rGO/persulfate metal-free catalytic system for the degradation of tetracycline: effect of reaction parameters

Dinh Trinh Tran and Van Noi Nguyen
Key Laboratory of Advanced Material for Green Growth, Faculty of Chemistry, University of Science, Vietnam National University, Hanoi; 334 Nguyen Trai Str., Hanoi, Vietnam
E-mail: trinhdt@vnu.edu.vn
Keywords: reduced graphene oxide, persulfate, metal-free catalyst, tetracycline, kinetics
Supplementary material for this article is available online

Abstract
Reduced graphite oxide (rGO) was synthesized from graphene oxide (GO) by reduction process with the aid of ascorbic acid. GO was synthesized from graphite precursor by modified Hummers method. The prepared materials were characterized in terms of surface morphology, structure, functional group, and elemental compositions by different methods such as SEM/EDS, XRD, FT-IR, Raman, and BET. rGO/K$_2$S$_2$O$_8$ system was used to study the impact of different reaction parameters on the degradation of tetracycline in water. The results showed that GO and rGO materials were successfully synthesized, with high purity. The prepared rGO promoted the degradation of tetracycline by sulphate radicals generated from K$_2$S$_2$O$_8$ with an efficiency of two-fold higher than sole K$_2$S$_2$O$_8$. More than 95% of 5 mg l$^{-1}$ tetracycline were removed by rGO/K$_2$S$_2$O$_8$ system after 40 min of reaction. The catalytic performance of rGO/K$_2$S$_2$O$_8$ system in the degradation of tetracycline was dependent on pH of the solution, catalyst loading, tetracycline initial concentration, and persulfate concentration. The optimal conditions for the degradation of tetracycline in water were at pH 10, with 5 mg l$^{-1}$ tetracycline initial concentration, 20 mg l$^{-1}$ of rGO, and 0.2 mM persulfate added. The catalytic performance of the system showed relatively stable, with about 75% tetracycline in solution were removed after 3 cycles. The degradation of tetracycline by rGO/K$_2$S$_2$O$_8$ system followed the pseudo-first order kinetics, with a typical coefficient of determination above 0.95 for all experimental conditions.

1. Introduction

Tetracycline (TC) has been wildly used for the prevention and treatment of infectious diseases in human and animals [1–3]. TC has been also used as animal growth promoter, used to control infections in aquaculture and agriculture [2]. Due to its extensive usage, large proportion excreted and released in active form into the environment after medication (more than 70%), and specific characteristics such as low volatility, strongly hydrophilic feature, and long half-life [2, 4, 5], TC usually ends up in different environments such as surface water [6–8], ground water [8, 9], soils [5–10], farm lagoons [2, 5, 8, 9], and sediments [2, 8, 9]. The main emission sources of TC to the environment are from human medicine and animal husbandry. TC can be released into environments from the discard of expired antibiotics in hospitals, of prescription antibiotics via the feces and urine of patients, residues in equipments/vials used for related treatments/tests. Regarding animal husbandry, the release includes (1) loss of the veterinary drugs during production processes, (2) discard of the expired drugs, (3) residues of used drugs, (4) residues in urine or feces from animals [5]. It is noted that, untreated animal manures used as agricultural organic fertilizer are usually one of the major pathways of antibiotic release into the soil environment [5, 8]. Once available in environments, antibiotics residues such as TC would enhance the development of antibiotic resistant microorganisms, thus inducing potential adverse impacts to human health by increasing the risk of certain infections [2, 3, 8, 11, 12]. Different research reported that the presence of TC...
antibiotics in the environment could inhibit the growth of and/or be toxic to some terrestrial and aquatic species [12–15]. In addition, the residues of such antibiotics could cause endocrine disruption of aquatic species [14, 16]. Because of its resistant nature, TC is difficult to be removed by conventional processes [2, 6, 14, 15, 17]. Most of the wastewater treatment plants are not capable of removing effectively the tetracycline antibiotics [14, 15, 17]. The removal efficiency of TC residues by conventional wastewater treatment plants was reported to be around 50% [14]. Therefore, there is a need to develop alternative processes to remove antibiotic residues from waters.

