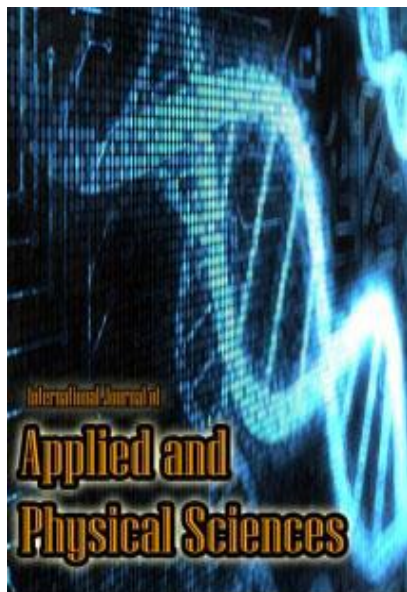


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RAPID CHEMICAL OXYGEN DEMAND ANALYSIS BY TOTAL ORGANIC CARBON CORRELATION

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Abstract. Chemical Oxygen Demand (COD) is a major parameter for wastewater treatment plant design and operation. The analysis takes two to three hours and produces toxic waste that is harmful to aquatic life. The online pollution monitoring system needs the analysis period as little as possible to report the effluent condition. Total Organic Carbon (TOC) analysis can be replaced with a response for the requirement of rapid analysis. The study had been done by digestion of total organic carbon to carbon dioxide gas to correlate to the COD in synthetic wastewater. Electrooxidation system and ultrasonic wave are the tools for TOC breakdown to carbon dioxide. Carbon dioxide gas was monitored by a non-dispersive Infrared (NDIR) type of analyzer. This study has shown that the COD analysis can be replaced by TOC digestion ($\text{CO}_2 \times 1.3\text{-}2.3 = \text{COD}$) in 15 minutes.

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INTRODUCTION

Total Organic Carbon (TOC) is representative of contaminants in water and wastewater. Nevertheless, TOC tests are unpopular because the analyzers are costly. Therefore TOC value is never specified in the standard of effluent merely Chemical Oxygen Demand test (COD) and Biochemical Oxygen Demand test (BOD_5) would be specified. BOD_5 [1], [2] is a conventional analysis method for wastewater that demands 5-day incubating period and by the reason of repeatability problems, frequently replaced by COD [3] for wastewater treatment plant design, operation and monitoring. COD analysis employs 2 hours to be completed but toxic substance generated and high content of chloride can be interfered.

The TOC consists of natural and synthetic sources, humic acid, fulvic acid, amines, and urea that are examples of Natural Organic Matter (NOM), some detergents, fertilizers, pesticides, herbicides, industrial chemicals and chlorinated organics that are examples of synthetic sources [4].

The analysis method was done by carbon dioxide gas measurement after combustion or wet chemical oxidation [5] while it has tendency switch to replace both the COD and BOD_5 tests due to being faster and potentially more accurate than the COD test. [6] TOC test has been developed for doing the analysis more precisely and reliably, furthermore for sophisticated materials such as industrial wastewater [7].

Ultrasonic wave or ultrasound was determined as the sound of a frequency that is beyond human hearing and is above 16 kHz. Sono-chemistry is a branch of science that deals with the chemical and mechanical effects of ultrasound; it is produced by ultrasonic wave in the particular range of 16-1000 kHz [8].

Chemical reactions acceleration and the oxidation - reduction process by ultrasounds were found in 1927. [9] Temperature of the cavitation gas bubbles was determined to be up to 5000 K [10] and the pressure can be increased up to several hundred atmospheres during ultrasonic wave distribution [9]. Ultrasound uses acoustic cavitation which helps to degrade organic pollutant, does not require chemicals and is easy to install and operate [12]. Sono-chemistry comprises of hotspot theory, electrical theory, and plasma discharge theory [13]. Nowadays, hot-spot theory or cavitation theory is widely accepted in sono-chemistry, all of the laboratory tests based on sono-chemical degradation of organics are being explained based on this cavitation theory alone [11], [12].

Electrochemical oxidation (EO) is widely used for organic removal from wastewater. The principle consists of carrying out the oxidation reaction on anode where toxic substances re-verse to non-toxic substances. The EO is used for degradation: industrial toxic substances, aromatic compounds, pesticide and other organics, the carbon dioxide gas (CO_2) and water (H_2O) will be generated. In the EO process, total organic carbon and toxic substances in wastewater are usually destroyed either by the direct or indirect oxidation process [14], [15]. In a direct anodic oxidation process, the contaminants are first absorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone or hydrogen peroxide can be regenerated by the electrochemical reactions during electrolysis. The contaminants are then destroyed in the bulk solution by oxidation reaction of regenerated oxidants. All the oxidants are generated in-situ and are utilized immediately.

