Removal and Mineralization of Bisphenol A by Ozonation Process

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Abstract─The removal of Bisphenol A (BPA) in water by ozonation was investigated by varying different operational parameters including initial concentration of BPA, alkaline pH effect and mineralization of BPA. The results obtained from the study showed that ozonation could be used effectively to remove BPA in contaminated water or industrial wastewater. The observed degradation rate increase with ozone dosage thus obtained 81.13% as the highest removal efficiency at pH of 8.25. The second order rate constant was determined for the reaction of BPA with aqueous ozone, indicating increase in rate constant as the concentration of BPA decrease from 2 to 0.75ppm i.e. $0.0120min^{-1}$, $0.0123min^{-1}$ and $0.0137min^{-1}$. Meanwhile at 0.5ppm, the rate constant decreased to $0.0113min^{-1}$. Mineralization was enhanced by alkalization from 8.25 to 11.0, which moderated the overall degradation process through the formation of radical species. Therefore, the total organic carbon removal at pH of 8.25 and 11 was 42.1% and 50.71% respectively.

Keywords---Bisphenol A, Ozonation, Mineralization, Oxidation.

I. INTRODUCTION

ENVIRONMENTAL pollutants currently released are called endocrine disrupting chemicals [24]. These pollutants have gained attention from the public, scientific agencies, government and non government bodies due to their environmental implications and public health effects. BPA is an organic compound with chemical formula of $(CH_3)_2C$ $(C_6H_4OH)_2$. Structurally, Bisphenol A BPA has two large phenyl groups as well as two electron rich •OH group and two methyl group. BPA has a low vapor pressure, high melting point and moderately soluble in water (300mg/L at room temperature) and it dissociates in alkaline environment pKa 9.9-11.3 [1]. Chemicals can be detected in wide range of concentration (ng/L-mg/L) and exposure leads to hormonal damage, birth defect, testicular cancer, organ damage, infertility etc. [19]. BPA is manufactured by the condensation of phenol with acetone in the presence of catalyst (Figure 1). BPA is primarily used in the synthesis of polycarbonate products and epoxy resin [19]. Epoxy resin are used for inner coating for food and beverages cans, car coating, PVC pipes, anti corrosion coating for floor and aerospace application while application of polycarbonate have been employed to manufacture many consumer products such as medical devices, drinking and food packaging, automotive lenses, motorcycle helmet, safety glasses and compact disk [11], [19]. Since 1960, BPA has been an industrial chemical used to strengthen many hard plastic bottles and metal-based food and can beverages [23]. BPA global production in 2003 was over 2million metric tons. Due to global demand, BPA annual consumption rate increased to 10% from 2003 to 2006 and the demand in consumption increased at annual rate of 7 to 8% in 2011[13], [18]. Over some decades BPA has been featuring in consumer products and several agencies have questioned its safety, due to application in consumer products used for food and packaging, medical devices etc.

In September 2008, National Toxicology Program in the United State issued a report about the adverse implications of BPA exposure on human development and reproduction. This report buttressed the potential effect of BPA exposure using a five level scale of concern: minimal concern, serious concern, and negligible concern, some concern and concern. The expressions of this level of concerns are based on the developmental changes experienced by humans. The report expressed 'minimal concern' exposure will affect the mammary gland or accelerate puberty in female's development. NTP further explained 'negligible concern' results in fetal or neonatal mortality in pregnant woman, causes birth defect and growth of their offspring. 'Negligible concern' causes reproductive effects in non-occupationally exposed adults and "minimal concern" for workers exposed to higher levels in occupational settings. A 2010 report from the United States Food and Drug Administration (FDA) raised further concerns regarding infants, fetuses and young children's exposure to this chemical. In September 2010, Canada declared BPA as toxic substance [9], [15]. European Food Safety Authority issued its report on the safety of BPA in November 2006 which established dose intake of BPA per day in kilogram of body weight meanwhile, 50ug of BPA per kilogram of body weight per day was established as safe dose of exposure without significant health implication on the basis of drink, food, air and water. Report found BPA exposure level in human blood, tissue and urine ranging from 0.1 to 10ppb while some are in ppm [13], [20]. Therefore it is called Endocrine Disrupting Chemical because BPA binds to estrogen receptor and exhibit estrogenic activity.