Different efforts made to develop feasible processes to effectively and efficiently remove TC residues discharged to the environment are, therefore, of great significance. Busto et al (2020) reported that under anaerobic conditions, amoxicillin could be totally removed by biological treatment conducted in a small reactor in laboratory. However, the same authors found that there were the formation of by products, and biogas production inhibition was observed [18]. Other research focused on the utilization of sorbents for the removal of antibiotics in aqueous media revealed good results. For instance, Premarathna et al (2019) synthesized clay-biochar composites for the removal of TC from water, and found the maximum adsorption capacity of 78.0 mg g⁻¹ [19]. Huang et al (2014) showed that activated carbon produced from lignin could removal TC from aqueous media, with a typical adsorption capacity of 475 mg g⁻¹ [20]. Although adsorption approach for the removal of antibiotics is usually easy to be deployed, desorption of pollutants and recovery of saturated sorbents are challenging. Some focused on the development of composite membranes for the removal of antibiotics in water [21, 22]. Pan et al (2015) showed that forward osmosis process could remove up to 97% of TC in aqueous solutions [21]. However, this technique is usually expensive and there are challenges linked with membrane fouling and/or decline in the membrane flux [22]. Advanced oxidation processes (AOPs) have been developed as alternative methods to ensure high degradation and mineralization of tetracycline antibiotics, and they have been shown to effectively degrade TC residues which are present in water media. Among advanced oxidation processes, Fenton and Fenton-like reactions, photocatalysis, and persulfate activation are studied and developed the most [23–28]. Yang et al (2018) examined the removal of Tetracycline by a Fe/N-C Hybrids/H₂O₂ Fenton-like system, and revealed that about 94% of TC were removed at optimal conditions, and the system presented good stability and good recycling ability, with 88% catalytic activity obtained after sixth cycle [23]. Hou et al (2016) studied on using a coupled ultrasound/heterogeneous Fenton process and found that the stability of catalyst was significantly improved when ultrasound was employed. Under optimal conditions, 93.7% of TC was removed after 60 min of treatment. The removal efficiency of the total organic carbon (TOC) at 60 min was 31.8% [24]. Photocatalytic degradation of TC has been also studied by several researchers [25–27]. Sulfate radicals (SO₄⁻) generated from the activation of persulfate (PS) by ultrasonication [4, 28], UV irradiation [29], heat [30], and transition metals-based catalysts [31, 32] have been revealed to be effective and environmentally friendly approaches in the treatment of pharmaceuticals [4, 28–34] due to their higher redox potential (2.5–3.1 V, depending on the pH) compared with hydroxyl radicals (HO·, 1.9–2.7 V). In addition, the lifetime of sulfate radicals is much longer than that of hydroxyl radicals in aqueous solutions (e.g., 300 μs versus ~40 μs) [35], and the operational pH range for sulfate radicals-based AOPs is large, ranging from acidic to basic [36], whereas hydroxyl radicals-based AOPs (Fenton process, for instance) presents high efficiency solely at acidic solutions [37]. Transition metals like Fe²⁺, Fe³⁺, Mn²⁺, Ni²⁺, Ru³⁺, and Co²⁺ can strongly enhance the oxidation capacity of a single system [34, 38, 39]. However, these metal ions may require additional treatments because of their unintentional presence in treated samples. In addition, the excessive catalysts or sequential additions of Fe³⁺, Mn⁴⁺ can also play an important role in quenching the formation of SO₄⁻. As regards the generation of SO₄⁻ by thermal activation approach, Li et al (2016) found that the increase in temperature and solution pH favored the removal of TC [40]. This would deter the application of thermal activation approach in real conditions. Recently, different research revealed that reduced graphene oxide (rGO) could be used as an efficient activating material for persulfate to generate sulfate radicals. Sun et al (2012) reported that rGO was more efficient than other carbon allotropes, including activated carbon, graphite, graphene oxide (GO), multiwall carbon nanotubes; and even better than Co₃O₄ in the degradation of methylene blue, phenol, and 2,4-dichlorophenol in water [41]. The activators of persulfates by rGO could be the zigzag edges which were produced depending on the orientation that C−C σ bonds are broken. The localized state at zigzag edge makes their π electrons between sp² carbon atoms in a basal plane not to be confined by the edge carbons, hence resulting in higher chemical activity [41]. Chemically reduced graphene oxide would lead to reduce oxygen functional groups at zigzag edges, which present a higher intrinsic activity than those located in terminal flat surface [42]. The oxygen functional groups, such as ketone (C=O), are rich in electrons, and thus having a great potential for redox process [41, 43]. Moreover, the delocalized π-electron systems in graphene structure would lead to a strong adsorption capacity regarding organic compounds by π−π stacking interactions [44], thus enhancing the degradation of organic pollutants by persulfates and rGO system.
The current work aims at producing rGO for the study on TC degradation by PS activation. The influence of different reaction parameters such as pH, catalyst dosage, PS concentration and initial concentration of TC will be examined. Finally the stability of the catalytic system will be also studied.

2. Materials and methods

2.1. Chemicals

Chemical and materials used in this work were analytical reagents, including H$_2$SO$_4$, NaNO$_3$, KMnO$_4$, and NaOH, HCl, NaCl purchased from Xilong Chem. Co., Ltd, China; H$_2$O$_2$, ascorbic acid, and TC purchased from Sigma-Aldrich; flake graphite powder 99.95%, 100 mesh, from Aladdin Chemicals, China.

