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THE EFFECT OF WATER QUALITY ON REMOVAL OF ACETAMINOPHEN IN SURFACE WATER BY OZONATION PROCESS

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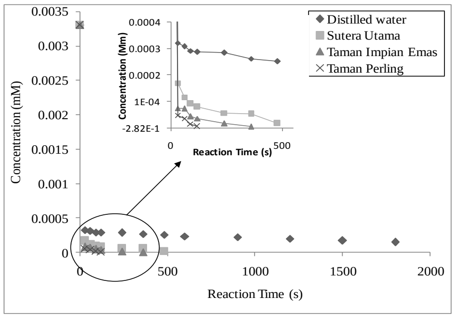
Graphical abstract



Abstract

The effectiveness of ozone to remove acetaminophen in surface water was studied. The results demonstrated that the removal of acetaminophen in surface water by ozone was achieved less than 30 minutes. Ozonation experiment was conducted with the initial concentration of 3.3 x 10^{-3} mM acetaminophen and *para*-cholobenzoic acid was selected as hydroxyl radical probe. The second-order rate constants for the reactions between acetaminophen and ozone have been evaluated in different quality of surface water. Based on the result obtained, ozone was reducing rapidly in water samples according to the level of water quality. The presence of various organic and inorganic compounds in the water samples, which greatly influence the decomposition of dissolved ozone, hydroxyl exposure and removal of acetaminophen. The rate constants showed the minimum value (7.34 x 10^{-4} M^{-1} s^{-1}) in lower water quality and maximum value (4.57 x 10^{-2} M^{-1} s^{-1}) in high-quality water.

Keywords: Ozonation, river water, acetaminophen

Abstrak

Keberkesanan ozon untuk menyingkir acetaminophen di dalam permukaan air telah dikaji. Keputusan menunjukkan bahawa penyingkiran acetaminophen di dalam permukaan air oleh ozon telah dicapai kurang daripada 30 minit. Kajian pengozonan telah dijalankan dengan kepekatan awal acetaminophen 3.3 x 10^{3} mM dan para-cholobenzoic asid telah dipilih sebagai "probe" radikal hidroksil. Pemalar kadar tertib kedua bagi tindak balas antara acetaminophen dan ozon telah dinilai di dalam permukaan air yang berbeza kualiti. Berdasarkan keputusan yang diperolehi, pengurangan ozon di dalam sampel air mengikut tahap kualiti air. Kehadiran sebatian organik dan bukan organik bersama-sama dalam sampel air yang amat mempengaruhi penguraian ozon, pendedahan hidroksil dan penyingkiran acetaminophen. Pemalar kadar menunjukkan nilai minimum (7.34 x 10^{-4} $M^{-1}s^{-1}$) di bawah air berkualiti rendah dan nilai maksimum (4.57 x 10^{-2} $M^{-1}s^{-1}$) dalam kualiti air tinggi.

Keywords: Pengozonan, air sungai, acetaminophen

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1.0 INTRODUCTION

Recently the presence of pharmaceuticals in water sources has been reported as an emerging environmental issue. This is due to some of pharmaceutical compounds are suspected to be able to affect the endocrine system of living organisms[1]. Acetaminophen is an anti-inflammatory and analgesics pharmaceutical compound which is most commonly detected in water. It is commonly known as paracetamol and chemically named N-acetyl-p-aminophenol. This compound is widely consumed as pain reliever and reducer such as headache, muscle aches, arthritis, backache, toothaches, colds, and fevers. The presence of acetaminophen in an aquatic environment is attributable to personal hygiene products, pharmaceutical industry waste, hospital waste and therapeutic drugs. Acetaminophen can enter the environment in many ways, such as via feces or urine after consumption by humans and animals, which is evidently more difficult to prevent [2].