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Among the oxidants, generation of hypochlorite is cheaper as most of the effluents have certain amount of chloride [16].

The objective of this experimentation was to study the TOC that is expressed in terms of carbon dioxide gas for COD comparison. The CO_2 concentration which is produced by electro-oxidation combines with non-ultrasonic/ultrasonic radiation and varied current (ampere) will be compared. The important parameters such as initial concentration of H_2O_2 (hydrogen peroxide), PH and electric potential difference (voltage) variation were also investigated.

MATERIALS AND METHODS

Experimental Setup

The laboratory scale experiment was done with a 200 ml stainless steel 316 L reactor with titanium cathode (-), anode (+) and a source of ultrasonic wave as shown in figure 1. The synthetic wastewater with standard COD 200 mg/l (TOC 80 mg/l) was prepared by using potassium hydrogen phthalate

($\text{KHC}_8\text{H}_4\text{O}_4$), 18 gram in deionized water 1000 ml. The reactor with diameter of 5 cm and 15 cm height, material is SUS 316L with acrylic cap to prevent the electrical current leakage. The electrodes with diameters 1.2 cm and length 10 cm are used and the clearance between cathode and anode is 1.0 cm.

AC-DC adjustable power regulator 0-6 volt, 0-5 ampere (Kenwood PW18-1T, U.S.A.) was used to supply the direct current 1, 2, 3, 4 and 5 volt with 1, 2, 3, 4 and 5 ampere respectively. Ultrasonic wave was achieved at frequency of 42 kHz (120 W) with ultrasonic generator (UCE ultrasonic UCE-220v-PCB50w/120w, China) with an ultrasonic transducer with diameter 4 cm fixed at the bottom of the reactor. Two stainless steel 316 valves were installed on top of reactor, one for sample hydrogen peroxide filled and another one for carbon dioxide gas analyzer (NDIR) tubing connection.

Analysis Method

COD was analyzed following the APHA standard method for water and wastewater examination (2005) [17].

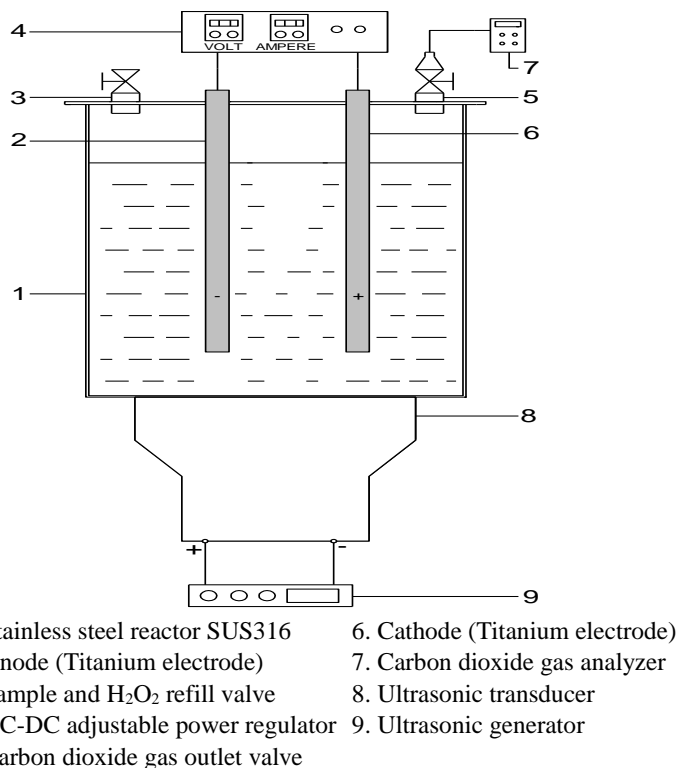


Fig. 1. Schematic diagram of electro-oxidation and ultrasonic wave reactor

Carbon dioxide gas was analyzed with a Haltech HCO 202 (USA), range of analysis 0-5000 ppm with sampling built-in pump. Each test was done in 15 minutes after switching on the adjustable power regulator and ultrasonic generator. All experiments were done in triplicate to assure reproducibility.

