

Removal of dissolved organic matter in sugar mill effluent by catalytic ozonation with activated carbon (O₃/GAC)

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Abstract

This study investigated removals of dissolved organic carbon (DOC) in natural surface water mixed effluent (NW-EFF) of sugar mill factory using O₃, granular activated carbon (GAC) and O₃/GAC as catalytic ozonation. Effects of O₃ flowrate and GAC dose on reductions of DOC and ultraviolet absorbance at 254 nm (UV₂₅₄) were examined. The DOC removals by O₃/GAC were the most efficient (85.5% – 88.0%), while those of O₃ and GAC were 41.2% – 61.7% and 0.6% – 14.2%, respectively. The UV₂₅₄ removals by O₃/GAC were 99.8%–99.9%, while those of O₃ and GAC were 92.7% – 97.2% and 4.9% – 28.5%, respectively. In O₃ experiment, the increases of ozone flowrate decreased the DOC removal. In O₃/GAC, during the first 60-min reaction time, the DOC removals by GAC doses of 0.1 g/L and 1.0 g/L were about the same drastic reductions of DOC observed at GAC dose of 2.5 g/L. After 60-min reaction time, the DOC concentrations gradually decreased at the same rate towards the end of the experiment for all GAC doses. The O₃/GAC reduced approximately 50% of specific ozone consumption compared to the O₃ alone for the same DOC removal. The enhancement factors (R) of all GAC doses are greater than 1.0 indicated that GAC doses have synergistic effects on the removal of DOC in NW-EFF. The O₃/GAC reduced the electrical energy per order (EEO) approximately 30% – 55% of those by the O₃ process. The present study shows that the O₃/GAC is suitable for treatment of NW-EFF of sugar mill factory due to DOC removal and energy efficiencies.

Keywords: Industrial effluent, Sugar mill, DOC, Advanced oxidation, Ozone, Reclamation

1. Introduction

Sugar mill industry is one of the most important industries in the world and global sugar demand tends to rise every year. In Thailand, the number of sugar mill factories has been continuously increasing during the last decade due to the rapid expansion of sugar business and sugar products. Therefore, water demand and wastewater increase as well. To reduce the natural raw water consumption in sugar mill factories, treated wastewater (effluent) has been stored in the storage pond combining with natural surface water. The natural surface water mixed effluent (NW-EFF) was used as raw water for water supply and productions in the factory. However, the NW-EFF still contains a large amount of dissolved organic matter (DOM) resulting in low quality of the mixed water and difficulty in water treatment. The DOM is a mixture of complex organic compounds, including natural organic matter (NOM) and effluent organic matter (EfOM). The presence of DOM causes many problems in water treatment processes such as the increased coagulant and disinfectant doses, promoted biological growth in the distribution system, and increased levels of complex heavy metals and adsorbed organic pollutants [1]. Generally, the EfOM is a mixture of NOM, soluble microbial products, and other organic compounds generated during water use and wastewater treatment [2]. Therefore, the NW-EFF, the mixture of natural surface water and secondary effluent, also contains a wide variety of organic matter as aforementioned. Thus, the organic matter in NW-EFF in this study was described as NW-EFF DOM. The NW-EFF DOM is a huge barrier to water utilization in the sugar mill factory because it produces an unpleasant color, odor and taste in water. To produce desirable qualities of water supply and utility water in the factory, the removal of NW-EFF DOM would be required.

In the previous studies, the conventional methods, such as adsorption, biological treatment, membrane filtration and coagulation, were applied to remove the organics in many natural water and secondary effluents. In the adsorption method, activated carbon is an effective adsorbent for removing organic and inorganic pollutants but the regeneration of the exhausted adsorbent and safe disposal of the used adsorbent are the major limitations of this method [3-5]. Applications of biological treatments were limited by long residence time for the EfOM degradation of industrial effluents [3, 6-8]. Membrane filtration processes was suffering from organic fouling which in turn increased the cost of membrane cleaning and replacement [3, 9-11]. The coagulation process, the simple and low operating cost technique, removed effectively high molecular weight (MW) organic matter, while smaller organic molecules tend to be more polar and more soluble. To force the organics to be coagulated, a higher coagulant dose was always required [11]. The high coagulant dose and large sludge formations are the major limitations of this process [3]. Importantly, the coagulation process can only remove DOM partially [11], while the residual organics could be a precursor of disinfection by-products (DBPs) during ozonation, chlorination or

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chloramination in the disinfection process [12, 13]. Therefore, to reduce the risk of NW-EFF DOM in produced water that used in the sugar mill factory, an advanced treatment technique is required to remove the DOM constituent in NW-EFF.