2.2. Material synthesis

Graphene oxide flakes were prepared by chemical exfoliation and oxidation reactions using the modified Hummers’ method [39, 45, 46]. First, a mixture of 1 g graphite powder and 0.5 g NaNO$_3$ was prepared and added to a 250 ml three-necked flask, cooled in an ice bath to achieve 0 °C. Then, 23 ml of concentrated sulfuric acid (H$_2$SO$_4$) was carefully added to the three-necked flask and the temperature of the mixture was controlled at less than 5 °C for one hour. Second, 0.2 g of KMnO$_4$ was added for the preoxidation. After stirring for 30 min, 2.8 g of KMnO$_4$ were added to the mixture and the temperature was controlled at 10 to 20 °C for 2 h to obtain a dark green suspension. Then, the three-necked flask was transferred to an oil bath at 35 °C for 2 h to obtain a brown suspension; 23 ml of water were added drop wise and the reaction temperature was controlled at 95 °C for 30 min, prior to being cooled down to about 50 °C by further water addition. The mixture was stirred and added with H$_2$O$_2$ solution until the mixture changed from brown to bright yellow. The supernatant was removed after centrifugation and the precipitate was washed with HCl 10% and distilled water until the pH of the supernatant reached 5–6. Finally, the precipitate was ultrasound treated for 3 h and then dried at 60 °C for 12 h to obtained GO.

The reduction of oxygen of graphene oxide (GO) to form reduced graphene oxide (rGO) using ascorbic acid. In a typical procedure, 1 g of ascorbic acid was dissolved in 100 ml of deionized water. The prepared solution was then mixed with 0.1 g GO. The mixture was then heated at 95 °C for 1 h. At the end of the heating process, the mixture was immediately treated by ultrasound for 30 min. The black precipitate was then simply filtered by vacuum filtration and subsequently washed with 0.5 M HCl solution and deionized water to reach neutral pH. The product is filtered and dried in a vacuum at 60 °C for 5 h.

2.3. Structural analysis of as-synthesized materials

The crystal structure of samples were characterized by x-ray diffraction spectroscopy (XRD, D8 Advance—Bruker) using Cu Kα radiation source (V = 40 kV, I = 40 mA) operated at a scan rate of 0.03°.s$^{-1}$ over a 2θ range of 5°–60°. The surface morphology and elemental composition of the samples were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) with the aid of a JEOL JSM 7000 F FEG-SEM. Infrared spectroscopy (IR) spectra of the synthesized materials were analysed by using an IR spectrometer Bruker IFS-28 (Bruker Optik GmbH, Ettlingen, Germany). Dried samples were mixed with the dried KBr and FT-IR spectra was recorded at a resolution of 4 cm$^{-1}$, ranging from 450 to 4000 cm$^{-1}$. Raman spectrometer Horiba Jobin-Yvon LabRam HR800 was employed for the characterization of as-synthesis regarding functional groups and structural defects. Finally, Brunauer–Emmett–Teller (BET) surface area analysis was conducted on a Micromeritics ASAP 2000 sorptometer. Nitrogen adsorption at liquid nitrogen temperature (77 K) was used to measure surface areas of pristine graphite and rGO. Before the adsorption measurement, samples were degassed at 100 °C to remove water.

The pH$_{pzc}$ of rGO sample was measured by pH drift method. pH$_{pzc}$ (point of zero charge) is the pH when the charges on the adsorbent surface is null. The procedure could be briefly described by the following steps. First, a series of 50 ml of NaCl 0.01 M solutions were prepared and poured into different tubes. Then, the pH values of the prepared NaCl 0.01 M solutions were adjusted between 2 and 12 with the aid of HCl 0.1 M or NaOH 0.1 M solutions, attributed to pH$_{initial}$. Subsequently, 0.2 g of rGO was added into each tube, then shaken for 12 h to reach equilibrium state. The pH of equilibrium solutions were measured and denoted pH$_{final}$, the pH$_{pzc}$ of rGO in solution was the value at which pH$_{final} = $ pH$_{initial}$.

2.4. Parameters influencing the treatment of TC by rGO/PS system

TC oxidation tests were performed in a series of 250 ml conical flasks at room temperature. In order to compare TC degradation capacity of sole rGO, PS, and rGO/PS, three series of experiments were conducted at the same reaction conditions in which one series for only rGO and TC solution, one for only PS and TC solution, and the other for both rGO and PS, and TC solution as target pollutant. The reaction conditions were designed as...
follows: 10 mg rGO particles were dispersed in 100 ml solution of 5 mg l\(^{-1}\) initial TC concentration, PS concentration were 0.2 mM, and pH of examined solutions were the same as the pH of 5 mg l\(^{-1}\) TC solution (6.5). The pH value was not controlled during all experiments. The suspension was shaked at 150 rpm for 2 min to reach the adsorption/desorption equilibrium between TC and rGO. Then, a defined amount of PS was added into the solution. 5 ml samples were taken at predetermined time timesteps, then filtered by 0.22 \(\mu\)m membrane filter to analyse the remained TC concentration by an Agilent UV-visible spectrophotometer (Model Cary 100). All experiments were performed in triplicate.

