



Adsorption and photocatalytic activity of biochar with graphitic carbon nitride (g-C₃N₄)



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ABSTRACT

Biochar has attracted significant attention for its potential as a carbon-neutral biowaste treatment and adsorbent. However, the adsorbed contaminants should be treated further. This study is intended to degrade or mineralize adsorbed contaminants using biochar. Among biowaste, nitrogen rich materials can produce graphitic carbon nitride (g-C₃N₄) with photocatalytic activity through pyrolysis. In this study, urea, glycine, L(+)-arginine, and puree were used to prepare photocatalytic biochars. XRD analysis and screening tests were performed to evaluate the production of g-C₃N₄. As model compounds, Orange G (OG) and Cr(VI) were oxidized and simultaneously reduced in a reactor by biochar. Additionally, biochar effectively activated persulfate to sulfate radicals. The oxidation rate of OG was enhanced by the addition of persulfate, where synergistic effects were observed. Therefore, photocatalytic biochar could be an alternative for treating environmental pollutants.

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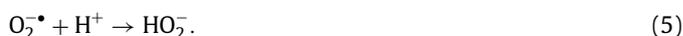
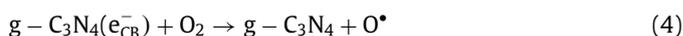
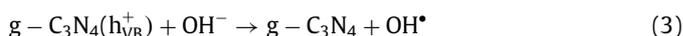
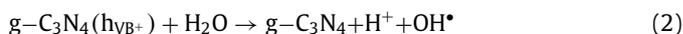
1. Introduction

Recently, enormous amounts of biowaste have been produced in agriculture, forestry, and food industries [1]. Biowaste is considered organic solid waste, and it has been treated by ocean dumping and incineration [2]. However, biowaste has been recognized as an organic resource and carbon sink. Biochar has attracted more attention due to its potential role in carbon sequestration, renewable energy, waste management, agricultural use, and environmental remediation [3–8]. Biochar is commonly used as an adsorbent, and contaminants adsorbed onto biochar remain problematic [9–13]. These contaminants must be degraded or mineralized.

Some nitrogen-rich organic matters have been used as single-source molecular precursors to obtain g-C₃N₄ under thermal treatment [1]. This material is a metal-free catalyst and has been widely studied as a photocatalyst with adsorption capacity [14,15]. Substances such as cyanamide, dicyanamide, melamine, thiourea, and urea have been used to prepare g-C₃N₄ [1]. Among these materials, urea derived material showed the highest quantum yield of 26.5% at 400 nm and the highest photocatalytic activity [16]. Urea consists of carbon and nitrogen, the most abundant materials on the

planet, so it is easily obtained and prepared [17]. Photolysis may mineralize the contaminants adsorbed on biochars or environmental contaminants without requiring further post-treatment [18,19].

Photocatalysts are activated in three steps: irradiation to move electrons from the valence band to conduction band, the formation of the electron-hole pair (EHP), and oxidation and reduction reaction on the photocatalyst surface [20,21]. More EHPs induce more photocatalytic activities, which induces oxidation and reduction.



In this case, the potential difference in the electron-hole space, commonly referred to as the band gap, has a unique value depending on the material and structure. In general, the band gap can be controlled by the crystallinity of the semiconductor. The g-C₃N₄ used in this study is active in the ultraviolet and visible light. The band gap is about 2.7 eV [22,23], which is lower than that of TiO₂ [24,25], and g-C₃N₄ can be activated by low energy.

