Ozonolysis of wastewater from rubber industry

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Abstract. The chemical industries currently release pollutants into air, soil, and water. For rubber industry, large amount of wastewater is produced resulting in huge energy demand for water treatment. However, there are several restriction factors for wastewater treatment i.e., contaminated oil from machinery and foul odour from organic matter caused by microbial enzymes. To overcome these problems, this research focused on wastewater treatment from rubber industry via ozonolysis. Two cases of experiments were carried out in a bubble column with capacity of 500 ml including with and without ozonolysis. Ozone concentration were maintained at 64 mg/L. Samples of 10 ml were collected every 4 h and then analyzed by GC-MS. The BOD, COD, and operating cost were investigated. The results showed that the BOD and COD decrease by 40% when ozonolysis was applied. The colour of wastewater become clear after ozonolysis. In addition, the operating cost of ozonolysis process is lower than that of without ozonolysis.

1. Introduction

Energy is currently used in all sectors in form of electrical and thermal energy. The use of energy increases as world’s economy growth. In the industrial production process, there are various problems from pollutions release to the environment i.e., air and water. Water pollution is the serious issue in the industry. Water treatment system is therefore required before discharge. Electrical energy must be added to solve these problems. Although many researches publishes a plenty of water treatment technique, the assessment of environmental benefits, especially energy consumption is rarely considered [1].

The wastewater treatment system currently used in rubber industry is anaerobic digestion [2]. It is used to reduce biochemical oxygen demand (BOD) and chemical oxygen demand (COD). This process is achieved through several stages i.e., hydrolysis, acidogenesis, acetogenesis and methanogenesis.
However, the problem of industrial wastewater treatment is as a result of oil contamination from machinery. Several techniques are utilised to eliminate oil [3, 4]. Moreover, the wastewater also has a foul odour from the organic matter which is caused by many reasons such as microorganisms, enzymes, physical characteristics and chemical reactions. [5]. Therefore, the odour treatment systems using microorganisms is normally utilized to decompose contaminants in the air to become a smaller molecule. Contaminants that microorganisms can decompose are classified as volatile organic compounds (VOCs).

VOCs are a wide group of pollutants comprising of more than 500 compounds that occur in the atmosphere in gaseous form including alkanes, alkenes, aldehydes, ketones, halogenated and aromatic hydrocarbons, esters and alcohols [6]. These compounds are extensively used by many industries, they can adversely affect both human health and the environment. VOCs are key ingredients in many consumer products such as fuels, paints, aerosols, refrigerants and pesticides. Thus, they are often abundant in wastewater [7].

Ozone known as oxidative substance is used for over the past 2 decades in the treatment of ground and industrial wastewaters [8-10]. The use of ozone can reduce the cost of both chemicals and energy. The objective of this study was focused on the wastewater treatment of rubber industry via ozonolysis technique. The BOD, COD, and energy used were investigated.

2. Methodology

Experiments were carried out in a bubble column with capacity of 500 ml as shown in figure 1. Temperature of wastewater obtained from the rubber industry in Rayong Province (after pre-treatment processes by scrubble method) was control at 25°C. Ozone was generated using a QLA-7G-M (320 x 250 x 525 mm) ozone generator fed with pure oxygen. The flow rate of oxygen and ozone concentration were maintained at 10 L/min and 64 mg/L, respectively. The inlet ozone concentration was analyzed using chemical technique. Samples of wastewater from the rubber industry of 10 ml were collected every 4 h and then analyzed by Gas Chromatograph-Mass Spectrometer (GC-MS, TSQ9K-VPI) equipped with TSQ™ 9000 Triple Quadrupole. Moreover, both BOD and COD were also investigated using titrimetric method.

![Flow diagram of wastewater treatment systems](image)

**Figure 1.** Flow diagram of wastewater treatment systems.

In this study, the experiments were divided into 2 cases as shown in figure 2. Case 1 involves treatment of wastewater with ozonolysis, where pure oxygen was fed to the ozone generator. Ozone
was then introduced to the bubble column. \( \text{Al}_2(\text{SO}_4)_3 \) and \( \text{NaOH} \) were added before analysis. The concentration of ozone was set at 64 mg/L. Whereas case 2 involves treatment of wastewater without ozonolysis, where pure oxygen was fed to the bubble column filled with wastewater. \( \text{Al}_2(\text{SO}_4)_3 \) and \( \text{NaOH} \) were then added before analysis.