The influence of different parameters such as pH of the solution, catalyst dosage, concentration of PS, and initial concentration of TC on the degradation of TC by rGO/PS were examined in this work. Regarding the effect of pH, the experimental procedure was similar to the above mentioned one. Only the pH of examined solution was adjusted to 4, 6, 7, 8, and 10 with the aid of NaOH 1 M and HNO\(_3\) 1 M solutions. Similarly, experiments for the effect of catalyst dosage were conducted at the optimal pH found, and catalyst concentrations were 5, 10, 20, 30 mg l\(^{-1}\). Effect of PS concentration on the degradation of TC was performed at optimal pH and catalyst dosage found previously, while PS concentration varied in the range of 0.1–0.4 mM. Once optimal value for PS was revealed, it was used along with optimal pH, catalyst load to study the influence of TC initial concentration in the range of 2–8 mg l\(^{-1}\).

3. Results and discussion

3.1. Structural and surface characterization

Graphite sheets (figure 1(a)) were transformed to corrugated form of GO (figure 1(b)) and more wrinkled structure of rGO (figure 1(c)). The size of GO and rGO and their chemical composition will be clarified in subsequent sections of the paper using surface analysis methods such as EDX, XRD, and FTIR.

EDS spectra of GO and rGO are shown in figure 2. There were solely the presence of C and O elements in prepared GO and rGO, suggesting high purity of or no significant contamination sources to the obtained products (less than 0.5% - the quantification limit by EDS technique).

The reduction process resulted in a decrease in the surface atomic percentage of oxygen from 38.4% (in GO) to 19.9% (in rGO), but an increase in C/O ratio from 1.60 (in GO) to 4.03 (in rGO). This suggests successful the reduction of oxygen functional groups (\(-\text{OH}, \text{−O−}, \text{−C=O and −COOH}\)). The obtained results were comparable with those reported by Park et al (2019) in an attempt to thermally reduce graphene oxide [47] while they were...
higher than the work conducted by Stobinski et al (2014), which revealed an average C/O ratio of 2.8 in rGO [48]. It should be noted that C/O ratio can largely be varied from one work to another due to discrepancies in reduction conditions [49]. Some work reporting high reduction levels of oxygen functional groups by relatively mild conditions, with C/O ratio in rGO up to 12.5 [49, 50].

Figure 3 shows the results of the x-ray diffraction analysis of the synthesized materials. The (002) peak at $2\theta = 27^\circ$ was attributed to pristine graphite [51] while the sharp (002) diffraction peak at $2\theta = 9.89^\circ$ corresponded to GO [48, 52]. After the chemical reduction by ascorbic acid, the (002) peak of GO disappeared while another broad peak of around 24.6° showed up. The disappearance of the sharp peak at around 10° can be attributed to the exfoliation of layered structures of graphite oxide. The broad peak at around 24.6 may be caused by partial restacking of exfoliated graphene layers to form crystalline structure [48, 53].

The samples were characterized by FTIR, and the corresponding spectra of graphite, GO, and rGO in the 4000–400 cm$^{-1}$ region are presented in figure 4. Broad peaks at the region of 3400–3600 cm$^{-1}$ can be attributed to OH group [53]. The absorption peaks at 1720 cm$^{-1}$ corresponding to carbonyl functional groups located on the edge of the graphene oxide sheets (COOH and C=O) [52] while the peak at 1620 cm$^{-1}$ was attributed to the C=C vibrations of the graphene skeleton [54, 55]. C–O vibration in hydroxyl or epoxy groups was observed at 1410 cm$^{-1}$ and 1060 cm$^{-1}$ [55, 56].
It is noted that all the intensities of the vibration peaks of oxygen functional groups in rGO were decreased compared to those in GO. This confirmed the successful reduction of GO by ascorbic acid but the reduction process was not complete.

Raman spectroscopy is a popular technique for characterization of carbon-based materials, especially C=C double bonds which result in high Raman intensities [57–59]. Raman spectroscopy is an essential tool for the study on structural and electronic properties of graphene, including disorder and defect structures, defect density, and doping levels [57, 59] a part from electron paramagnetic resonance (EPR) and photoluminescence (PL) [60, 61]. Raman spectroscopy of graphene is generally characterized by two main features: the G-peak, resulting from first-order scattering of the E_2g phonon from sp² carbon atoms, which is known to appear at 1575–1583 cm⁻¹ for bulk graphite, and the D-peak (at ~1350 cm⁻¹), resulting from breathing mode of κ-point photons of A_1g symmetry [57]. The results in this work showed G-band and D-band of GO at 1587 cm⁻¹ and 1329 cm⁻¹, respectively (figure 5). Along with other methods presented previously, the Raman spectra also support structural changes before and after the reduction of GO by ascorbic acid. Indeed, in the Raman spectrum of rGO, the D-band and G-band were broadened and shifted to around 1320 cm⁻¹ and G band shifted to 1580 cm⁻¹ (figure 5). In addition, rGO presented a slightly higher D/G integrated intensity ratio (1.43) than showed GO (1.32). This suggests the introduction of sp³ defects after functionalization and an increase in bonding defects or formation of large number of smaller sized sp² bonded carbon domains during the reduction process [57–59].