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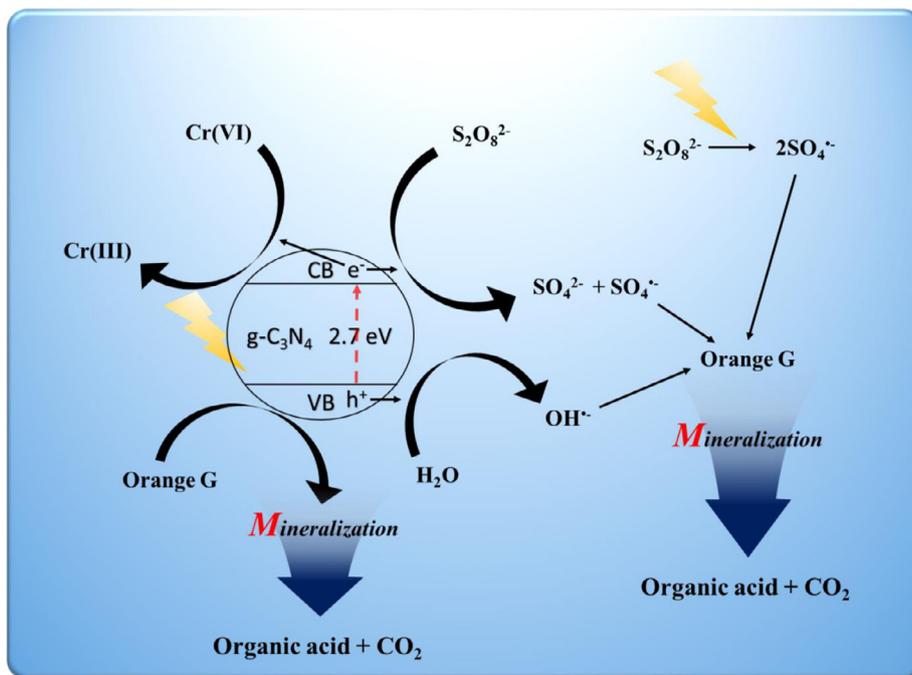


Fig. 1. A schematic diagram of the oxidation and reduction of organic pollutants and Cr(VI) by photocatalyst and persulfate (PS) under UV light.

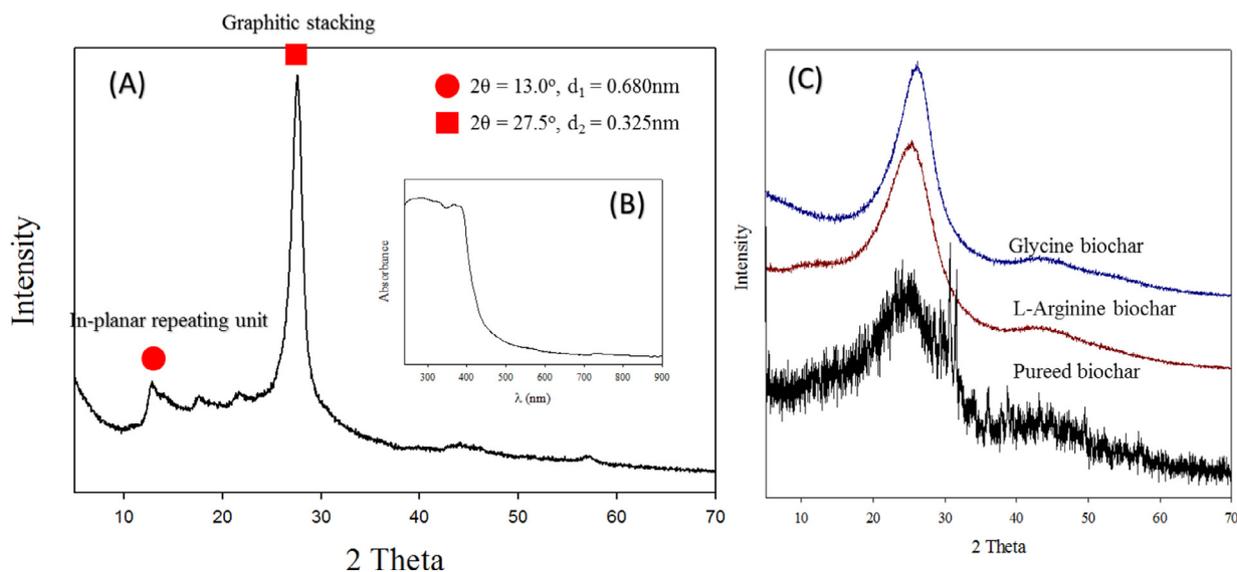


Fig. 2. XRD of urea biochar (A), UV-vis diffuse-reflectance spectra (b) and glycine, L-arginine, pureed biochar XRD patterns (C).