Bisphenol A is a pseudo persistent chemical, despite its short half-life is ubiquitous because of continuous release to the environment [20]. Chemicals can be spilled into the environment through transport, manufacture and processing. The sources are discharges from municipal and industrial wastewater, combustion of domestic waste, leaching from landfill and natural breakdown of plastics in the environment

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[2], [12], [21]. These chemicals are persistent in the environment through industrial discharge, research institutes, leaching from landfills, incineration etc. [22]. BPA have been found in different sectors of the natural environment like surface water, sediment, atmosphere [5], [10]. Ozonation treatment of wastewater are among advanced oxidation (AOP) methods which are based on generation of hydroxyl radicals ˙OH. Ozonation as advanced oxidation process, (AOP) technique is used in water and wastewater treatment processes for complete mineralization of pollutants, subsequently, destruction of bacteria can be achieved through ozonation treatment systems. The conventional treatments have proved abortive in removal of endocrine disrupting compounds and derivatives such as specific micro-pollutants which are resistant to different stages of conventional treatment therefore, appropriate physicochemical processes must be employed in order to meet the water quality standard required for wastewaters effluent discharge contaminated organic pollutants [8].

Studies around the world and US have reported existence of BPA in the environment including rain water, sediment samples from river, lakes and channels; treated drinking water; leachate from hazardous waste landfills; and tissues of aquatic animals[4], [25]. Laboratory studies on animals and humans have showed the estrogenic potency, thyroid hormone disruption, obesity promoting effect, and prevalence increase in cardiovascular disease and liver-enzyme abnormalities [13], [14]. Some studies use various physical techniques to remove EDCs such as ultrasonic, membrane methods and activated carbon. However, ozonation has shown its ability to effectively remove phenol, phthalates, bisphenol A and other organic contaminants [6]. Ozonation reaction occurs when organic pollutant undergo sequential oxidation processes by ozone and hydroxyl radical formed by the decomposition of O_3 in water. In some cases toxic by product may be generated. [7] Reported the degradation of bisphenol A by ozonation at slightly acidic medium with several operational parameter including ozone addition, mass transfer rate, contact time, BPA concentration reaction kinetics, rate constant and by products. Total mineralization is most rapid before complete conversion of BPA and much slower thereafter; implying ozone reaction with the intermediate is slow. Mineralization enhanced by alkalization pH 10.8, facilitate the overall degradation process via the formation of radical species that were less selective than ozone. Effect of pH, alkalinity is another water quality parameter and could affect the effectiveness of ozonation techniques for treatment of organic pollutant. pH is an important factor on self decomposition of ozone in water which affects total organic carbon (TOC) removal of BPA in aqueous solution more significantly. Ozone decomposition is slower at low pH values apparently, the main reaction between organic compounds and molecular ozone. At high pH values, TOC conversion increases due •OH radicals production [6]. Considering the wide spread contamination of BPA in the environment, the main objective is to investigate the degradation of BPA during ozonation at different operational parameters and also, total mineralization of BPA at different pH condition.
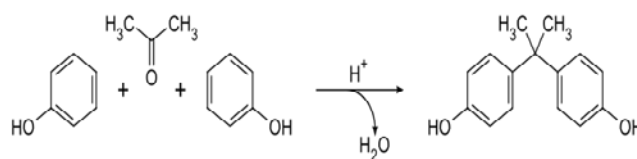

Fig 1. Reaction of Phenol and Acetone to produce BPA in the presence of Catalyst

II. EXPERIMENTAL APPROACH

A. Material and Reagents

All chemicals and reagents used were in analytical grades. Bisphenol A was purchased from Merck. Ultra-pure water obtained from Sartorious 61316 and 611UV ultrapure water system, Methanol and NaOH (Merck). Acetonitrile and Methanol were all liquid chromatography in grades, pH meter (WTW series pH720).

B. Analysis

Concentration measurement was analyzed by high pressure liquid chromatography (HPLC Shimadzu. LC-20AD coupled with UV system Shimadzu SPD-20A and Autosampler Shimadzu SIL-20A.) The separation was made by the column synergy 4μ C18 CTO-10AS VP, 50 x 20mm x 4μm at a flow rate of 1mL/min. The mobile phase was acetonitrile and ultrapure water, Elutes signals were monitored at 280nm. The column temperature is kept at 40°C. Sample injection by autosampler (SIL-20A Shimadzu) equipped with control vial needle stroke (52mm) and 10μL loops were eluted by acetonitrile and water (10:90) mixture at 1mL/min. The detection limit was about 0.1ppm.