Pharmaceuticals including acetaminophen have been receiving great attention due to its potential as bioactive chemicals in the environment [3].They are considered as emerging pollutants in water because they still remain unregulated or are currently undergoing a regularization process, although the directives and legal frameworks are not set-up yet. Pharmaceuticals are continuously discharged into the water bodies and normally found at low concentrations, commonly in the range of micrograms per liter to nanograms per liter [4]. In high concentration, their existence had potential to affect water quality and subsequently gives impact to drinking water supplies, ecosystem and human health [5]. Although no specific indications of acetaminophen toxicity towards test organisms have been so far documented, based on precautionary principle, its removal should be achieved in all water sources for human use [1].

Considerable research interest has recently been shown in the application of ozone for removal of acetaminophen. Ozonation is a potential chemical treatment process for the oxidation of numerous sorts of organic compounds in water. Ozonation has been demonstrated effectively in the purification of water for the purpose of disinfection and oxidation because to its high oxidation potential [6, 7]. Decomposition of ozone resulting in the formation of hydroxyl free radicals [8-10] .However, the stability of ozone and the formation of hydroxyl radical strongly depends on the water matrix, especially its pH, alkalinity, type and content of natural organic matter [11]. This is because the presence of various organic and inorganic matters in water matrix can act as promoter, inhibitor and initiator during ozonation process which simultaneously affects the removal efficiency of target compounds.

During ozonation process in water, the oxidation can occur via two ways; through direct reactions with molecular ozone and through indirect reactions with hydroxyl radicals. While molecular ozone selectively attacks organic compounds with unsaturated bonds such as double bonds, aromatic systems, and deprotonated amines, whereas hydroxyl radicals react relatively unselectively with organic contaminants [11, 12]. However, ozone and hydroxyl radical have short lifetime, depending on the water quality, the half-life of ozone is in the range of seconds to hours [13, 14].

To assess the removal efficiency of acetaminophen during ozonation, it is necessary to determine the rate constants for the reaction of acetaminophen with ozone and hydroxyl radicals. The present study aims to investigate the removal efficiency of acetaminophen in surface water and to study the decomposition of ozone and hydroxyl radical exposure in different quality of surface water. The results of this investigation are presented in this paper.

2.0 EXPERIMENTAL

2.1 Chemicals

Acetaminophen, *para*-chlorobenzoic acid, sodium thiosulfate, potassium indigo trisulfonate, sodium hydrogen phosphate, sodium dihydrogen phosphate and potassium iodide were supplied by Sigma-Aldrich. Analytical grade chemicals were used for this experiment except for acetonitrile, methanol and water were supplied from Merck was HPLC grade.

2.2 Natural Water Samples

Water collected from three different sites along Sungai Skudai which located at Sutera Utama, Taman Impian Emas and Taman Perling. Water samples were filtered (0.45 µM membrane filter) and kept at 4°C prior to the ozone experiments. Water quality characterizations, were conducted for natural samples filtered on 0.45 µM following the standard methods.

2.3 Ozonated Water

Ozone gas (40-50 mg/L) produced by Anseros ozone generator (Model COM-AD-02) was bubbled into 1 L deionized water in gas washing bottle. The dissolved ozone levels were controlled via adjusting the duration of bubbling and the flow rates (45 and 90 ml/s). Residual ozone gas in the effluent of the gas washing bottled was quenched by into a glass bottle containing 300 ml of 2% potassium iodide (KI) solutions.

2.4 Analytical Methods

2.4.1 Ozone Concentration

The concentrations of dissolved ozone stock solutions were measured by UV spectrophotometer at wavelength 258nm. The ozone concentration is determined by the Beer's Law according to the following equation:

$$[O_3]= \frac{48(1000)(A_{258})2}{(\varepsilon)(b)}$$

Where, $[O_3]$ represents ozone concentration (mg/L), MW represents the molecular weight of ozone (g/mol), A_{258} represents absorbance of solution at 258 nm, b represents cell length (cm) and ε represents extinction coefficient, L mol-1cm-1. Dissolved ozone concentration in the reaction solutions was determined by the indigo colorimetric method [15] using UV-Visible spectrophotometer at wavelength 600 nm. The ozone concentration was determined using the following equation:

$$[O_3]= \frac{(V^T)(A_{258})}{(V^S)(f)}$$

Where, ΔAbs represents the difference in absorbance at 600nm between sample and blank, V^T represents the total volume of sample plus indigo (mL), V^S represents sample volume (mL) and f is 0.42 L (mg O_3)$^{-1}$ cm^{-1}.