Table 1
Experimental conditions.

Exp	OG (mM)	Cr(VI) (mM)	PS (mM)	Light sources	Biochar solid-liquid ratio	Time (min)
1	0.05	0	0	Sunlight	5 g/l - Urea biochar, g/l - Glycine, L-Arginine, Pureed soybean biochar	300
2	0	0.3	0	15W UV lamp	5 g/l Urea biochar	720
3	0.05	0	0			
4	0	0.3	0	15W UV lamp	5 g/l Urea biochar	360
5	0.05	0.3	0			
6	0.05	0	0	15W UV lamp	5 g/l Urea biochar	360
7	0.05	0	1			
8	0.05	0	1	Without biochar		

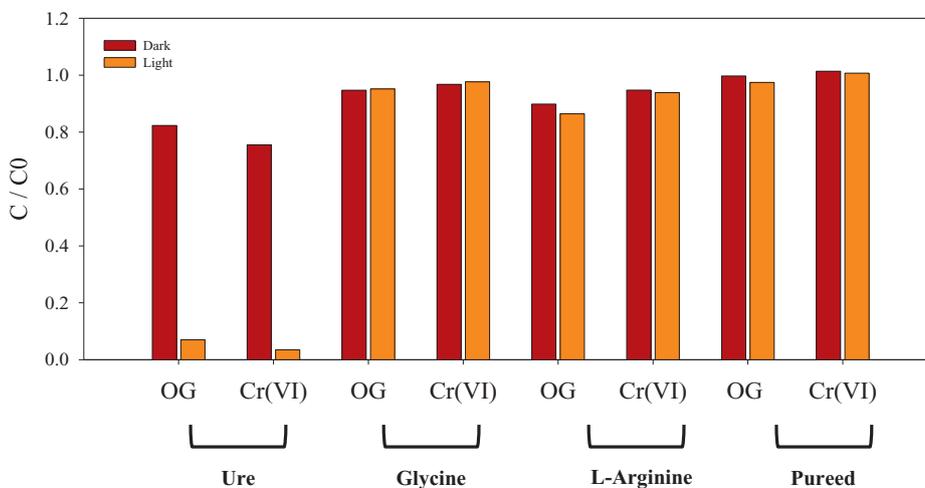


Fig. 3. Oxidation and reduction screening test of OG and Cr(VI) using urea, glycine, L-arginine and pureed biochar.