C. Ozonation Procedure

The ozonation of the phenols mixtures were conducted with synthetic solutions in distilled water with the variation of the initial organics concentration .The reactor was a semi-batch type (0.500 L). Initial ozone concentration was 27- 30 mg L^{-1}. The ozone-oxygen mixture flow was 0.5-L min^{-1}. All experiments were carried out at 20°C with agitation by bubbling of an ozone-oxygen mixture and by a magnetic agitation (operated at 120 rpm). The pH variation was performed with sulfuric acid and sodium hydroxide (0.05N). For all experiments, aliquots of 3 mL reaction solution were withdrawn at desired time intervals from the reactor for sequent analyses

D. Ozone Generation

Ozone gas was generated from oxygen using OPAL OG 400 model ozone generator with a maximum production capacity of 400mg/h of ozone. During a typical experiment performed, the solutions were prepared in ultrapure water for different concentrations ranging from 0.5 to 2ppm. The samples were subjected to ozone for 120minutes. 1mL of samples was drawn at time interval of 0, 5, 10, 20, 30, 60, 90 and 120 minutes for concentration measurement. Initial pH of the solution was maintained throughout except in case of studying the effects on mineralization by ozonation thus the pH of the sample solutions was increased to 11 by sodium hydroxide NaOH.

E. Mineralization Measurement

TOC-V$_{CPN}$ Analyzer (Shimadzu) coupled with automatic autosampler was used for total organic carbon measurements. Total Organic Carbon analysis made with purging sample 5 minutes with dry air. After that samples introduced into an oxidation tube filled with PtO_2 catalysts with a temperature of $700^{o}C$. NPOC method is developed for quantitative measurement.

III. RESULTS AND DISCUSSION

A. Effect of initial BPA concentration

The impact of initial BPA concentration was investigated based on the following parameters (Ozone gas concentration, flow rate and pH were kept constant). The effects of initial concentrations ranging from 0.5 to 2ppm were measured on BPA removal. The result obtained show the removal efficiency increases as the concentration decrease from 76.35 to 81.13% at 2-0.75ppm and later reduced to 75.01% at 0.5ppm. This is because as the initial concentration of BPA decreases from 2ppm to 0.5pm there was an increase in the ozone dosage which lead high rate of removal perhaps the ozone dosage was predominantly excess in 0.5ppm. The ozonation process involves indirect ozone attack and radicals are formed during the reactions resulting in high degradation rate but when applied excess, radical formation and interaction are slow which may inhibit the reaction rate depending on the pH medium. At the end of 10minutes about 1.4×10^{-3} mol of ozone was absorbed. The result of BPA removal end at 120minutes where the highest efficiency is 81.13%.

B. Effect of pH

Fig.1 represents the impact of pH on BPA treatment by ozonation. Various impacting factor which include Initial BPA concentration, influent ozone gas concentration and sodium hydroxide concentration were kept constant at 1ppm, 6.67mg/L and 0.1N respectively. At pH of 8.25 the removal of BPA was 78.48% at the end of reaction time 120minutes while 78.6% were removed at pH of 11.
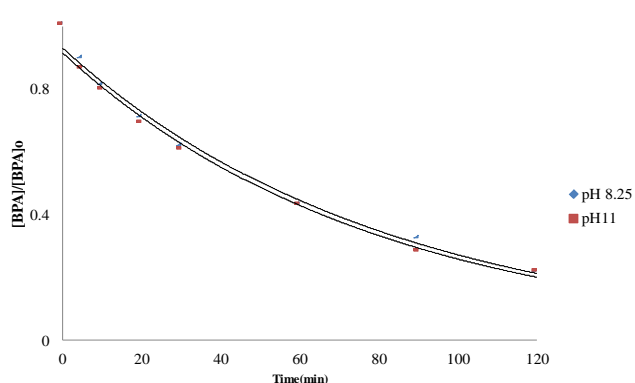

Fig.1. Effect of pH on BPA treatment

However, this result shows that there was no significant increase in degradation rate reason been that the alkalinity of the solution was high at pH of 11, there fore, the production of •OH radical was excess and crowdedness could inhibit or slow the reaction. The results show that alkalinity can either promote or scavenge the reaction. Thus, the minute different

between pH of 8.25 and 11 could be attributed to an increase in •OH scavenger by the sodium hydroxide which predominantly occupy the reaction at higher pH levels [6].