![Diagram of experimental set up of case 1 and case 2.](image)

**Figure 2.** Experimental set up of case 1 and case 2.

3. **Results and discussion**

3.1. **Substances found in the wastewater**

The wastewater obtained from the rubber industry was analysed by the GC-MS as shown in figure 3. All substances can be classified as VOCs. The results show that the major substance found in the wastewater is acid (2-ethylhexanoic acid) with the composition of 36.34% as listed in table 1. This substance causes air pollution problem that affect people's health. Other substances are glycol ester group, heterocyclic compounds group, heptadecane, and hexanal with the composition of 29.05%, 13.05%, 2.71%, and 2.49%, respectively.

| No. | Retention time | Name of the compound | Molecular formula | Molecular Weight | Peak area % |
|-----|----------------|----------------------|-------------------|-----------------|-------------|
| 1.  | 12.14          | Hexanal              | \( \text{C}_6\text{H}_{12}\text{O} \) | 100.16          | 2.49        |
| 2.  | 14.85          | Heptadecane          | \( \text{C}_{17}\text{H}_{36} \) | 240.48          | 2.71        |
| 3.  | 15.48          | 2H-Tetrazole, 5-((thiophen-2-yl)methyl | \( \text{C}_6\text{H}_3\text{N}_4\text{S} \) | 166.02          | 13.05       |
| 4.  | 11.50          | Ethanol, 2-(2-butoxyethoxy)- | \( \text{C}_6\text{H}_{14}\text{O}_3 \) | 134.07          | 29.05       |
| 5.  | 10.96          | 2-ethylhexanoic acid | \( \text{C}_8\text{H}_{16}\text{O}_2 \) | 144.21          | 36.34       |
3.2. Comparison of wastewater treatment efficiency

The BOD and COD of wastewater from the rubber industry after pre-treatment by scrubber system were analyzed. The values of BOD and COD are $34,320 \text{ mgO}_2/\text{L}$ and $216,000 \text{ mgO}_2/\text{L}$, respectively, which exceeds the standards set by the Pollution Control Department. Electricity used for pre-treatment processes provided by the rubber industry is $471,183.63 \text{ kWh/ year}$ ($1,696,261 \text{ baht/year}$).

After treatment via case 1 (ozonolysis), the results show that the BOD and COD values are 5,970 and 128,000, respectively, while such values are 13,560 and 160,000 after treatment via case 2. As shown in table 2, the reduction of BOD and COD values of case 1 is approximately 40% higher than that of case 2. Moreover, the color of wastewater changed from brown (pre-treatment) to clear (case 1) as shown in figure 4. This means that ozone can treat the wastewater by reducing the BOD and COD values and purify the color.

| Waste water treatment | BOD (mgO$_2$/L) | COD (mgO$_2$/L) |
|-----------------------|---------------|---------------|
| Pre-treatment         | 34,320        | 216,000       |
| Case 1                | 5,970         | 128,000       |
| Case 2                | 13,560        | 160,000       |

Table 2. Comparison of BOD and COD values before and after treatment.
Figure 4. Characteristics of wastewater treatment: (a) Pre-treatment; (b) Case 1 and (c) Case 2.

In addition, after treatment via both case 1 and 2 and analysed by the GC-MS, the results show that the reduction of concentration of VOCs was observed. This means that ozone can oxidize the VOCs.

3.3. Energy efficiency in ozone treatment process

The wastewater treatment process (case 1) requires electricity to produce ozone. Chemicals are also used to settle and neutralize. Electricity used for the ozone generator and air compressor are list in table 3. Chemicals cost used in the treatment are also summarized in table 3. The operating cost of laboratory and full scale are 31,476.3 baht/year and 220,334.1 baht/year, respectively. The BOD and COD of wastewater obtained from the rubber industry after pre-treatment processes are still higher than the standard. Therefore, extra cost of 1,696,261 baht/year must be invested to treat wastewater disposal. However, the operating cost of 1,475,926.9 baht/year can be reduced by applying ozonolysis technique as summarized in table 4. Other than cost, this treatment process can produce wastewater to meet the standard prior to discharging.

| Item                        | Lab scale          | Full scale         |
|------------------------------|--------------------|--------------------|
| Electrical energy of the ozone generator (kW/year) | 7,008 (25,228.8 bath) | 49,056 (176,601.6 bath) |
| Electrical energy of the air compressor (kW/year) | 876 (3,153.6 bath) | 6,132 (22,075.2 bath) |
| Acid chemical cost (bath)    | 27.9               | 195.3              |
| Base chemical cost (bath)    | 3,066              | 21,462             |

Table 3. Summary of operating cost.

| Item                        | Cost (bath/year) |
|------------------------------|------------------|
| Wastewater disposal cost in industry | 1,696,261 |
| Ozone treatment wastewater    | 220,334.10       |
| Saving cost                  | 1,475,926.90     |

Table 4. Summary of saving cost.
4. Conclusion
Wastewater produced from the rubber industry affects the environment because BOD and COD values are higher than the standard. Using ozonolysis technique can reduce both BOD and COD values by over 40%. Moreover, the reduction of VOCs and purify water can be observed. In case of economic analysis, ozonolysis technique can reduce the operating cost of 1,475,926.9 Baht/year compared with per-treatment processes.

Acknowledgment
We would like to thank the Faculty of Science, energy and environment, King Mongkut’s University of Technology North Bangkok (Rayong Campus) for financial support.

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