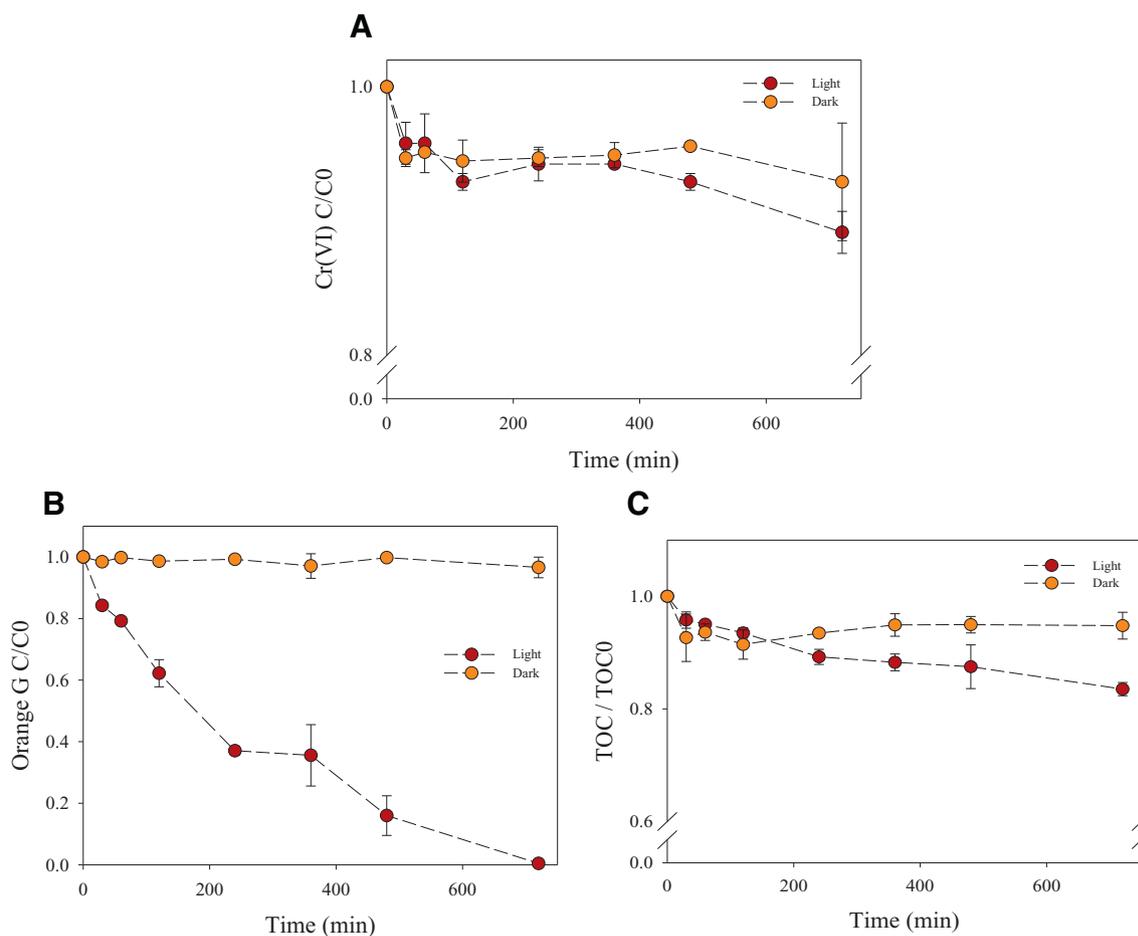
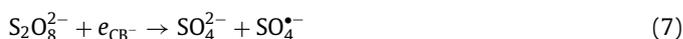


Fig. 4. Individual reduction and oxidation of Cr(VI) or OG under 15W UV lamp or dark condition. (A) Reduction of Cr(VI), (B) oxidation of OG, and (C) removal of TOC.

Even though photolysis can mineralize organic contaminants, mineralization takes a long time to complete. Additional oxidants can be used to enhance the mineralization rate. PS is an oxidizing agent used in the oxidation process. PS is activated to sulfate radical to induce oxidation, and UV light can be used to activate PS to sulfate radicals [26–28]. The reactive radical intermediates ($\text{SO}_4^{\bullet-}$) produced by reaction with photo-generated electrons exert dual functions as strong oxidizing agents and as electronic scavengers to inhibit electron-hole recombination at the semiconductor surface [29]. Therefore, we hypothesized that PS could be activated

by photocatalysts as well as by UV. We anticipated that addition of PS to photolysis would synergistically enhance oxidation of organic pollutants.