Ozonation is one of the most cost-effective method and widely used for the removal of recalcitrant pollutants [14-16]. However, some intermediate products from reaction between DOM and ozone were relatively refractory to ozone and more difficult to be further mineralized [17]. Thus, more ozone dosage is generally required for enhancing DOM mineralization. To improve the performance and reduce the ozone consumption, some catalysts such as transition metal ions, alumina and alumina-based supports catalyst, cerium-based supports catalyst, carbon and carbon-based supports catalyst, have been applied in the ozonation process to produce hydroxyl radical (HO•) which is a stronger oxidant than ozone [3, 18]. Among various catalysts, granular activated carbon (GAC) has received quite attention due to, great efficient and environmentally friendly, low cost and high specific surface area [19]. In the GAC catalytic ozonation (O₃/GAC), the GAC can accelerate the ozone decomposition to promote HO• generation, while the increases of GAC dose increase the ozone decomposition rate [20]. However, an excessive amount of the GAC inhibits the reaction resulting in the decreasing removal efficiency of organic contaminant as well [21]. Ozone and GAC doses have been reported as important factors for the design and operation of the O₃/GAC system. The appropriate ozone and GAC doses varied greatly on types of organics and water matrixed.

O₃/GAC has been successfully applied to remove dye, pesticides, humic acid and several industrial effluents [19-21]. Therefore, the O₃/GAC has potential for treating sugar mill industry. Thus far, utilization of O₃/GAC for the removal of dissolved organic matter in the real water matrixed of sugar mill factory has never been reported. The objective of this study is to investigate the removal of DOM in NW-EFF of sugar mill factory by O₃/GAC process. The influences of O₃ and GAC dosage on dissolved organic carbon (DOC) and UV absorption at wavelength of 254 nm (UV₂₅₄) removal were examined during ozonation of NW-EFF after coagulation pretreatment in the presence of GAC. O₃ and GAC alone were also compared. The synergistic effect of GAC on DOC removal and the electrical energy per order (EEO) were determined.

2. Materials and methods

2.1 Materials and reagents

All the chemicals used in this study were analytical grade. FeCl₃·6H₂O and Na₂S₂O₃·5H₂O were purchased from QReC, New Zealand. KI was obtained from RCI Labscan Ltd., Thailand. Potassium indigotrisulfonate was purchased from ACROS Organic™, Belgium. All chemical solutions were prepared by deionized (DI) water. Granular activated carbon (GAC; 8×30 mesh size, iodine number of 750) was purchased from EUNICARB activated carbon, Taiwan.

2.2 Water sampling and characterization

A NW-EFF sample used in this study was collected on July 11, 2020 from a storage pond of sugar mill factory, Northeast region, Thailand. The NW-EFF was pretreated by coagulation/sedimentation using FeCl₃ (10 mg/L) to remove turbidity and consequently filtered through a 1.2 μm glass-fiber filters (Whatman, England) to remove particulate organic matter and colloids. The NW-EFF and pretreated NW-EFF were analyzed for pH, turbidity, color, DOC and UV₂₅₄. The characteristics of the sugar mill NW-EFF before and after coagulation pretreatment are shown in Table 1.

Table 1 Characteristics of the sugar mill NW-EFF before and after FeCl₃ coagulation

Parameters	Before FeCl ₃	After FeCl ₃
pH	7.92 ± 0.08 ^a	7.67 ± 0.21 ^b
Turbidity (NTU)	10.85 ± 0.50 ^a	0.83 ± 0.28 ^b
Color (ADMI)	17.5 ± 2.1 ^a	13.5 ± 2.1 ^b
DOC (mg/L)	6.46 ± 0.17 ^a	5.15 ± 0.15 ^b
UV ₂₅₄ (cm ⁻¹)	0.1381 ± 0.0083 ^a	0.1043 ± 0.0024 ^b

Note: Data were reported in average, "±" represented standard deviations ^a; n = 2, ^b; n = 7

2.3 Experimental procedure

The pretreated NW-EFF was stored in dark condition until it was used for ozonation (O₃), ozonation with granular activated carbon (O₃/GAC) and GAC adsorption experiments. The GAC was prepared before used in the experiments followed by these steps. Firstly, soaking 100 g of GAC with 1.0 L of ultrapure water for 3 times, boiling with a 1.0 L for an hour, rinsing with 1.0 L of ultrapure water for 3 times, after that, dried at 105 °C for 24 h in a hot air oven and cooled to room temperature in a desiccator, respectively. The dried GAC was stored in an air-locked bag until used.

