radicals on the SMX degradation efficiency was evaluated by varying the initial PMS loading. As shown in Fig. 4c-d an increase in PMS loading from 0 to 4.0 g/L led to a rise in the reaction rate constants from 0.003 to 0.089 min\(^{-1}\). This trend could be attributed to the increased diffusion of PMS on the surface of the catalyst accelerating the generation of more species thus increasing the SMX removal efficiency.

Fig. 4 shows the influence of various reaction parameters on the catalytic reaction. Fig. 4a-b depicts the effect of the initial dosage of catalytic discs on SMX oxidation. The number of discs varied from 0 to 150 discs/L (equivalent to 0 – 0.075 g/L catalyst loading). It can be noted that as the loading increased, the rate of reaction increased, and the corresponding rate constants increased from 0.002 to 0.150 min\(^{-1}\). Such an increase in SMX degradation efficiency could be explained by the increased number of active sites enhancing the electron transfer from the catalysts’ surface for the generation of reactive radicals.

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Fig. 4. Impact of reaction parameters on the efficiency of SMX degradation: (a) catalysts dosage, (c) PMS loading, (e) solution pH, (g) reaction temperature, corresponding pseudo-first-order reaction kinetics: (b), (d) and (f), and (h) evaluation of activation energy.
suitability for practical application. For this study, the pH of the solution was adjusted by the addition of a dilute aqueous solution of NaOH or HCl.

Fig. 4g-h depicts the effect of the reaction temperature in a range of 25 – 55 °C. SMX degradation efficiency increased with the increase in reaction temperature. 100% SMX degradation was achieved in 60, 45, 30 and 20 min when the reaction temperature was set at 25, 35, 45 and 55 °C. This confirmed that the reaction was endothermic. The Arrhenius equation was used to estimate the activation energy (Ea), which was found to be 26.49 kJ/mol. The low activation energy can be attributed to the high activity of rGNTCN discs, making them suitable for practical use in wastewater remediation processes.

3.2.2. Catalyst reusability and stability

Fig. 5a shows the stability and reusability of rGNTCN discs after each run. The stability and reusability of the catalysts are vital factors to consider before their practical applications [32]. Herein, rGNTCN discs were tested over four runs before regeneration followed by two successive runs to evaluate their stability. After each run, the discs were collected by a simple decantation process and washed with ultrapure water for 3 h with continuous replacement of water every 15 min. The discs were subject to vacuum drying at 60 °C for 12 h before their reuse in subsequent runs. For regeneration, the discs were washed using PMS solution for 30 min following by the above washing procedure before annealing under a nitrogen atmosphere at 100 °C for 1. After the first run, the efficiency decreased by 14%. In the second and third runs, the degradation efficiency further dropped by 19% and 30% respectively. After regeneration, 92% efficiency was achieved in the first run followed by 82% in the second run after regeneration. The slight reduction in efficiency can be attributed to the accumulation of intermediates during the SMX degradation process, which may block or occupy the active sites [24]. Despite being used for four runs, the discs showed substantial SMX degradation efficiency remaining high, which can be attributed to the successful synthesis of the catalyst. This suggests that the discs have the potential for practical application in wastewater treatment plants.

To assess the role of nitrogen in the degradation of SMX, XPS analysis was conducted on both the pristine and used catalysts. Generally, the activation of PMS involves the cleavage of the superoxide O-O bond for the transfer of electrons between the catalyst and the oxidant [40]. From Fig. 5 (b-c), it can be noted that nitrogen was fitted into three peaks (pyridinic N, pyrrolic N and graphitic N). The analysis concluded that pyridinic N and pyrrolic N decreases after the reaction while graphitic N increases suggesting that the latter two could be the active sites in the activation of PMS [12]. Generally, pyridinic N and pyrrolic N are considered to be associated with catalysis due to their lower energy barrier for the adsorption of reactants on the adjacent carbon atoms thereby accelerating the rate-limiting first electron transfer [34].