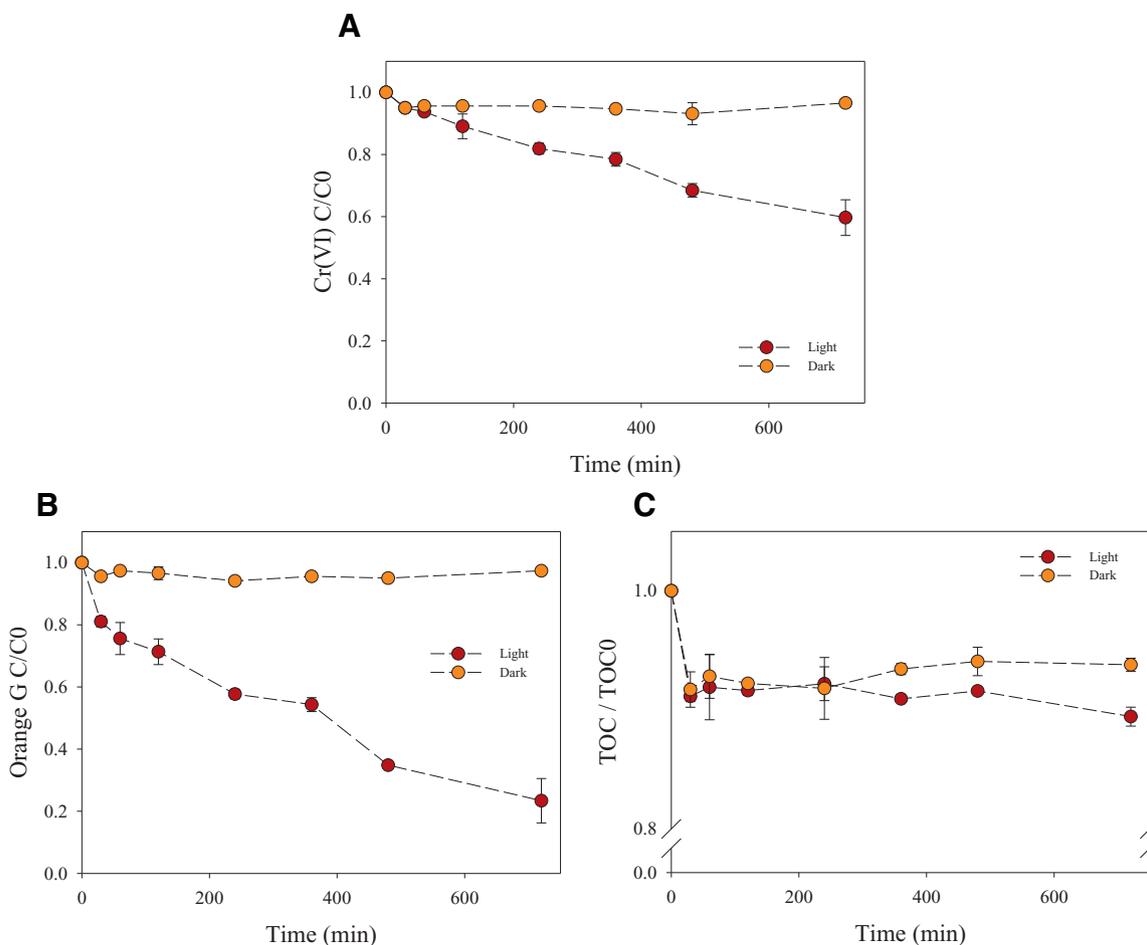


Fig. 5. Simultaneously reduction and oxidation of Cr(VI) and OG under 15W UV lamp or dark condition. (A) Reduction of Cr(VI), (B) oxidation of OG, and (C) removal of TOC.

Azo dye and hexavalent chromium were used as target contaminants. Azo dye should be oxidized by the photocatalyst [30] while hexavalent chromium should be reduced [31]. In this study, it was hypothesized that nitrogen rich biomass could be used to prepare biochar containing $g\text{-C}_3\text{N}_4$ structure including glycine, L(+)-arginine, and nitrogen rich soy bean puree. This study involved simultaneous treatment of azo dye and Cr(VI) by biochars with $g\text{-C}_3\text{N}_4$ using radicals produced according to Eqs. (2)–(8). The reduction ability on conduction band was also assessed (Fig. 1).