BET analyses were carried out under nitrogen atmosphere to figure out porous features of the prepared rGO materials, which are presented in figure 6. The adsorption/desorption plots of graphite and rGO showed a common type II isotherm with H3 hysteresis loop. This behaviour was probably linked to non-rigid aggregates of plate-like particles with slit-like pores [62]. Furthermore, the BJH analysis revealed a wide distribution of hierarchical pores with diameters in the range of meso - macro pore (figure S1 is available online at stacks.iop.org/MDX/7/075501/mmedia); the pore volume for graphite and rGO were respectively 0.047 and 0.035 cm³ g⁻¹. It is noted that the specific surface area of the prepared rGO (4.33 m² g⁻¹) was close to that of pristine graphite (7.89 m² g⁻¹). The former was largely lower than previously reported results (up to 1000 m² g⁻¹) on specific surface area of rGO [43, 63, 64] on the one hand, but it was comparable with several reported work on the other hand [65]. This can be explained by the fact that, in solid form, rGO sheets interact to form aggregates which become more compacted when solvents are evaporated by drying processes [66]. As a result, specific surface area of rGO in solid form is not representative for that of rGO in solution which was used in this work. To overcome this challenge, several research groups proposed different techniques to quantify surface area of rGO in solution including the measurement of the amount of methylene blue adsorbed on the surfaces of rGO in solution with the aid of optical spectroscopy observation of new absorption bands that were indicative of the formation of MB/GO conjugates [66], or by the measurement of rheology-based method recently developed by Zhang et al (2020) [67].
3.2. Comparison of degradation efficiency of TC by PS, rGO, and rGO/PS system

In order to compare the degradation efficiency of TC by PS, rGO, and rGO/PS system, experiments were performed with 100 ml TC solution of 5 mg l\(^{-1}\), at initial pH = 6.7 without any adjustments; PS and rGO concentrations applied for all experiments were respectively 0.2 mM and 10 mg l\(^{-1}\). Three experimental series were carried out for the degradation of TC with solely PS, rGO, and rGO/PS, respectively. The obtained results are presented in Figure 7.

The results showed that the TC removal efficiency of rGO alone reached 20% after 40 min of reaction while PS resulted in better performance, with around 50% of TC removed. With the aide of rGO as a catalyst to generate more radicals from PS decomposition by equation (1), the rGO/PS system treated about 95% of TC in solution after 40 min, implying that rGO assisted the degradation of TC by PS. A plausible mechanism of PS activation by rGO can be explained by a process of three steps as follows [28, 43]: (1) rGO as an electron rich material, in particular at various sites where situated oxygen functional groups such as the ketone group (C=O) can easily transfer electrons to generate \(-\text{SO}_4^\cdot\) from PS decomposition by equation (1); (2) the subsequent reaction between \(-\text{SO}_4^\cdot\) and H\(_2\)O resulted in the formation of HO\(^\cdot\) radicals (equation (2)); and both \(-\text{SO}_4^\cdot\) and HO\(^\cdot\) radicals involved in the degradation of TC (equation (3)).

\[
\text{rGO} + \text{C} = \text{O} + \text{S}_2\text{O}_8^\cdot \rightarrow \text{rGO} - \text{C} = \text{O}^* + \text{SO}_4^\cdot \\
\text{SO}_4^\cdot + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2^-} + \text{HO}^\cdot + \text{H}^+ \\
(\text{SO}_4^{2-}, \text{HO}^\cdot) + \text{TC} \rightarrow \text{intermediates} + \text{CO}_2 + \text{H}_2\text{O}
\]

However, it is noted that a complete understanding of persulfate activation by graphene and its derivatives is still not fully revealed and there is a need for further research on mechanism [68, 69]. It has been reported that the activation mechanism is not only by radicals but also a non-radical pathway leading to the formation of persulfate radicals. Currently, three theories for PS activation are presented by different authors [70–72] (1) electron-rich ketone group; (2) defective edges of boundary of carbon network; and (3) sp\(^2\) carbon along the
Our obtained results were comparable with other work previously reported. The charge of TC in solution also played an important role; for pH below 3.3 TC was in protonated, resulting in positively charged which are more easily to be attacked by anion radicals and hence the degradation of organic compounds in water.