C. Determination of rate constant for reaction of BPA

Second rate order has been reported in several treatment techniques employed to determine the rate constant between ozone and organic pollutants. Both direct oxidation method and competitive kinetics can be use to determine the rate constant [6]. Various method of generating •OH include gamma- radiolysis, UV/H$_2$O$_2$, O$_3$/H$_2$O$_2$, Fenton method, Walling's method [6]. In the present study, direct oxidation method was applied to determine the second rate constant. At constant ozone concentration, the degradation rate dependent on the initial concentration of BPA. The reaction was second rate order as reported in several literatures [6]. But in this study, second rate order was observed because ozone attack was not predominant and is dependent on initial concentration of BPA. Figure 2 depicts the influence of initial concentration with respect to time.
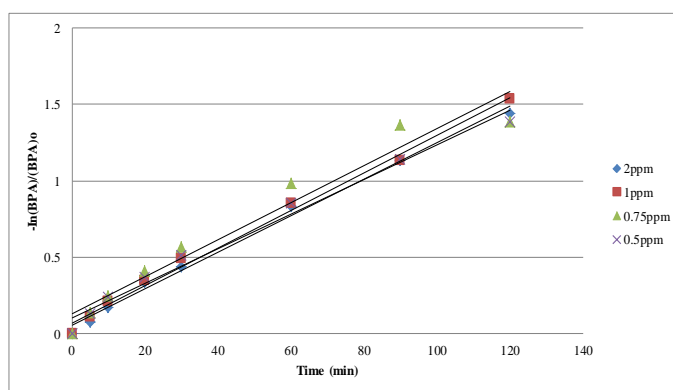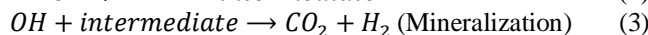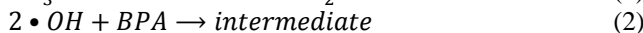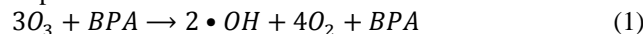

Fig.2. Second order plots for BPA degradation at various concentrations by ozone alone. $[BPA]_o$ = 1ppm, $[O_3]$=6.67mg/L, pH=8.25.

Under the alkaline pH condition, ozone decomposition rate increases in water. The half-life of ozone in water was about 2-3minutes thus the •OH radical dominate the system as reaction intermediate. Therefore, degradation of BPA may occur with •OH radicals while molecular ozone can be ignored. Therefore the proposed rate of degradation of BPA can be expressed to established second order kinetics based on this assumption:

$$3O_3 + BPA \rightarrow 2 \bullet OH + 4O_2 + BPA \qquad (1)$$
$$2 \bullet OH + BPA \rightarrow intermediate \qquad (2)$$
$$OH + intermediate \rightarrow CO_2 + H_2 \text{ (Mineralization)} \qquad (3)$$

Combining rate order of (1) and (2) is equal

$$\frac{d[BPA]}{dt} = -k_{\bullet OH}[BPA]_o[\bullet OH] - k_{O3}[BPA]_o[O_3] \qquad (4)$$

Where $k_{\bullet OH}$ is the reaction rate constant of BPA with •OH while k_{O3} is the reaction rate constant with aqueous ozone.

$$-k_{obs} = [BPA]_o\{k_{\bullet OH}[\bullet OH] + k_{O3}[O_3]\} \qquad (5)$$

Therefore the above equation can be simplify to

$$\frac{d[BPA]}{dt} = -k_{obs}[BPA]_o \qquad (6)$$

$$In\frac{d[BPA]}{[BPA]_O} = -k_{obs}t \qquad (7)$$

Where k_{obs} the pseudo-first order rate is constant for BPA degradation during ozonation $[BPA]_O$ is the initial

concentration of BPA and $[BPA]$ is the residual concentration at time. A straight line was obtained through the plot of $-In\frac{d[BPA]}{[BPA]_O}\ vs\ t$ with slope k_{obs} .