2.4.2 *Water Quality Analyses*

The alkalinity of the water samples was performed using HACH reagent followed APHA standard method. HACH. The Shimadzu TOC-VCSH analyzer was used for dissolved organic carbon (DOC) measurements. The pH value was measured using pH meter and temperature of the sample was determined using thermometer.

2.4.3 *Sample Analyses*

Acetaminophen and *p*CBA were measured using Ultra High Performance Liquid Chromatography (UHPLC) system with diode array detector (DAD). Analysis was performed using 150 x 2.1 mm Zorbax SB-C18column. pCBA was eluted using an isocratic mobile phase of 55% methanol: 45% 10 mM phosphoric acid buffer at 0.2 mL/min, UV-detection at 234 nm and the temperature was maintained at 25°C. Acetaminophen was eluted using a mobile phase consisting of 90 % acetonitrile: 10 % 10mM phosphoric acid buffer with a flow rate of 0.5 mL/min and detected at 280 nm at 40 °C

2.5 Ozone Experiments

All bench-scale experiments were performed using three surface waters that differed in alkalinity and dissolved organic carbon concentration. All ozonation were performed in a semicontinous stirred in 1 liter glass bottle by injecting 5mg/L of the ozone stock solution into the sample solution contain a known amount of acetaminophen and pCBA. All experiments were performed at original condition of water samples and were carried out at room temperature. Three replicates were performed for each compound.

3.0 RESULTS AND DISCUSSION

3.1 Removal of Acetaminophen

Surface water was characterized by analytical techniques described previously and the results are presented in Table 1. The results correspond to averages of analyses done for three sampling points along Sungai Skudai.

Table 1 Water quality analysis of Sungai Skudai

Water sample	Sutera Utama	Taman Impian Emas	Taman Perling
Dissolved organic carbon (mg/L)	6.19	6.52	9.17
Alkalinity (mg/L)	30	40	45
Temperature	25	26	25
pH	6.76	6.83	6.77

All water samples contained organic and inorganic compounds, but in all such cases, the detected concentrations were much lower than the concentration spiked during the bench-scale experiments. Based on the water quality analyses, the temperatures of in all water samples were in the range of 25 to 26 and pH was in the range of 6.8. The results shows, all water samples have high concentration of alkalinity and dissolved organic carbon and it was found that water sample in Sutera Utama area less polluted, followed by surface water at Taman Impian Emas and Taman Perling.

Initial concentration of 5 mg/l ozone was completely remove (100%) of 3.3 x 10^{-3} mM acetaminophen in surface water. Figure 1 shows the removal trend of acetaminophen in surface water. It was found that the removal of acetaminophen was mostly completely removed less than 1800 seconds. The results indicated the degradation rates of acetaminophen in ozonation were varied with the different quality of surface water. As expected, fast removal of acetaminophen was found in water samples at Taman Perling followed by surface water at Taman Impian Emas and Sutera Utama which was completed in the first 240 seconds, 480 seconds and 600 seconds respectively.