2. Materials and methods

2.1. Materials

Urea ($\text{CH}_4\text{N}_2\text{O}$, $\geq 99\%$), glycine ($\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$, $\geq 99\%$), L(+)-arginine ($\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2 \geq 98\%$), acetone (CH_3COCH_3 , $\geq 99.5\%$), and sulfuric acid (H_2SO_4 , $\geq 95\%$) were purchased from Samchun Co., Korea. Orange G ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$), potassium persulfate ($\text{K}_2\text{O}_8\text{S}_2$, $\geq 99\%$), sodium nitrate, (NaNO_3), and 1,5-diphenylcarbazide ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$) were provided by Sigma-Aldrich. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was obtained from Junsei Chemical Co., Ltd., Japan. The photocatalyst was prepared using nitrogen-rich puree. All reagents were used after being dissolved in deionized water. Raw materials (urea, glycine, L(+)-arginine, and puree) were used to prepare biochar, including $g\text{-C}_3\text{N}_4$. The materials were dried at 80°C for 24 h and pyrolyzed under nitrogen at 550°C for 3 h at $5^\circ\text{C}/\text{min}$ [14].

2.2. Adsorption and photoreaction

The experimental conditions are shown in Table 1. Screening tests were conducted to evaluate the photocatalytic ability of produced biochar. Sunlight experiments were performed between 11:00 and 16:00 during August at a latitude of $35^\circ 43'$ North and longitude of $126^\circ 59'$ East (Jeonju, Korea). Photolysis was performed under a 15W UV lamp with a dominant wavelength of 380 nm. Based on the results, photo-oxidation of OG and photoreduction of Cr(VI) were evaluated. Simultaneous photo-oxidation and photoreduction were then carried out. Additionally, the same experiments were performed in the dark to examine the adsorption capacity of biochar. Finally, activation of persulfate using biochars was evaluated to investigate the synergistic effects on oxidation of OG.

2.3. Analytical method

X-ray diffraction spectroscopy (XRD, PANalytical, Holland) was used to assess the structure of $g\text{-C}_3\text{N}_4$ in biochar. The ultraviolet-visible diffuse reflection spectra were measured by UV/Visible/NIR (SolidSpec-3700, Shimadzu, Japan). The OG and Cr(VI) in samples were analyzed by a UV/Visible spectrophotometer (HS3300, HUMAS, KOREA). OG was analyzed at 478 nm and Cr(VI) was analyzed by the diphenyl carbazide method [32–36]. The concentration of PS was estimated by analyzing sulfate concentration using ion chromatography (Futecs Co, Korea). The residual total organic carbon (TOC) was analyzed by a total organic carbon an-