The experiments of O₃ and O₃/GAC were carried out using a semi-batch mode as shown in Figure 1. Two liters of pre-treated effluent were added to a 2-L borosilicate glass bottle reactor. The O₃ gas was generated by corona-discharge using ozone generator (OZ-1060 SW, EBASE Corp., Ltd. Thailand) with O₂ (98%) as feed gas. Noted that the ozone generator can be operated at fixed power (60 W, 220 Vac, 50 Hz), amount of ozone added to the reactor was adjusted by the O₃ gas flowrate. The O₃ gas was continuously bubbled at the bottom of reactor by a glass porous diffuser and completely mixed by a magnetic stirrer. The water samples of 50 mL were taken out for analysis at reaction times equal to 0, 5, 15, 30, 60, 90, 120, 150 and 180 min. Of 50 mL, a 5-mL aliquot of the water samples is split for dissolved ozone analysis, while a 45- mL water sample is filtered through a 0.45 μm cellulose acetate filter (prewashed 3 times by DI water) for DOC and UV₂₅₄ analysis. The concentration of the O₃ in liquid phase was measured by indigo method, while the gaseous phase was measured by iodometric method as described in Standard Methods [22]. The GAC experiments were carried out with the same O₃ and O₃/GAC procedure without O₃ gas feed to the reactor.

In O₃ experiment, the O₃ gas flowrate was controlled by adjusting oxygen feed flowrate at 2, 4 and 6 L/min which yielded O₃ concentrations (in gas) of 11.28 ± 0.76, 9.68 ± 0.14 and 7.04 ± 0.00 mgO₃/L_{gas}, respectively, while the specific ozone dose rates were 11.28 ± 0.76, 19.36 ± 0.28 and 21.12 ± 0.00 mgO₃/L-min, respectively (section 2.5, Eq 3).

In O₃/GAC experiment, the O₃ gas flowrate with the highest DOC removal from the O₃ experiment was selected for O₃/GAC experiments with the GAC doses of 0.1, 1.0 and 2.5 g/L. In order to investigate DOC and UV₂₅₄ removal by GAC alone, adsorption experiments were conducted using the same GAC doses and the same reactor as O₃/GAC experiments.

2.4 Analytical methods

In this study, the DOC concentration was determined by TOC analyzer (Multi N/C 3100, Analytik jena, Germany), while UV₂₅₄ was determined by UV spectrophotometer (Agilent, USA) as described in Standard Methods [22].

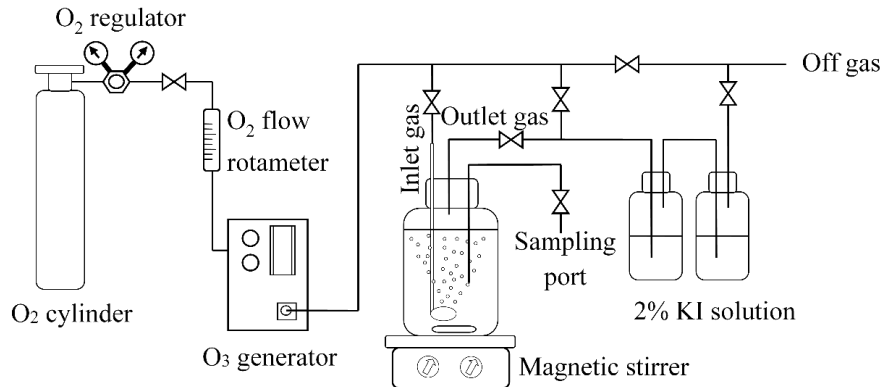


Figure 1 Schematic diagram of the experimental setup

2.5 Parameters for semi-batch ozonation

In the present study, the important parameters and their relationships in semi-batch ozonation system at steady state were calculated according to Eq. 1 – 4 as follows [23]: Applied ozone dose (I , mg/L):