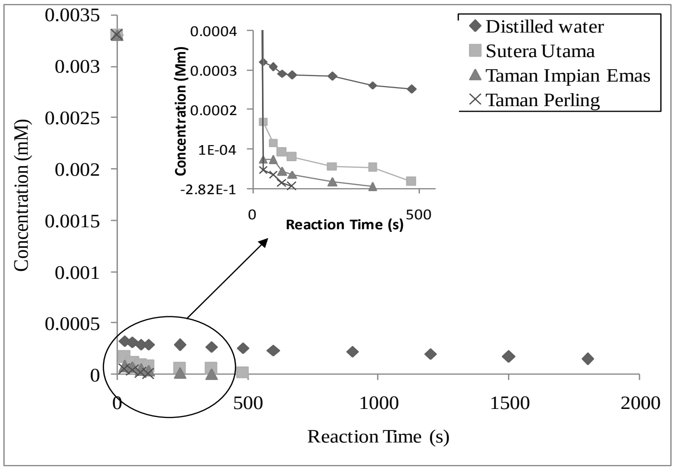

Figure 1 Removal of acetaminophen in different area water sample

Second-order rate constant for the reaction of acetaminophen was determined in buffered ultrapure water and natural water during ozonation process. Ozonation experiments were duplicated and undertaken at pH 7. The second order rate constants are compiled in Table 2. Overall, reaction rate constants varied from 4.57 x 10^{-2} M^{-1} s^{-1} to 7.34 x 10^{-4} M^{-1} s^{-1}. The second-order rate constants revealed that acetaminophen was found to be easily removed from water by ozone treatment. It was noted that the rates of acetaminophen removal were higher at Taman Perling and lowest in distilled water. This is believed to be due to the involvement of organic and inorganic compound presence in the water sample.This is because the water samples contain mainly differ in alkalinity and dissolved organic carbon, which is corresponding to the natural organic material (NOM) in natural water. Depending on the nature of the foreign compound in natural water, it can react solely as the initiator, promoter, inhibitor, or simultaneously [16]. According to the literature, the oxidation of organic micropollutants by ozone is an efficient process only for compounds with functional groups such as amino groups, activated aromatic systems or double bonds [17].

Table 2 Second-order rate constant and reaction time for removal of acetaminophen

Sample	Acetaminophen Degradation rate (M^{-1} s^{-1})	Removal of acetaminophen (seconds)
Distilled water	7.34 x 10^{-4}	1800
Sutera Utama	6.56 x 10^{-3}	600
Taman Impian Emas	1.22 x 10^{-2}	480
Taman Perling	4.57 x 10^{-2}	240

3.2 Ozonation of Acetaminophen in Surface Waters

3.2.1 Decomposition of Ozone

The decomposition of dissolved ozone for three filtered surface waters are presented in Figure 2. It was found that, all surface water to have similar decomposition trends. In all experiments, the ozone residual experienced a fast decay rate at initial period followed by slower decay rate. The fast initial decay rate of ozone was believed to be due to the reaction of organic and inorganic compounds with ozone. As expected, the decomposition of ozone is faster in water samples in a Persisiran Perling area followed by Taman Impian Emas and Sutera Utama area.

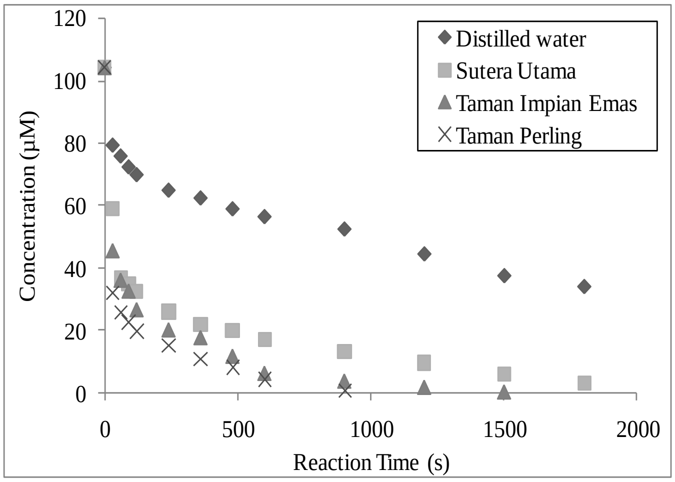

Figure 2 The decomposition of dissolved ozone in different water samples

Ozone residuals decreased faster in Taman Perling surface waters with decomposition rate of 4.06 x 10^{-3} s^{-1} compared to Taman Impian Emas surface water 2.96 x 10^{-3} s^{-1}, Sutera Utama surface water 1.49 x 10^{-3} s^{-1} and distilled water 4.90 x 10^{-4} s^{-1} as shown in Table 3. The decomposition rates of ozone decrease as the quality of water samples increase. This is because the decomposition of ozone, mainly depending on the nature of the water sample. The presence of organic and inorganic solutes in water sample affects the decomposition rate of ozone and generally controlled by a radical-type chain reaction [18].