Statistical Analysis

Data was presented as mean and significant letter at $p < 0.05$. Statistical comparisons were performed using SPSS 16.0 by SPSS Inc. The significant difference in each condition was tested using a One-way ANOVA with a Duncan's Multiple Range Test (DMRT). A $p < 0.05$ was considered statistically significant.

RESULTS

Ultrasonic and Non-Ultrasonic Effect on CO₂ Production

The effect of applied ultrasonic into reactor was investigated and the results have been displayed in Figure 2. The ultrasonic has a capability to increase the carbon dioxide production of EO process. CO₂ concentrations of non-ultrasonic experiment with 1, 2, 3, 4 and 5 A of electric current were 14.7,

20.3, 27.3, 35.7 and 38.0 ppm, respectively. Therefore, using ultrasonic gave the better performances. CO₂ concentrations of ultrasonic experiment with 1, 2, 3, 4 and 5 A of electric current were 19.3, 33.0, 42.3, 49.7 and 65.7 ppm, respectively. Then the optimum condition of ultrasonic and electric current were used as following experiment condition by using ultrasonic and 5A electric current.

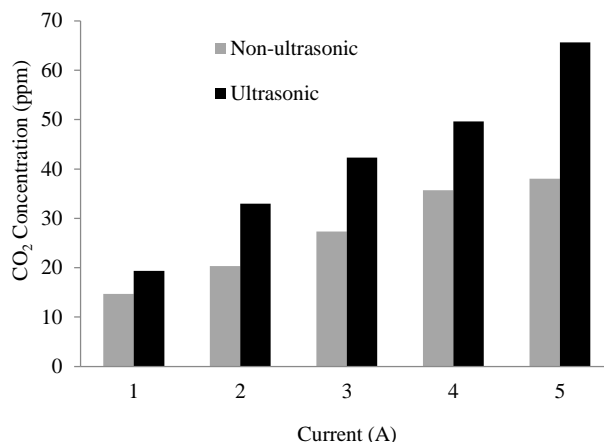


Fig. 2. Comparison of produced CO₂ concentration (PPM) of experiment setups with ultrasonic and without ultrasonic by various electric current (A)

Effect of Various Experimental Parameters

Voltage

Various electric voltages were applied to the electrodes; CO₂ yields were illustrated in Fig. 3. The result showed that the produced CO₂ concentrations were likely increased proportionally

to the increasing of applied electric voltage. The average CO₂ concentrations were 27, 43, 67, 75 and 86 ppm for 1, 2, 3, 4 and 5 V of applied voltage respectively. Highest yield of CO₂ production was achieved at 5V but the statistical analysis showed no significant difference between 4V and 5V ($p < 0.05$).

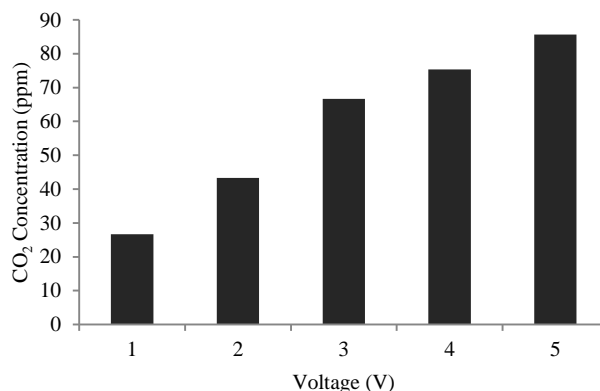


Fig. 3. Comparison of produced CO₂ concentration (PPM) of experiment setups with ultrasonic by various electric voltage (V)

H₂O₂

By varying the initial H₂O₂, CO₂ concentrations were investigated and illustrated in Fig.4. The results shared the identical trend; increasing H₂O₂ concentration will escalate the

CO₂ yield. The average CO₂ concentrations were 29, 39, 59, 62, 73 and 76 ppm for 0, 5, 10, 15, 20 and 25 ml of initial H₂O₂ respectively. Highest yield of CO₂ was achieved at 25 ml of initial H₂O₂.