3.3. Factors influencing the degradation of TC by rGO/PS system

3.3.1. Effect of pH

The influence of initial solution pH on the TC removal efficiency of rGO/PS system was conducted at the following conditions ([PS] = 0.2 mM, [TC] = 5 mg l⁻¹, [rGO] = 10 mg l⁻¹), and the obtained results were presented in figure 8. The results showed that TC removal efficiency increased when the solution changed from acidic to neutral to alkaline. Within the examined conditions in this work, the rGO/PS system presented the best TC removal efficiency (about 98% of TC were removed after 40 min, and reaction rate constant = 0.079 min⁻¹) at pH4 whereas at the lowest TC removal efficiency observed at pH10 (only 77% of TC were removed after 40 min, with a corresponding reaction rate constant = 0.041 min⁻¹). TC removal efficiency of the system at pH7 and pH8 were relatively comparable, with around 95% of TC removed after 40 min and reaction rate constant in the range of 0.057–0.062 min⁻¹ (figure 8).

TC removal efficiency of rGO/PS system at different pH could be explained by the involvement of free radicals (HO·, SO₄²⁻), surface charge of catalyst (rGO) and charge of TC in solution which largely varied as a function of pH. In acidic solutions, SO₄²⁻ was the main free radical generated from PS while in neutral solutions both HO·, SO₄²⁻ were present, and in more basic pH, HO· radicals were predominant as in base solutions SO₄²⁻ will react with HO⁻ to produce HO²⁻ according to the following reaction [4, 73, 74]:

$$\text{SO}_4^{2-} + \text{HO}^- \rightarrow \text{SO}_4^{2-} + \text{HO}^-$$  \hspace{1cm} (4)

The charge of TC in solution also played an important role; for pH below 3.3 TC was in protonated, resulting in positively charged [75], hence be more vulnerable to be attacked by SO₄²⁻ because the latter was an anion radical. In pH within the range 3.3–7.7, TC was in the form of zwitterion + – 0 while above 7.7, TC was in the form of monovalent anion, + – –, or a divalent anion, + – [75]. Furthermore, the obtained results in this work showed that pHpzc of rGO was 4.1, suggesting rGO surface was positively charged in solutions with pH < 4.1, and negatively charged in pH > 4.1 solutions. At pH4, although there were certain sites on TC molecules positively charged which are more easily to be attacked by SO₄²⁻ the in solution, the positive charges of rGO prevent TC molecules from being adsorbed on rGO surface (electrostatic repulsion) where concentration of SO₄²⁻ would be higher than other places in the solution due to the activation of PS by rGO. In addition, in pH4 solution, there were higher concentration of H⁺ which more mobile than TC molecules, therefore there was concurrence in electrostatic attraction between SO₄²⁻ anion radicals and positively charged sites on the TC molecules and ion H⁺. Those parameters might results in lowest TC removal efficiency of rGO/PS system at pH4. Regarding pH6, PH7, and pH8 solutions, different processes (electrostatic repulsion/attraction, generation of both HO· and SO₄²⁻) influenced the TC removal efficiency by rGO/PS system. The results revealed there were no significant discrepancy between the system performance at pH7 and pH8.

Regarding basic solution at pH10, HO· were predominant and TC removal efficiency was highest compared with other pH in this work. This could be attributed to more radicals generated by PS in base solutions [36, 74]. Our obtained results were comparable with other work previously reported [4, 33].

Figure 8. Effect of pH on TC degradation by rGO/PS (a), and pseudo-first order kinetics (b). (Reaction conditions: [rGO] = 10 mg l⁻¹; [TC]₀ = 5 mg l⁻¹; [PS] = 0.2 mM).
3.3.2. Effect of rGO loading

Catalyst concentration can influence the degradation of organic pollutants as it provides more active sites available to react with the oxidant species, hence fortifying the generation of radicals being responsible for degradation of pollutants. In this section, rGO concentration of 5, 10, 20, and 30 mg l\(^{-1}\) while other reaction conditions fixed such as pH of TC solution (6.5), \([TC_0] = 5\) mg l\(^{-1}\), \([PS] = 0.2\) mM were used for comparison. The results showed that the more catalyst loading the better TC degradation performance of the rGO/PS system (figure 9). After 40 min, almost 100% of TC were removed by the system with catalyst loading \(= 20–30\) mg l\(^{-1}\) whereas this value for the system working with catalyst of 5 mg l\(^{-1}\) reached only 80% (figure 9(a)). The corresponding constant rate were around 0.10 min\(^{-1}\) and 0.036 min\(^{-1}\), respectively. The TC degradation efficiency for catalyst loading \(= 20\) mg l\(^{-1}\) was comparable (almost 100% of TC degradation reached after 40 min and constant rate \(= 0.097\)) with that obtained for catalyst loading \(= 30\) mg l\(^{-1}\); therefore 20 mg l\(^{-1}\) was selected as optimal catalyst loading. This results are in agreement with the results reported by other work [4, 32].