Table 3 The dissolved ozone consume by acetaminophen in and ozone decomposition rate

	Dissolved ozone consumed within at first 30 seconds (100%)	**Ozone Decomposition rate (s^{-1})**
Distilled water	24	4.90×10^{-4}
Sutera Utama	43	1.49×10^{-3}
Taman Impian Emas	56	2.96×10^{-3}
Taman Perling	69	4.06×10^{-3}

Complete decomposition of ozone in Taman Perling surface waters Taman Impian Emas Sutera Utama surface waters was found in 2100 seconds, 1800 seconds and 1200 seconds respectively. Taman Perling surface waters water was more reactive, as shown by a higher initial demand (69%) than in Taman Impian Emas surface water (56%), Sutera Utama surface waters (43%), distilled water (24%). This observation is consistent with their respective DOC concentration which induces a significant difference in ozone residual profile in all water samples. The biggest determining factor in ozone demand is dissolved organic carbon. The concentration of dissolved ozone varied considerably with different value dissolved organic carbon of the sample. Higher dissolved organic carbon value increases the ozone demand in ozonation process. This difference might be due to the significant alkalinity in water samples which already acted as hydroxyl scavengers. Bicarbonate/carbonate are known to inhibit ozone decomposition due to their ability to scavenge hydroxyl radicals [18].

3.2.2 Hydroxyl Exposure

Upon ozone oxidation process, micropollutant can be oxidized by ozone molecule itself and also hydroxyl radical. Hydroxyl radical the most significant role as an oxidant to elevate the degradation efficiency of many inorganic and organic compounds in water [11] and reacts very rapidly with many organic species .The hydroxyl radical exposure can be determined using R_{ct} concept which can be established using the relationship of ozone exposure ($\int[O_3]dt$) and hydroxyl radical exposure ($\int$[HO.dt) according to the following equation.

$$Rct = \frac{\int [HO.]\ dt}{\int [O3]\ d}$$

The experimental approach of using an hydroxyl radical probe compound to measure the hydroxyl radical exposure and *para*-cholorobenzoic acid (pCBA) was used as the probe compound for hydroxyl radical exposure due to slow reaction rates with ozone ($k_{O3}<1 M^{-1}s^{-1}$), but fast oxidation kinetics with the hydroxyl radical ($k_{OH,pCBA} = 5x10^9 M^{-1}s^{-1}$). The decomposition of the probe is an indirect measure of the hydroxyl radical concentration.

The degradation of pCBA in surface water is shown in Figure 3. For three water sample, a two-stage pattern of decomposition of pcba was found, which has been commonly observed for the ozonation of natural water [19-21] and different decomposition rate were observed for each water sample. The decomposition of pCBA in water samples were very fast at first 30 seconds and slowly decrease. The drastic dropped in the first 30 seconds was due instantaneous reaction between ozone and acetaminophen and organic and inorganic matter in the water sample.