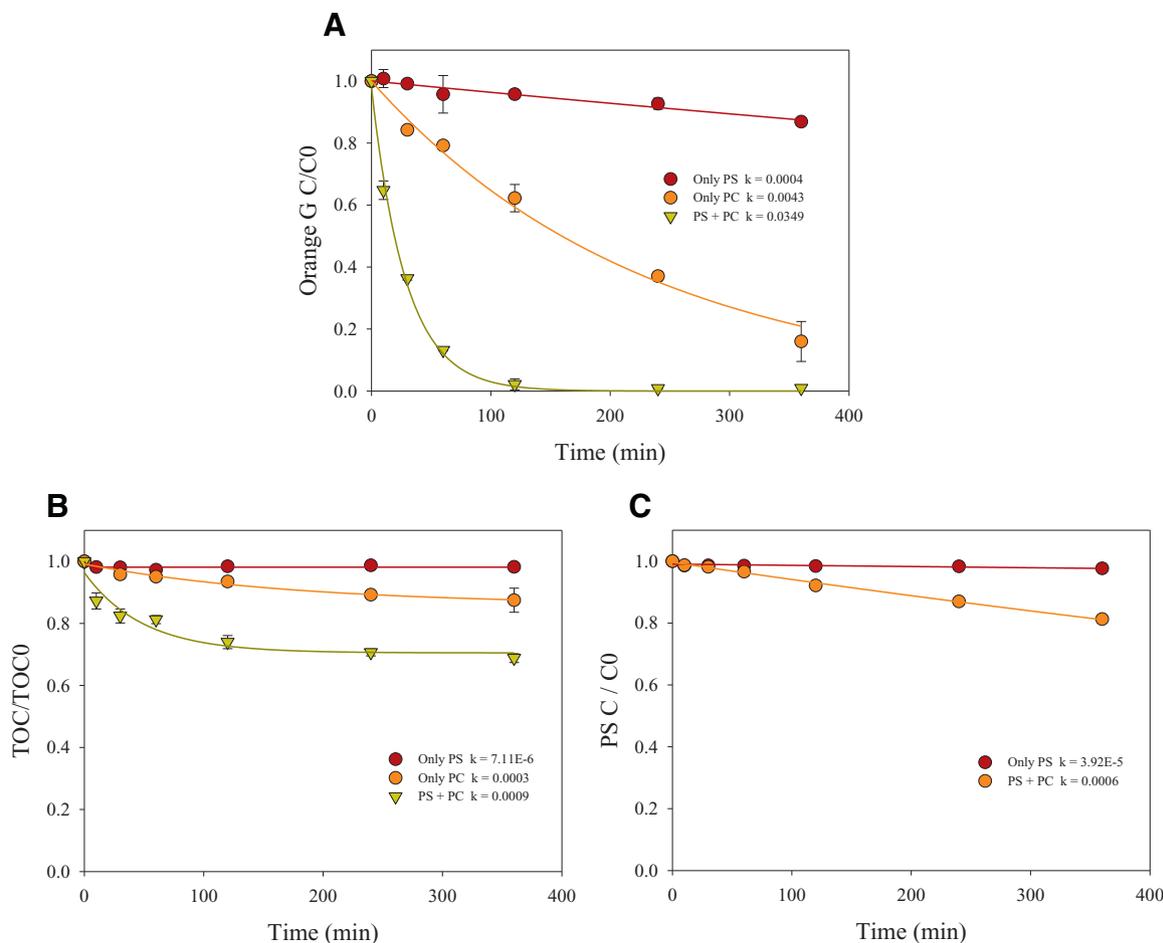


Fig. 6. Degradation ratio of OG when PS and/or biochar including $g\text{-C}_3\text{N}_4$ as a photocatalyst (PC) is used. (A) Degradation of OG, (B) degradation of TOC, and (C) degradation of PS.

alyzer (H544352, Shimadzu, Japan) after decomposition of organic material.

3. Results and discussion

3.1. Production of the biochar including $g\text{-C}_3\text{N}_4$

XRD was used to analyze biochar structure (Fig. 2(a)). Urea biochar had an in-planar repeating unit showing structure repeatability with crystallinity at 13° , and graphic stacking was observed at 27.5° [22]. However, in-planar repeating units and graphitic stacking were not observed in biochars prepared by glycine, arginine, and puree (Fig. 2(c)). Evaluation of the photocatalytic activity of biochars shows that urea biochar including $g\text{-C}_3\text{N}_4$ can oxidize and reduce over 90% OG and Cr(VI) (Fig. 3), and the biochar did not have adsorption capacity for contaminants. Other biochars did not show any photocatalytic activity even though sunlight was used, and slight adsorption was observed. As a result, photocatalyst was not prepared by other biochars, and only urea can be used to prepare the photocatalyst.

Urea biochar including $g\text{-C}_3\text{N}_4$ was investigated by UV-vis diffuse reflectance spectroscopy, and the results are shown in Fig. 2(b). The $g\text{-C}_3\text{N}_4$ has a pattern of typical organic semiconductors in which band gap absorption was strongly expressed at about 420 nm. This corresponds to pale yellow, as already reported in the literature [37,38].