$$I = \frac{Q_G \cdot C_{G0}}{V_L} \cdot t_R \quad (\text{Eq.1})$$

Specific ozone dose rate ($F(O_3)$, mg/L-min):

$$F(O_3) = \frac{I}{t_R} = \frac{Q_G \cdot C_{G0}}{V_L} \quad (\text{Eq.2})$$

Specific ozone-transfer efficiency ($\eta(O_3)$, %):

$$\eta(O_3) = \frac{C_{G0} - C_{Ge}}{C_{G0}} \times 100 \quad (\text{Eq.3})$$

Ozone consumption, ($D(O_3)$; mg/L):

$$D(O_3) = \left[\frac{Q_G}{V_L} (C_{G0} - C_{Ge}) t_R \right] - C_{Ltr} \quad (\text{Eq.4})$$

Where, Q_G is the O₃ gas flowrate (L_{gas}/min), V_L is the reactor liquid volume (L), t_R is the reaction time (min), C_{Ltr} is the dissolved O₃ at reaction time t_R (mg/L), C_{G0} and C_{Ge} are the O₃ concentration in the inlet and outlet gas (mg/L_{gas}), respectively.

To evaluate the synergistic effect of GAC doses in the O₃/GAC experiments, the DOC removals by O₃, O₃/GAC and GAC were compared, while the synergistic effects were represented by an enhancement factor (R) which was calculated according to Eq. 5 (modified from [24]).

$$R = \frac{\Delta DOC_{O_3/GAC}}{\Delta DOC_{O_3} + \Delta DOC_{GAC}} \quad (\text{Eq.5})$$

Where, R is the enhancement factor (unitless), $\Delta DOC_{O_3/GAC}$, ΔDOC_{O_3} and ΔDOC_{GAC} are the DOC removal (%) in the O₃/GAC, O₃ and GAC adsorption experiments, respectively.

The electrical energy efficiency was assessed in terms of electrical energy per order (EEO) which can be calculated according to Eq.6 (modified from [25]).

$$EEO = \frac{P \times t}{V \times \log\left(\frac{DOC_o}{DOC_f}\right)} \quad (\text{Eq.6})$$

Where, EEO is the electrical energy per order (kWh/m³), P is the electric power of O₃ generator (kW), t is the reaction time (h), V is the reactor liquid volume (m³), DOC_o and DOC_f are the initial and final concentration of DOC in the water samples (mg/L), respectively.

3. Results and discussion

3.1 Effects of the O₃ flow rate in O₃ experiment

In O₃ experiments, the effects of O₃ flowrate through reactor on DOC and UV₂₅₄ removal were carried out. With O₂ feed gas of 2, 4 and 6 L/min, the O₃ concentrations in generated gas were 11.28 ± 0.76, 9.68 ± 0.14 and 7.04 ± 0.00 mg/L, respectively. The DOC removals (Figure 2a) during those O₃ gas for flowrate of 2, 4 and 6 L/min at 180-min reaction time were 61.70%, 50.87% and 41.25%, respectively. The specific ozone transfer efficiencies at 180-min reaction time decreasing with increased O₃ flowrate (Figure 3a) were 34.56%, 29.41% and 25.00%, respectively. The decreased DOC removal was from less amount of ozone transferred in which it could be from two possible reasons. The first reason was the decrease of O₃ gas concentration as flowrates increased. With O₃ feed gas of 2, 4 and 6 L/min, the O₃ concentrations in generated gas were 11.28 ± 0.76, 9.68 ± 0.14 and 7.04 ± 0.00 mg/L. In this present study, O₃ can only be produced by the electrical discharge ozone generator at fixed voltage. Therefore, increased flowrate consequently diluted the O₃ gas concentration. This in turn reduces driving force of ozone mass transfer according to the film theory [23, 26]. The other reason was, too high O₃ gas flowrate created large bubbles (less contact surface area) in the turbulent/bubble flow regime. Therefore, this will actually reduce the ozone mass transfer [23, 26]. As a result, the dissolved ozone concentrations in the aqueous solution of O₃ flowrate of 2 L/min were higher than those of 4 and 6 L/min (Figure 3b). Figure 2b shows the UV₂₅₄ removal within 180-min reaction time in different O₃ gas flowrates. The result shows that UV₂₅₄ was quickly removed over 80% within the first 30-min reaction time, then slightly changed after 120-min reaction time. The rapid reductions of UV₂₅₄ were similar to the previous reports [21, 26-28], suggesting that the ozone preferentially reacted with some organic compounds (such as humic acid, C=C organic compounds and aromatics) in the pretreated NW-EFF samples. Although most of UV₂₅₄ absorbing compounds were almost fully removed (>90%) from the samples by single ozonation within 120-min reaction time, some intermediate products and some small-molecule organic acids (such as oxalic and formic acids) were indicated by the remaining DOC level. These compounds were quite refractory to ozone and difficult to be further mineralized [17, 29]. The increase in the O₃ dosage can enhance the degradation of the intermediate products but the excessive O₃ can also react with hydroxyl radicals which may inhibit the degradation of organic compounds [17]. Therefore, the mineralization of DOC was slow after the reaction time of 120 min.