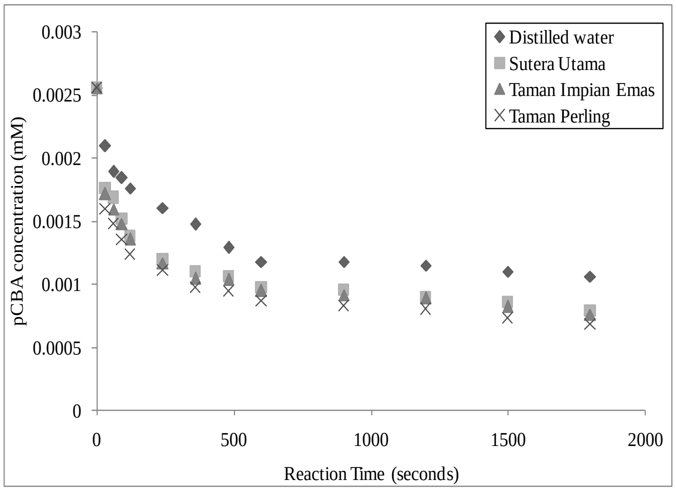

Figure 3 The degradation of pCBA in different water samples

Figure 4 shows the ozone exposure and hydroxyl radical exposure determined from experiment in different water sample quality and two-stage Rct pattern was observed. The initial high Rct was believed to be due to the instantaneous formation of hydroxyl radical generated from the reaction of fast-reacting initiation functional groups in bulk NOM with ozone. It has been suggested that phenolic and amine moieties in the NOM macromolecule could contribute to the high initial Rct value [14].

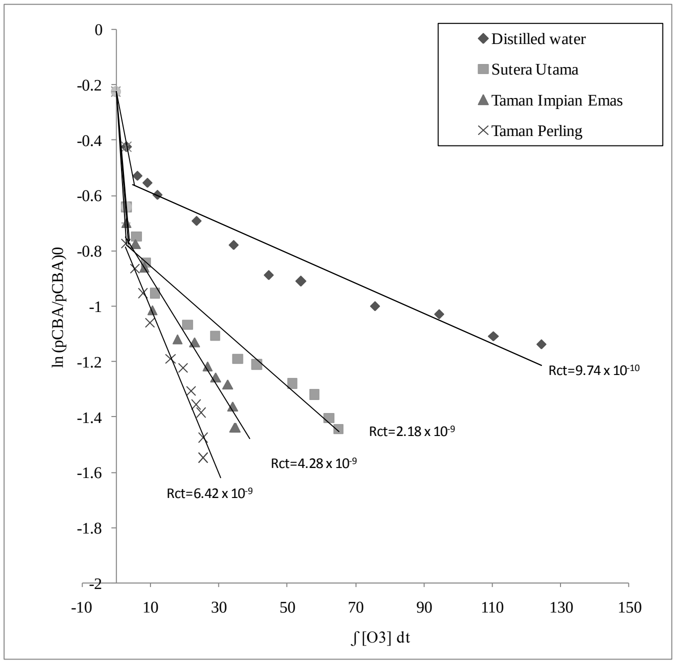

Figure 4 The ozone exposure and hydroxyl radical exposure in different water samples

Since limited data points (< 2) could be obtained during the initial period of the first Rct stage (< 30 s), only the second stage Rct was considered for the determination of rate constants. The results show that decreasing water quality increases the Rct value. The Rct value is directly proportional to hydroxyl exposure, which means that for a given condition, hydroxyl exposure increase as the Rct value increases. Based on the Rct diagram, the Rct value increases from 9.74 x 10^{-10} M^{-1} s^{-1} to 6.42 x 10^{-9} M^{-1} s^{-1} as the concentration of dissolved organic carbon and alkalinity increase. In natural water, NOM and carbonate alkalinity are commonly compound that can significantly affect the Rct value [22]. NOM contributes simultaneously to the initiation, promotion and inhibition in ozonation [16] whereas carbonate alkalinity can only serve as the inhibitor [23].

4.0 CONCLUSION

The overall results indicate that, 5 mg/L of ozone were effectively remove 3.3x10^{-3}mM acetaminophen in surface water less than 30 minutes. However, in ozonation process, the effectiveness of acetaminophen removal strongly depends on the water matrix. In this study, higher dissolved organic carbon and alkalinity value accelerates the decomposition of ozone and increase the removal rate of acetaminophen in ozonation process

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