Further, Fig. 5 (d-g) depicts the high convoluted spectra of carbon and oxygen. As seen, carbon was fitted into three peaks at 283.75, 284.55 and 286.03 eV which correspond to C–C/C–C, C-OH/C–O and C–N/C–O moieties respectively. Oxygen was fitted into two peaks at 531.20 and 532.51 eV corresponding to the C=O and C-OH/C–O–C moieties. From both carbon and oxygen spectra, it can be deduced that C–O (ketonic) and C=N moieties decreased as a result of their conversion to C=C and/or C=C-O-C groups during the PMS activation suggesting that nitrogen atoms played a vital role in the catalysis [54].

3.2.3. Practical application of rGNTCN discs/PMS system

Among various antibiotics consumed, a fixed dose of sulfamethoxazole and trimethoprim (TMP) mixed in a ratio of 5:1, commonly known as co-trimoxazole, has been administered to patients as a medication for the treatment of various bacterial infections [36]. Further, co-trimoxazole has been proven to be highly effective and relatively cheap resulting in its vast usage. Owing to the continuous usage of this drug, traces of it have been found in municipal wastewater causing great concern [10]. As such, herein, SMX and TMP were mixed in the fixed commercial ratio of 5:1 and used as the target pollutant. From Fig. 6a-b, it can be noted that when SMX and TMP are used as the target pollutants in a singular system, 100% degradation is achieved in 60 and 20 min respectively. However, when used together in a binary system, 100% degradation of TMP is achieved in 30 min while 88% degradation of SMX is achieved in 60 min. Further, TOC analysis was conducted to investigate the degradation of intermediates. As seen in Fig. 6c, 95% and 72% TOC removal was achieved in 60 min when TMP and SMX were degraded in singular systems. Further, when degradation is performed in a binary system, about 58% TOC removal has been achieved owing to the high activity of the rGNTCN discs suggesting its potentiality in commercial wastewater treatment technologies.

Further, to investigate the degradation efficiency in a continuous flow, a packed bed column reactor was employed as described in Text S3. A similar amount of catalyst loading was used in the column reactor as in the batch reactor to compare the efficiency and practical applicability. The results shown in Fig. S3 suggest that about 90% SMX removal efficiency was obtained even after continuously running for 2 h. This mimic experiment could be further exploited for commercial application.

3.2.4. Detection of active species and degradation mechanism

In AOPs, PMS is generally activated for the degradation via radical or non-radical pathways. Herein, the identification of the generated ROSs was done via EPR experiments and selective radical quenching tests. DMPO was employed to trap the SO•− and •OH radicals while TEMPO was employed to trap singlet oxygen (1O2) [55]. The EPR spectrograph in Fig. 7a depicts strong peaks of DMPO–•OH and DMPO–SO•− suggesting the co-existence of both radicals. Further, when TEMPO was employed (Fig. 7b), sharp peaks of TEMP–1O2 were observed suggesting the existence of a non-radical pathway.

The synergistic effect of radical and non-radical existence was further verified with selective radical quenching tests. Fig. 7c-f shows the degradation efficiency curves of SMX when various quenching agents were employed and their corresponding pseudo-first-order reaction rate constants presented in Fig. S4. Methanol (MeOH) and tert-butanol (tBA) were employed to quench oxidative SO•− and •OH radicals while p–benzoquinone (p–BQ) was used to quench superoxide radicals (O2•−) [52]. When 50 mM MeOH was added as a quencher, 79% SMX degradation efficiency was achieved while further reduced to 54% upon the addition of 100 mM suggesting the presence of SO•− and •OH radicals. This was further confirmed by the addition of 50 mM and 100 mM of tBA which resulted in 84% and 63% degradation efficiency. On the other hand, 95% and 88% degradation efficiency were achieved when 5 mM and 10 mM p-BQ was employed respectively suggesting the negligible role of superoxide radical. To verify the role of the non-radical pathway, sodium azide (NaN3) was used to quench singlet oxygen. 69% and 50% SMX degradation efficiencies were noted when 5 mM and 10 mM NaN3 were added to the degradation system suggesting the presence of 1O2. Based on the above discussions, it can be noted that both radical and non-radical pathways were present in the rGNTCN/PMS system.