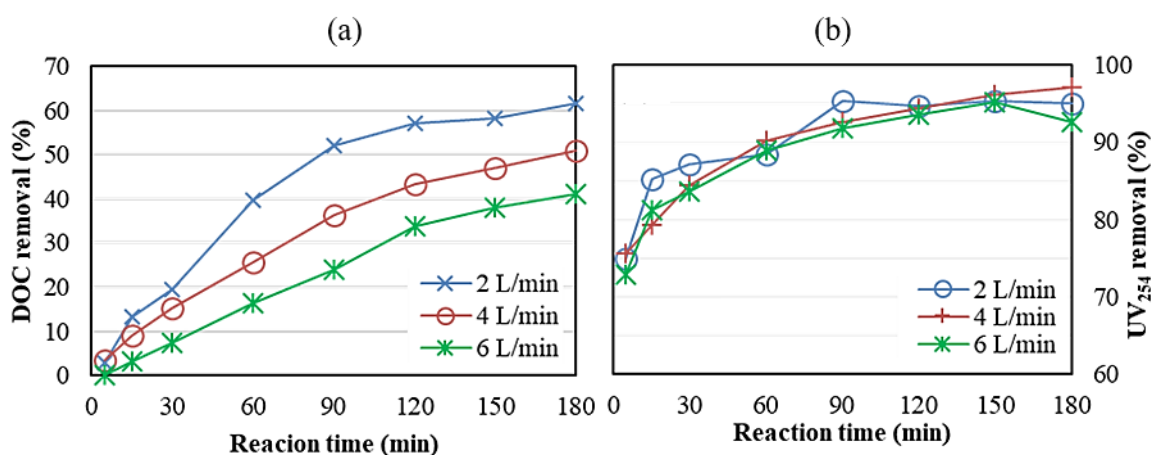


Figure 2 The removal of (a) DOC (b) UV₂₅₄ with various reaction times during the different flowrates of O₃ in ozonation process

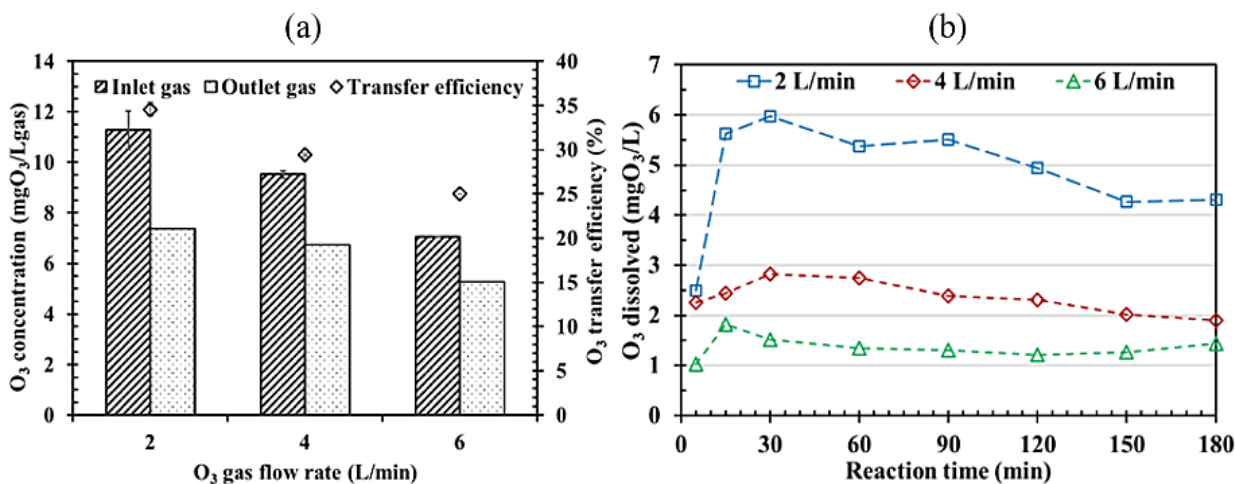


Figure 3 The (a) O₃ concentration in inlet gas, outlet gas and O₃ transfer efficiency with different flowrates at 180-min reaction time (b) dissolved O₃ with various reaction times