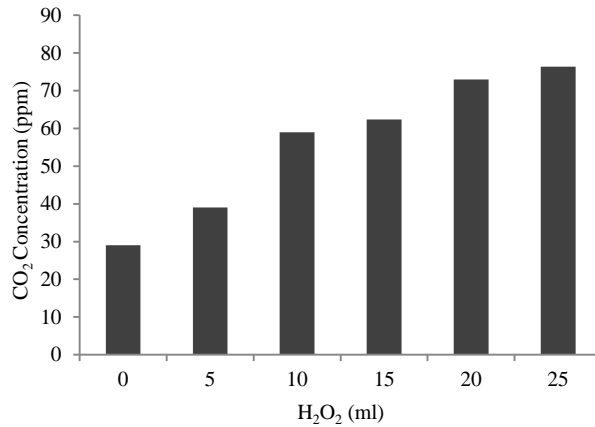


Fig. 4. Comparison of produced CO₂ concentration (ppm) of experiment setups with ultrasonic by various H₂O₂ (ml)

PH

Changing the initial pH conditions was conducted in 5 conditions such as pH 2, 4, 6, 8 and 10. The produced CO₂ concentration has been investigated and displayed in Fig. 5. The

results indicated that the pH range 6-8 provided appropriate CO₂ concentration which was above 70 ppm while acidity or strong basicity will decrease the CO₂ production.

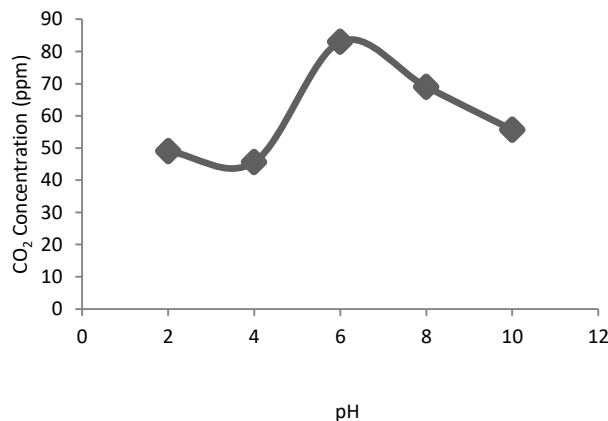


Fig. 5. Comparison of produced CO₂ concentration (PPM) of experiment setups with ultrasonic by PH

DISCUSSION AND CONCLUSIONS

Effect of Ultrasonic

The ultrasonic not only degrades TOC but also promotes faster degradation through millions of cavitation events occurring throughout the reactor during any particular point of time. It completely breaks down organic pollutants into simple molecules such as water and carbon dioxide and therefore produces no sludge. The formation of intermediates and their composition may vary, depending on treatment time and cavitation intensity. The most volatile organic compound undergoes degradation first, followed by the next most volatile and so on [18].

Effect of Various Operating Parameters

Increasing of electric current (A) was directly enhancing the EO activity at anode of the reactor which led to higher yield of CO₂. Another study also claimed that, increasing the current

tends to increase the rate of oxidation [19] due to production of oxidant such as H₂O₂ solution. Increasing generation of oxidant is proportional to current density, which eventually increases the pollutant degradation [20]. The extent of oxidation (and therefore the degree of direct BOD/COD reduction) typically depends on the amount of hydrogen peroxide used. However, complete digestion of the organic compounds to carbon dioxide and water is not needed. Partial oxidation to intermediate compounds minimizes chemical consumption and often results in substantial reductions in BOD and COD and toxicity [21].

Another study showed the same results, organic removal efficiency under the basic condition with pH value from 8.2 – 11.0 was higher than acidic condition with pH < 6.6. The optimum pH value range was from 6.6 – 8.2. The pH values are greatly affecting the CO₂ yield by involving the composition rate

of substance in the solution and affecting the distribution of exiting state of all organic compounds in the wastewater [22].

COD and TOC Correlation

According to this study, CO₂ had related with COD and the breakdown of TOC that contains carbon atom will produce the CO₂ by combining with excessive oxygen from H₂O₂ following the experimentation. Therefore, COD concentration can be reverse calculated by multiplying CO₂ concentration by 2.5. A previous study showed that the relationship between TOC and COD is the strong linear relationship which supports the potential use of TOC as alternative measurement for COD [23].

CONCLUSION

This study presented the method where the rapid COD analysis can be replaced by TOC digestion to carbon dioxide gas analysis due to COD/TOC relativity. Effect of CO₂ concentration on various operating parameters e.g. electric current, applied voltage, initial H₂O₂ concentrations and initial pH were studied in this experiment. The results indicated that this method is capable of being applied as COD monitor system and also can be related to BOD. However, this research is only a preliminary study in laboratory and the analyzer must further study for commercial terms consideration.

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