3.3.3. Effect of initial PS concentration

It was shown that when the initial PS concentration increased from 0.1 mM to 0.3 mM, the the degradation performance of the system also augmented, with the time required for complete TC removal was 40 min for PS concentration \(= 0.3\) mM whereas only about 85% of TC was removed at the same time for PS concentration \(= 0.1\) mM (figure 10). However, when initial PS concentration reached 0.4 mM, the degradation efficiency decreased compared with those obtained when the system used PS concentration \(= 0.2\) mM or 0.3 mM. Those could be explained by the increase in initial PS concentration led to more free radicals generated, hence more TC removed. However, there was an optimal PS concentration in catalytic oxidation because more elevated free radical levels would provoke self-quenching and recombination of radicals by the following reactions [76]:

\[
\text{SO}_4^{2-} + S_2O_5^{2-} \rightarrow \text{SO}_4^{2-} + S_2O_6^{2-} \quad k = 5.5 \times 10^5 \text{ M}^{-1} \text{s}^{-1}
\]  (5)
In addition, Ghauch et al 2012 [77] revealed that self-scavenging effect of SO$_4$$^-$ by equation (5) was not significant as SO$_4$$^-$ consumed for oxidation reactions were more important. The explanation for our obtained results could be attributed to the fact that excessive concentrations of SO$_4$$^-$ generated at PS concentration = 0.4 mM led to free radical scavenging effect by equation (4).

In this work, the efficiency for the removal of TC at PS = 0.3 mM was only slightly higher than at PS = 0.2 mM, and after 40 min of reaction, almost the same level of TC removal (around 97%) was obtained for both initial PS concentration. The rate constants of rGO/PS system at initial PS concentration = 0.2 mM and 0.3 mM were respectively 0.0764 and 0.0908 min$^{-1}$. Therefore, we will use PS = 0.2 mM as optimal condition for future trials.

3.3.4. Effect of initial TC concentration

To examine the effect of initial TC concentration, a series of test were performed with initial TC concentration varied from 2 to 8 mg l$^{-1}$; other optimal conditions revealed from previous tests were deployed, [PS] = 20 mM; [rGO] = 20 mg l$^{-1}$, pH value = 6.7 of the TC solution was not adjusted. The obtained results are presented in figure 11. It was observed that the more diluted TC solution the better TC removal efficiency. At TC concentrations of 2–3 mg l$^{-1}$, almost 100% of TC were removed after 40 min of reaction while more than 95% of its content were removed after 30 min (figure 11(a)). When the initial TC concentration increased to 7–8 mg l$^{-1}$, the TC removal efficiency dramatically decreased. Only around 60% of TC were removed after 40 min of reaction. The rate constant of rGO/PS for the degradation of TC at 2–3 mg l$^{-1}$ were about 1 min$^{-1}$ while these values for the degradation of TC at 7–8 mg l$^{-1}$ were 0.027 min$^{-1}$. As the removal performance of the system for initial TC concentration at 5 mg l$^{-1}$ was slightly lower than those obtained for the system at TC = 7–8 mg l$^{-1}$ (95% of TC were removed after 40 min of reaction and rate constant = 0.0676 min$^{-1}$), initial TC concentration = 5 mg l$^{-1}$ was selected as optimal condition.

For evaluating the stability and reusability of the catalyst, after the TC treatment test, rGO were separated from the solution by using 0.22 micron-filters, rinsed with distilled water, dried at 105°C for 24 h and then used as the catalyst in the next cycle of degradation experiments. The results showed that the performance of rGO (20 mg l$^{-1}$)/PS (0.2 mM) for the catalytic degradation of TC (5 mg l$^{-1}$) at neutral pH decreased from 98% of TC removed for 1st run to 80% for the 2nd run after 40 min (figure S2). After the third cycle, 76% of TC were removed after 40 min, suggesting that more time and/or other recycling methods were needed to improve the catalytic performance of rGO/PS system. Ultrasonication and thermal treatments after each cycle will be examined in our future work.

4. Conclusions

Surface morphology, structure, and elemental analyses revealed the conversion of GO to rGO. After the reduction process, the obtained rGO presented C/O ratio much higher than that in GO precursor (4.01 versus 1.60). In addition, the analyses by FT-IR and Raman spectroscopy also revealed oxygen element was reduced in rGO, confirming successful reduction of oxygen functional groups in GO to form rGO, and structural defects of GO and rGO. Specific surface of rGO calculated by BET was within the range of values reported previously by other research, but quite low (4.33 m$^2$ g$^{-1}$) due to the formation of aggregation of rGO sheets which became
more compacted when solvents were evaporated by drying processes. The measurement of rGO surface would be more precise when it is conducted in solution.