3.2 Effect of the granular activated carbon dose in O₃/GAC experiment

From the result in O₃ experiment, the O₃ gas flowrate of 2 L/min with O₃ concentrations in generated gas equal to 11.28 ± 0.76 mgO₃/L_{gas} (specific O₃ dose rate of 11.28 ± 0.76 mg/L-min) was selected for O₃/GAC experiment. The effects of GAC dose on DOC and UV₂₅₄ removal were carried out at 0.1 g/L, 1.0 g/L and 2.5 g/L. Figure 4a shows the DOC concentrations with various reaction times among different processes. For O₃/GAC experiments, nearly 60% reduction of DOC concentration was observed within 90 min while it took 180 min for O₃ alone. The ozone consumptions in O₃/GAC with GAC doses of 0.1, 1.0 and 2.5 g/L (at 90-min reaction time) were 410, 495 and 627 mg/L, respectively, while those in O₃ alone (at 180-min reaction time) were about 698 mg/L (data not shown). Therefore, the present of GAC in O₃/GAC process can reduce about 50% of the ozone consumption for the same DOC removal compared to O₃ alone. During the first 60 min in the O₃/GAC experiment, the DOC removals by GAC doses of 0.1 g/L and 1.0 g/L were about the same drastic reductions of DOC observed at GAC dose of 2.5 g/L. After 60-min reaction time, the DOC concentrations gradually decreased at the same rate towards the end of the experiment for all GAC doses. These results suggested that the GAC might accelerate O₃ decomposition to form hydroxyl radicals in an aqueous solution enhancing the reduction of DOC. The increase of GAC dose will also lead to more active sites for oxidation reactions and facilitate the production of more hydroxyl radicals [17, 30, 31]. However, the excessive O₃ and GAC amount can also react with the hydroxyl radicals that may inhibit the degradation of organic compounds [17] thus the trend in DOC removal did not increase significantly with GAC dose after 60 minutes. It should be noted that, an optimum amount of GAC would be favorable to catalyze the oxidation of organics by creating oxidative radical species but if the GAC amount exceeded a certain quantity, then its role might be inhibited [27, 32].

As shown in Figure 4a, two stages of the DOC decreasing trends with all GAC doses in O₃/GAC experiments were observed. In the early stage of the reaction (0 – 150 min), the DOC concentration decreases rapidly due to the elimination of high MW organic compounds that favor react with O₃ and more HO• expected to be generated due to both GAC and DOM [33, 34]. Both O₃ and HO• are ready to react with DOM [35], leading to the rapid oxidation of the NW-EFF DOM during O₃/GAC. In the latter stage (after 150-min reaction time), the formation of reaction products from the early stage (such as low MW carboxylic acids) was still produced during O₃/GAC with the reaction prolonged [35]. These low MW carboxylic acids are more difficult to be oxidized than NW-EFF DOM due to low the reaction rate constant between these carboxylic acids and either O₃ or HO• [26, 35].

Figure 4b shows the UV₂₅₄ in O₃ and O₃/GAC experiments. In the O₃ experiment, the UV₂₅₄ decreased rapidly in the first 15-min reaction time, and then gradually decreased, while it became constant approximately 0.005 cm⁻¹ (95% removal) after 90-min reaction time. In the O₃/GAC experiment, the UV₂₅₄ was decreasing rapidly in the first 15-min reaction time, and then could be removed completely at the end of experiments. During the first 120-min reaction time in O₃/GAC experiment, the UV₂₅₄ removal by GAC doses of 1.0 and 2.5 g/L were more efficient than that by GAC dose of 0.1 g/L. High removal of UV₂₅₄ in high GAC doses (1.0 and 2.5 g/L) indicated that the high UV₂₅₄ adsorbent DOM in NW-EFF might be favor adsorbed on GAC and easy to further oxidized by HO• on the GAC surface. Xing et al. [30] reported that the HO• oxidation in bulk solution dominated with a lower AC dose, but surface oxidation dominated with a higher AC dose. Therefore, the GAC has a significant effect on the enhancement of UV₂₅₄ and DOC removal in the O₃/GAC process.