As a result of the synergistic existence of radical and non-radical pathways, a proposed SMX degradation mechanism was established as shown in Fig. 8. The electron transfer process and the activation of PMS by rGNTCN discs for SMX degradation can be described in the reactions below. Firstly, for the radical pathway, PMS could be attached to the surface of rGNTCN discs via chemical bonds where the discs could act as electron donors leading to the formation of SO• and •OH by breaking the O – O bonds as shown in Eqs. (1),(2) [56]. Additionally, the SO• could react with the as-produced OH− leading to the formation of •OH (Eq. (3)). As for the non-radical pathway, the positively charged C atoms could lead to an attraction between PMS and the catalyst leading to the generation of SO• (Eq. (4)) which would further react with H2O resulting in the formation of 1O2 (Eq. (5)) (21,28). Alternatively, SO• could undergo self-reaction forming 1O2 (Eq. (6)) [53]. Conclusively, the
Fig. 5. (a) Reusability test and high convoluted XPS spectra of pristine and used catalysts; (b-c) N1s, (d-e) C1s and (f-g) O1s. Reaction condition: [SMX]₀ = 20 ppm, [Catalyst]₀ = 100 discs/L, [PMS]₀ = 2.0 g/L and T = 25 °C.
possible SMX degradation by both radical and non-radical pathways could be summarized in (Eq. (7)).

\[
\begin{align*}
\text{HSO}_5^- + e^- & \rightarrow \text{•OH} + \text{SO}_4^{2-} \\
\text{HSO}_5^- + e^- & \rightarrow \text{OH}^- + \text{SO}_4^{2-} \\
\text{SO}_4^{2-} + \text{OH}^- & \rightarrow \text{SO}_3^- + \text{•OH} \\
\text{HSO}_4^- + \text{C} & \rightarrow \text{H}^+ + \text{C} + \text{SO}_4^{2-} \\
4\text{SO}_4^{2-} + 2 \text{H}_2\text{O} & \rightarrow 4\text{HSO}_4^- + 3\text{O}_2 \\
\text{SO}_4^{2-} + \text{SO}_4^{2-} & \rightarrow 2\text{SO}_2^2 + \text{O}_2 \\
\text{SO}_4^{2-}/\text{•OH}/\text{O}_2 + \text{SMX} & \rightarrow \{\ldots\text{multiple steps}\ldots\} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

(7)

3.2.5. Mineralization of organic pollutants

The mineralization of the organic pollutants and the identification of the possible intermediates were analyzed via HPLC chromatograms as shown in Fig. 5a. The sharp peak at \(t_0\) of 1.40 min represents SMX. It can be noted that after the addition of PMS, four small peaks were noted at \(t_0\) of 0.80, 2.60, 2.85 and 3.20 min and labelled as I₁, I₂, I₃ and I₄ representing four possible intermediates. Interestingly, I₂ was mineralized completely after 30 min suggesting that it could have a short life and could have possibly been converted to more stable compounds ([22, 44]).