The degradation of TC by sole rGO, PS, and rGO/PS system revealed rGO foster the formation of sulfate radicals, thus resulting in much better TC removal efficiency. More than 95% of TC (5 mg l⁻¹) were removed by rGO/PS system whereas around 50% and only 20% of TC were removed by sole PS, and rGO, respectively. The degradation of TC in solution occurred better in basic solution might be attributed to more radicals form in solutions with higher pH. In contrast, in acidic solutions, the performance of rGO/TS system for the removal of TC was less important. Only 77% of TC 5 mg l⁻¹ were removed at pH₄ after 40 min whereas this value for the system working at pH₁₀ was 98%. The reaction constant rate at pH₁₀ was almost twice the one at pH₄ (0.079 min⁻¹ versus 0.041 min⁻¹). At acidic solutions, there were electrostatic repulsion effect between rGO and TC, and a concurrence between H⁺ and positive sites of TC with radical anion SO₄⁻ by electrostatic attraction. TC initial concentration negatively correlated with degradation efficiency by rGO/PS while rGO loading resulted in positive correlation with degradation efficiency. Persulfate presented an optimal concentration for the treatment of TC, and for all experimental conditions the degradation of TC followed the pseudo-first order kinetics, with a typical coefficient of determination higher than 0.95.

The stability test revealed catalytic performance of rGO/PS for TC degradation reduced significantly after 3 cycles. Further research needs to be conducted to overcome that challenge to make the catalytic system more feasible.

Acknowledgments

This research is funded by the Ministry of Science and Technology of Vietnam under the project code NDT.75. CHN/19.

Conflict of interest

The authors declare that they have no conflicts of interest.

ORCID iDs

Dinh Trinh Tran @ https://orcid.org/0000-0001-9936-1823

References

[1] Kordick D L, Papich M G and Breitschwerdt E B 1997 Antimicrob. Agents Chemother. 41 2448–55
[2] Daghrir R and Drogui P 2013 Environ Chem. Lett. 11 209–27
[3] Chopra I and Roberts M 2001 Microbiol Mol. Biol. Rev. 65 232–60
[4] Safari G H, Nasseri S, Mahvi A H, Yaghmaeian K, Nabizadeh R and Alimohammadi M 2015 J. Environ Health Sci. Eng. 13 76
[5] Chang P-H, Jiang W-T, Li Z, Jean J-S and Kuo C-Y 2015 J. Pharm. Anal. 4 86–111
[6] Danner M-C, Robertson A, Behrends V and Reiss J 2019 J. Environ. Pollut. 255 113140
[7] Havelkova B, Beklova M, Kovacova V, Hlavkova D and Pikula J 2016 Sci. Total Environ. 664 793–804
[8] Reichert G, Hilgert S, Fuchs S and Azevedo J C R 2019 J. Environ. Pollut. 255 113140
[9] Pan S-F, Zhu M-P, Chen J P, Yuan Z-H, Zhong L-B and Zheng Y-M 2015 J. Environ. Pollut. 212 501–11
[10] Havelkova B, Beklova M, Kovacova V, Hlavkova D and Pikula J 2016 Neuro Endocrinol. Lett. 37 38–44 (Suppl. 1)
[11] Milakovic M, Vestergaard G, Gonzalez-Plaza J J, Petrović I, Simatović A, Sentić I, Kublik S, Schloter M, Smalla K and Udiković-Kolić K 2019 Environ. Pollut. 248 11–22
[12] Zhao H, Shi S, Zhao H, Gao H and Lu F 2019 RSC Adv. 9 41628–38
[13] Giebultowicz J, Nałęcz-Jawecki G, Hannisz M, Kucharski D, Korzeniewska E and Plaza G 2020 Molecules 25 1470
[14] Rodríguez-Mozañ S et al. 2020 Environ. Int. 140 105733
[15] Sbarbaro A, Ademollo N, Pescatore T, Rauseo J and Patrolecco L 2019 Front. Environ. Sci. Eng. 13 46
[16] Boxall A B, Johnson P and Smith E 2006 J. Agric. Food Chem. 54 2286–97
[17] Premarathna K S D, Rajapaksha A U, Adassoriya N, Sarkar B, Sirimuthue N M S, Cooray A, Ok Y S and Vithanage M 2019 J. Environ. Manage. 238 315–22
[18] Huang L, Wang M, Shi C, Huang J and Zhang B 2014 Desalination Water Treat. 52 2678–87
[19] Pan S-F, Zhu M-P, Chen J P, Yuan Z-H, Zhong L-B and Zheng Y-M 2015 Sep. Purif. Technol. 153 76–83
[20] Oh S-H, Jeong S, Kim I S, Shin H K and Jang A 2019 J. Environ. Manage. 247 385–93
[21] Yang Y, Zhang X, Chen Q, Li S, Chai H and Huang Y 2018 ACS Omega 3 15870–8
[22] Hou L, Wang L, Royston S and Zhang H 2016 J. Hazard Mater. 302 458–67
[23] Yan Q, Xu M, Lin C, Hu J, Liu Y G and Zhang R 2016 Environ. Sci. Pollut. Res. 23 14422–30