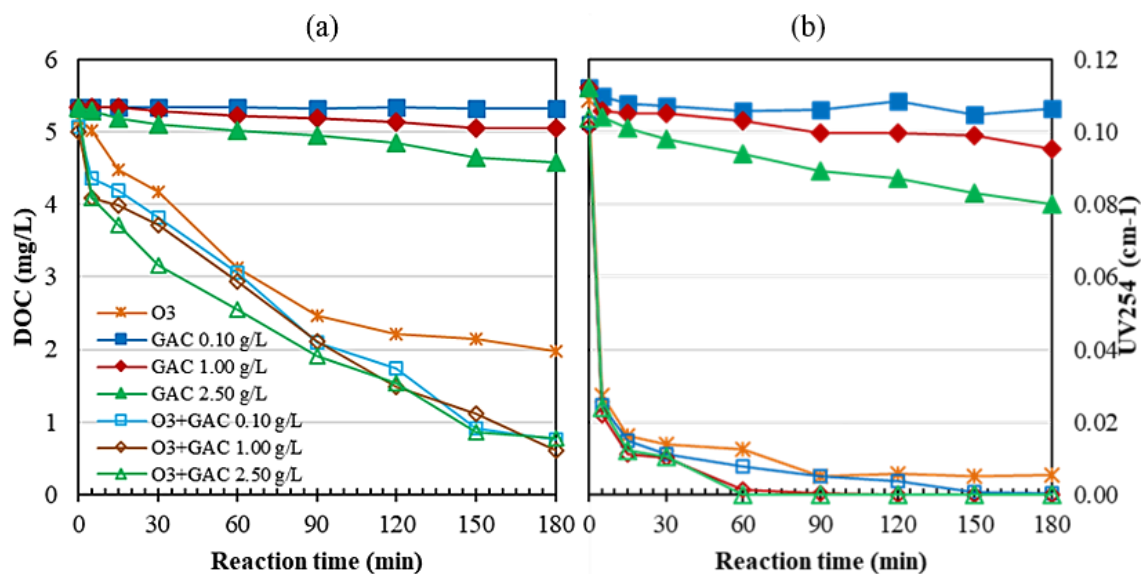


Figure 4 (a) DOC and (b) UV₂₅₄ with reaction time during the course of the O₃, GAC, and O₃/GAC experiments (specific O₃ dose rate of 11.28 ± 0.76 mgO₃/L-min)

3.3 Performance comparison of O₃ and O₃/GAC

Figure 5a shows the DOC removal after 180-min reaction time, the present of GAC enhanced the DOC removal from 61.70% (in O₃) to 85.04%, 88.00% and 85.50% (in O₃/GAC) with GAC doses of 0.1 g/L, 1.0 g/L and 2.5 g/L, respectively. GAC alone removed 0.56%, 5.61% and 14.21% at the end of experiment for GAC doses of 0.1 g/L, 1.0 g/L and 2.5 g/L. The result showed that, the NW-EFF DOM was more eliminated by O₃/GAC than O₃ process. This may be due to the acceleration of aqueous ozone decomposition into HO• by GAC [17, 30, 31]. The *R* values with GAC doses of 0.1 g/L, 1.0 g/L and 2.5 g/L at 180-min reaction time were 1.37, 1.31 and 1.13, respectively. All of the *R* values greater than 1.0 indicated that the GAC had synergistic effects on the removal of DOC in NW-EFF by the O₃/GAC process.

Figure 5b shows the UV₂₅₄ removal after 180-min reaction time. UV₂₅₄ absorbing compounds were fully removed (>99%) by O₃/GAC with all GAC doses, while the maximum removal of UV₂₅₄ by O₃ was approximately 95%. The UV₂₅₄ removals by GAC adsorption at GAC doses of 0.1 g/L, 1.0 g/L and 2.5 g/L are 4.91%, 14.90% and 28.55%, respectively. This indicates that the unsaturated organic matter in the treated effluent could be adsorbed on the surface of GAC.