3.2. Degradation of the pollutants using biochar including $g\text{-C}_3\text{N}_4$

The kinetics of photo-oxidation was investigated using urea biochar and OG. OG was degraded within 360 min under 15 W UV light (Fig. 4). This is comparative to TiO_2 , the most popular photocatalyst. Only 13% of OG was removed for 150 min under sunlight [39]. Although Cr(VI) was completely reduced in screening tests under sunlight, only 11% of Cr(VI) was reduced during 360 min under 15 W UV light (Fig. 4(a)). The low reduction is likely due to weaker UV light compared to sunlight. During the experiments, UV light was turned off for 1 h, and for that time the photocatalytic reaction was stopped. This is direct evidence indicating that urea biochar is a photocatalyst. Experiments conducted in the dark confirmed that adsorption played a slight role in the removal of pollutants.

Simultaneous reduction and oxidation were investigated using OG, Cr(VI), and urea biochar under 15 W UV light (Fig. 5). Oxidation and reduction occurred simultaneously. In this case, Cr(VI) and OG were slightly reduced and oxidized without light. Organic acids produced by the partial oxidation of OG may serve as electron donors for reduction of Cr(VI). Cr(IV) was not reduced without OG, so it must have been reduced by the organic acids that are byproducts of OG degradation.

OG is a large molecule compound, and azo bonding in the molecule could break first. However, the partially oxidized compound could be secondary pollutants [30]. Therefore, total organic carbon (TOC) was analyzed to evaluate secondary pollutants as indicators (Figs. 4(c) and 5(c)). Although OG was mostly removed, only about 19% of the TOC was removed when OG was individually

removed. A total of 40% of the TOC was removed when OG and Cr(VI) were simultaneously removed. The degradation rate of OG and removal rate of TOC without Cr(VI) were slightly lower than those with Cr(VI) because of synergistic effects.

3.3. Activation of the PS using biochar including $g\text{-C}_3\text{N}_4$

Even though biochar showed photocatalytic activity in the oxidation of OG, the reaction rate is still low. This indicates that it requires a long residence time to treat OG in the reactor. Therefore, persulfate was added to enhance the oxidation rate of OG. The oxidation rate of OG was 0.0004 min^{-1} with PS only, 0.0043 min^{-1} with urea biochar only, and 0.0349 min^{-1} with simultaneous application of PS and biochar (Fig. 6). Simultaneous application enhanced the oxidation rate of OG 10–100 times compared to the single application. Likewise, the TOC degradation rate constants were $7.11\text{E-}6\text{ min}^{-1}$ with PS only, 0.0003 min^{-1} with biochar only, and 0.0009 min^{-1} with the simultaneous application. The simultaneous application of biochar and PS showed synergistic effects on oxidation of OG and enhanced complete oxidation of the partially oxidized compounds of OG. Although UV light could activate PS to sulfate radicals, PS was not activated by UV light due to the weak light intensity. The results indicate that biochar activated PS to sulfate radicals, and the radicals enhanced oxidation of OG.

4. Conclusions

Photocatalytic biochars were prepared by pyrolysis. Screening tests for photocatalytic ability and XRD analysis showed that urea based biochar had the structure of $g\text{-C}_3\text{N}_4$ and photocatalytic ability. Biochars prepared from other materials did not show any photocatalytic activity. Urea biochar reduced Cr(VI) and oxidized orange G. Oxidation and reduction occurred simultaneously in a reactor. Organic matter enhanced the reduction of Cr(VI), that is, intermediates of orange G oxidation. The addition of persulfate, an oxidizing agent, greatly enhanced the oxidation rate of orange G. This indicates that the biochar could effectively activate persulfate to sulfate radical. Additionally, persulfate addition resulted in synergistic improvement of the oxidation rate compared to the sum of individual applications of persulfate and biochar. Results indicate that biochar containing $g\text{-C}_3\text{N}_4$ could be a green and sustainable material used to degrade or detoxify environmental contaminants. This material could be utilized as a green photocatalyst.

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