TABLE I
SECOND-ORDER RATE CONSTANT FOR THE REACTION
BETWEEN OZONE AND BPA

Concentrations BPA (ppm)	Rate Constant k(min^{-1})	R^2
2	0.012	0.9933
1	0.0123	0.9938
0.75	0.0137	0.9895
0.5	0.0113	0.9833

D. Mineralization (TOC) of BPA by Ozonation Process

TOC removal as a function of reaction time is shown in Fig.3. This process was under reaction conditions of ozone dosage of 6.67mg/min and BPA initial concentration of 1ppm are kept constant and varying the effects of pH on the TOC removal. As seen in Fig.3 the maximum TOC removal of 42% was achieved at 120 minutes reaction. The reaction proceeds very fast for the first 20 minutes leading to fast consumption of ozone molecules and also, fast removal of TOC. At the end of the reaction the pH dropped to 3.20 meaning there are formation of organic acids which are non degradable linear by products during the process as reported by [3] that muconic acid derivatives, benzoquinone, 2-(4-hydroxyphenyl)-propan-2-ol, orthoquinone, catechol compounds and acids or aldehydes are possible by-products of BPA ozonation.
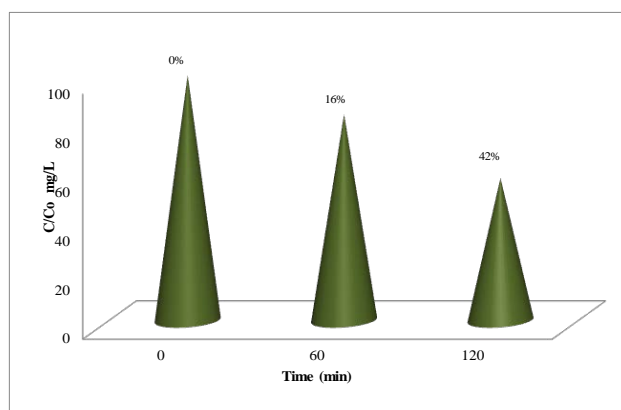

Fig. 3. Effects of pH on TOC removal: [pH] = 8.25 [BPA]$_o$=1ppm and [O$_3$]= 6.67mg/min

Meanwhile as seen in figure 4 below, at pH of 11 the solution falls to 3.4 indicating present of organic acids. The maximum TOC achieved was 50.7% at 120minutes. Therefore, complete mineralization was not achieved due to the presence of some organic acids which are the by products. The TOC removal at pH 11 is more pronounce than pH of 8.25 this is because more •OH radical is formed subsequently attacking the pollutants resulting in high TOC removal.
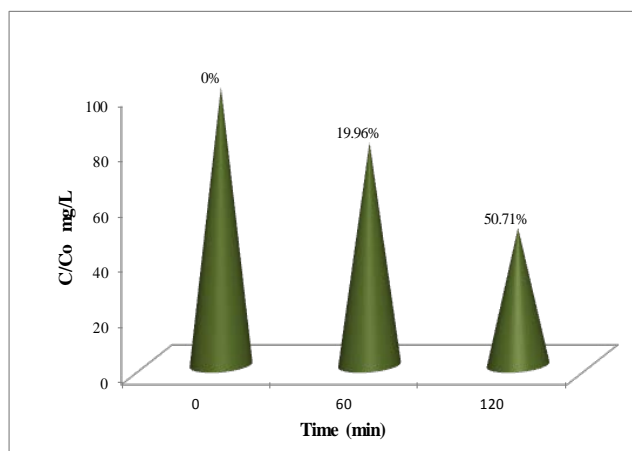

Fig.4. Effects of pH on TOC removal: [pH] =11.0 [BPA]o=1ppm and [O3]= 6.67mg/min

IV. CONCLUSION

The ozonation process is a successful method of EDCs treatment in water although complete degradation was not obtained. The rate of BPA removal increases as ozone dosage increase with time. The highest k value obtained at 0.75 ppm was 0.0137 min^{-1} which gives the best degradation efficiency of 81.13% at pH of 8.25. pH as an important factor on self-decomposition of ozone in water, which affects TOC removal of BPA more significantly. At low pH values ozone decomposition is slower and the main reactions are between organic compound and molecular ozone. In contrast, higher pH generates more •OH radicals while TOC conversion was higher. TOC removal of the BPA was conducted in alkaline pH. The highest TOC mineralization obtained was 50.71% of BPA at 120 minutes. Therefore, presence of organic acids was assumed in the reaction which are accumulated in the oxidation process, although the by-product may not be toxic than the parent compound. It was observed that kinetics follow second order reaction rate. However, mineralization of BPA may require more powerful oxidation process. Ozonation has proved to be the best technique suitable for BPA degradation due to it fast reaction rate and shorter decomposition time (20minutes). Meanwhile the fast reaction ozonation processes aided the degradation efficiency. In addition, necessary operational conditions might aid complete mineralization if more powerful techniques were introduced. Obviously, the ozonation process employed in this study is very effective. In wastewater treatment, ozonation serves as disinfectant, oxidant of organic pollutants and control method of odor and taste.

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