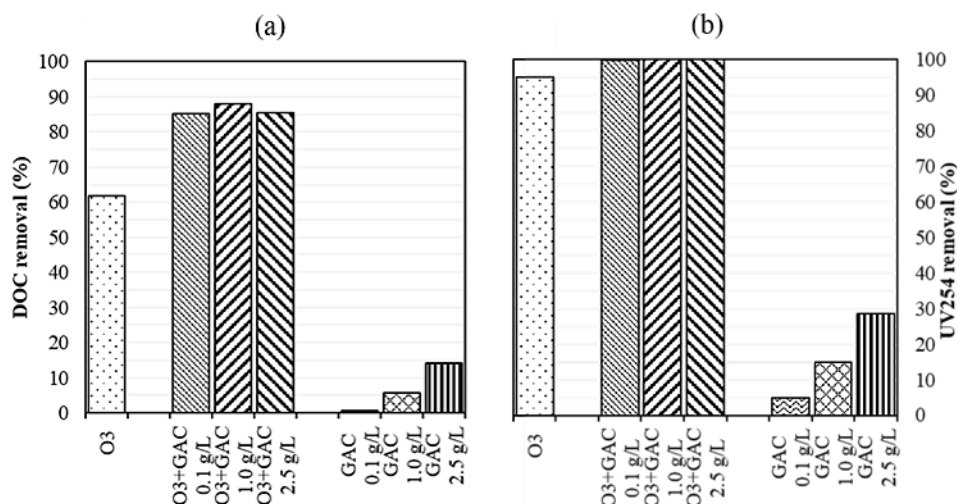


Figure 5 The removal of (a) DOC (b) UV₂₅₄ during O₃, O₃/GAC, and GAC adsorption experiments at 180-min reaction time (specific O₃ dose rate of 11.28 ± 0.76 mgO₃/L-min)

In addition, engineering practices should be energy-efficient competitive. In this case, the EEO of O₃ and O₃/GAC processes should be considered. Generally, most of water treatment plants operated the O₃ process with reaction time less than 30-min. However, the EEO with the maximum DOC removal efficiency should be known. Thus, the EEOs of the O₃ and the O₃/GAC (GAC dose of 1.0 g/L) processes were assessed and compared based on the DOC removal with 30-min and 180-min reaction times. The EEO of O₃ and O₃/GAC at 180-min reaction time were 215.92 kWh/m³ and 97.74 kWh/m³, respectively, while those 30-min reaction time were 160.68 kWh/m³ and 115.99 kWh/m³, respectively. The results showed that the O₃/GAC process reduced the EEOs approximately 30% - 55% of those from the O₃ process. The significantly reduction of EEO by the O₃/GAC process suggested that the O₃/GAC was more energy-efficient for the removal of DOC in NW-EFF than that by the O₃ process.

4. Conclusions

The differences in DOC removal among O₃, O₃/GAC and GAC experiments were observed in this study. The result shows that there is a certain catalytic effect during the oxidation of NW-EFF from sugar mill factory by O₃/GAC. In O₃ experiment, at the 180-min reaction time, the DOC removals during O₃ gas flowrates of 2, 4 and 6 L/min were 61.70%, 50.87% and 41.25%, respectively. Specific ozone transfer efficiencies with those gas flowrates and 180-min reaction time were 34.56%, 29.41 and 25.00%. The UV₂₅₄ was quickly removed over 80% within the first 30-min reaction time and almost fully removed (>90%) in 120-min reaction time for all of O₃ gas flowrates.

In the O₃/GAC experiment, nearly 60% reduction of DOC concentration was observed within 90-min reaction time for all GAC doses, while it took 180 min for O₃ alone. The present of GAC reduced approximately 50% of the specific ozone consumption compared to the O₃ alone for the same DOC removal. The *R* values with GAC doses of 0.1 g/L, 1.0 g/L and 2.5 g/L at 180-min reaction time were 1.37, 1.31 and 1.13, respectively. All of the *R* values greater than 1.0 showed that the GAC doses had synergistic effects on the removal of DOC in NW-EFF. The electrical energy requirement in terms of EEO reduced from 215.92 kWh/m³ (in O₃) to 97.74 kWh/m³ (in O₃/GAC) at 180-min reaction time. The finding of this study shows that the O₃/GAC is a potential treatment process for removal of dissolved organic matter in natural surface water mixed effluent of the sugar mill factory.

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