Based on the above discussions, the synergistic existence of both radical and non-radical pathways, and a vast literature study, a possible mineralization pathway for SMX is proposed in Fig. 5b. As discussed earlier, the radical pathway was characterized by \text{SO}_4^\cdot^- and \text{•OH} radicals while the non-radical pathway was characterized by \text{O}_2. In the sulfate radical-based mineralization, it is proposed that \text{SO}_4^\cdot^- would hydrolyze SMX molecule to form P₁ (N-(5-methylisoxazol-3-yl)-4-nitrobenzenesulfonamide) [48]. With the continuous attack of \text{SO}_4^\cdot^-, the S–N bond in hydrolysed P₁ molecule would the cleavage resulting in the formation of P₂ (3-amino-5-methylisoxazole sulfonic acid) and P₃ (aniline) which would further be oxidized to form P₄ (3-amino-5-methylisoxazole) and P₅ (phenol) [43,48]. Finally, P₄ and P₅ would be mineralized to \text{CO}_2 and \text{H}_2\text{O} [51]. On the other hand, in a hydroxyl radical-dominated pathway, \text{•OH} could attack SMX and cleavage the S–N bond forming P₆ (sulfanilic acid) and P₇ (3-amino-5-methylisoxazole). After a series of continuous \text{•OH} attacks, P₆ would form P₈ followed by P₉ (4-Aminophenol) while P₇ would form P₁₀ (Hydrolyzed 3-amino-5-methylisoxazole) [3]. Finally, P₉ and P₁₀ would be mineralized to \text{CO}_2, \text{H}_2\text{O}, and other small-chain by-products [29]. In a non-radical-based pathway, it is proposed that the singlet oxygen would attack the SMX molecule resulting in the isoxazole ring opening (P₁₁) [26]. The further attack of the ROS would cleavage the
SN bond resulting in the formation of P12 (4-Nitrosophenol – identified as I4 on HPLC chromatogram) and P13 (3-amino-5-methylisoxazole) \[37,7\]. P12 would further be broken down to P14 (nitrosobenzene) by breaking the hydroxyl functional group followed by P15 (p-benzoquinone) which was identified as I1 in the HPLC chromatogram \[7\]. On the other hand, the continuous attack of ROS on P13 would lead to the opening of a pentagonal ring leading to the formation of short-chained aliphatic acid, CO\(_2\), H\(_2\)O, and other simpler by-products \[29\].

4. Conclusions

In conclusion, a series of binary and ternary composites of graphene-based macro discs were successfully synthesized via hydrothermal and simple green pressing techniques. The discs were then characterized to evaluate their physiochemical properties, and their ability to activate PMS for the degradation of SMX in a batch reactor. Results indicated that the ternary discs (rGNTCN) had the highest SMX degradation efficiency with an activation energy of 26.49 kJ/mol, thanks to their larger surface area and nitrogen-containing functional groups. The system was optimized by evaluating various reaction parameters such as oxidant and catalyst dosage, pH, and temperature. Catalyst reusability and stability were also evaluated, with rGNTCN discs demonstrating up to 70% degradation efficiency. The system’s commercial feasibility was evaluated by simultaneously degrading SMX and TMP in a binary system.

Fig. 7. EPR spectra; (a) DMPO• OH and DMPO• SO\(_4^–\), and (b) TEMP• O\(_2\), the role of different quenchers on SMX degradation efficiency; (c) MeOH, (d) tBA, (e) p – BQ and (f) NaN\(_3\). Reaction condition: [SMX]\(_0\) = 20 ppm, [Catalyst]\(_0\) = 100 discs/L, [PMS]\(_0\) = 2.0 g/L and T = 25°C.
resulting in the degradation of 88% of the commercially approved SMX-TMP antibiotic in 60 min. Radical quenching tests and EPR analysis were performed to identify the role and existence of ROSs, and a possible SMX degradation pathway was proposed. In conclusion, this study could provide novel insights into the recovery and reusability of the heterogeneous catalysts after the degradation and a possible cost-benefit analysis could be performed to commercialize the above system for the remediation of organically polluted wastewater.

Environmental implication

Release of antibiotics in water has become overwhelming and such continuous exposure has led to the evolution of resistant bacteria causing adverse effects on human health. There is therefore an urgent need to exploit feasible techniques to eradicate these pollutants. Advanced oxidation systems (AOPs) have shown excellent degradation of such antibiotics but have a major shortcoming, i.e., catalyst recovery and reusability. To address this challenge, nanocatalysts have been modified to macro discs for the removal of antibiotics. The study has proven that this technique is feasible and could be possibly applied in real wastewater remediation processes.

CRediT authorship contribution statement


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

Data will be made available on request.

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Appendix A. Supplementary material

The Supplementary Data are available free of charge at.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.132400.

References


