Ozonation and ozone / UV process for industrial wastewater treatment:
comparison between two types of wastewater

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Abstract

This study investigated the degradation of organic and inorganic matters of wastewater by conventional ozonation and ozone/UV AOPs. The experiments performed with two types of wastewater (synthetic and industrial) having the same chemical oxygen demand COD, varying solution pH and employing UV clearly showed that oxidation during ozonation process was dominated by OH reactions. Conventional ozonation with 2 g/hr maximum ozone dose led to 56% COD removal efficiency in synthetic wastewater, while 52% was estimated from industrial wastewater, both having the same initial COD value of almost 50 ppm and contact time of 80 min. In meanwhile, using UV improved the utilization efficiency of oxidation by reducing the OH scavenging contribution of oxidants, 62% and 70% were the efficiencies of industrial and synthetic respectively in ozone/UV applications. Therefore, combined ozone/ AOPs shows better removal efficiency of toxic contaminants than using ozone alone.

Keywords: industrial wastewater, ozonation, ozone-based process, AOPs, COD.

1. Introduction

New compounds are manufactured and developed in today’s industry to meet human’s ever-increasing demand. Thus, new hazardous molecules, could not be considered as a small amount, are added continually to water bodies through effluents of different manufacturing units. The wastewater normally comes from chemical-producing industries like pharmaceutical, pesticides and petro-chemical and other industries containing complex molecules that are recalcitrant in nature; thus, cannot degrade completely by conventional treatment processes. Due to regulation authorities, these effluents have to be treated to a safe
dischargeable limit through various of method including physical, chemical and biological treatments (Kusvuran and Erbature, 2004; Thiruvenkghsh et al., 2007).

The operated processes involved in wastewater treatment consisting of primary (screening, mixing, flocculation, sedimentation, flotation and filtration) secondary (aerobic, anaerobic, etc.) and tertiary or advanced treatment (adsorption, disinfection, oxidation, etc.) (Babuponnusami and Mathukumar, 2012; Gogate and Pandit, 2004).

AOPs are processes involved in generation and use of hydroxyl free radicals OH as a strong oxidant toward compounds that cannot be oxidized by conventional processes. These radicals react with dissolved constituents to initiate oxidation reactions leading to almost complete mineralization to CO₂ and H₂O (Adewuyi 2005; Hua and Hoffmann 1997).

In order to overcome the limitations and difficulties of individual AOPs toward a specific pollutant and enhancing oxidation efficiency, combined AOPs termed as hybrid methods are used such as ozone/hydrogen peroxide and ultraviolet irradiation (Adewuyi 2005; Gorgate and Pandit 2004b; Pang et al., 2011).

In the present study, an investigation has been made to predict COD removal efficiency of conventional ozonation and hybrid ozonation methods, and make a comparison depending on the water quality. The effect of ozone dose, solution pH and contact time were taken into consideration to find the optimum conditions.

2. Material and Experimental procedure

Since the water quality is evaluated by the amount of organic and inorganic pollutant present in water, which termed as chemical oxygen demand COD test, two types of wastewater having the same COD value were operated.

2.1 Water samples

1. Industrial Wastewater

Industrial wastewater effluents were carried out from petroleum refinery plant south Baghdad, Iraq. Normally it undergoes a mechanical and physical treatment before operation to reduce the concentration of oil and other impurities that affect the ongoing process. Following Table 1 shows the characteristics of the effluents before and after pre-treatment. Industrial wastewater was characterized to have a 350 ppm COD concentration, which been reduced after pre-treatment to 53 ppm.
Table 1 characteristics of wastewater before and after pre-treatment methods

| Item   | Inlet | Outlet |
|--------|-------|--------|
| PH     | 7     | 6.8    |
| T.D.S  | 967   | 87     |
| Turbidity | 62.3 | 19.3   |
| Phenol | 1.99  | 137    |
| SO₄    | 294   | 375    |
| OIL    | 65.2  | 35.3   |
| COD    | 349   | 53     |
| CL⁻    | 275   | 297    |

2. Synthetic Wastewater

To simulate industrial effluents main characteristics, synthetic wastewater was prepared to have almost the same COD value of real industrial wastewater, after its been pre-treated, of 50 ppm. It has been made by adding 1 ml of glycerin to 20 L of deionized water (DW) for 300 ppm COD elaboration and then titrated to the adjusted value. The composition of the mixture was selected to appropriate structural properties, regardless of the presence of other materials.

2.2 Experimental procedure

The ozonation included air pump, ozone generator and bubble reactor. Highly efficient corona-discharge ozone generator was used to produce pure ozone gas, this initially provide ozone at a mass flow rate of 1.0 to 2.0 g/hr using a dry air as a feed gas. Laboratory scale ozone bubble reactors were cylindrical-shape reactors with 5 L hold-up volume and 6 L operation capacity (internal diameter 18 cm, height of 75 cm), made of acrylic vessel. The bottom of the reactor was designed to have a porous diffuser to produce small fine bubbles and provide a good agitation of solution for the reaction. The inlet fresh air was pumped at max flow 18 L/min. Fig. 1. shows the flow diagram of the experimental batch mode apparatus. The AOP procedure is carried out as following:

1. Filling the reactor with 1 litres of wastewater and run the air pump at the maximum flow of 18 L/min to provide the required amount of air for ozone
generator. Produced ozone is then applied by the porous diffuser on the operated wastewater as fine bubbles for better mass transfer.

2. The AOP involved:
   a. pH regulation of the reaction using 1N of each sodium hydroxide and hydrochloric acid.
   b. Modification of ozone concentration flow rate ranging from 1 g/hr to 2 g/hr.
   c. Reaction time starts from 20 min to 80 min, which was found to be the optimum condition.

3. Each step presented in section 2 were also considered when the hybrid method is used (ozone/UV).

4. UV lamp of 15 cm long, 6 watt and 215 mm wavelength is adjusted at the top of the reactor.

5. When ozonation starts, samples were taken after each 20 min to undergoes COD analysis test.

![Figure 1: schematic diagram of the ozonation system, 1. Gas outlet, 2. Bubble reactor, 3. Inlet Gas bubbles, 4. Samples outlet, 5. Diffuser, 6. Ozone generator, 7. Air pump.](image)

2.3 Analysis
The COD test was performed by testing the effluent samples before and after being treated. An oxidizing agent, like \( \text{K}_2\text{Cr}_2\text{O}_7 \), was added to the collected samples and left to 120 min and a temperature of 150 °C for digestion in (Lovibond COD reactor RD 125).

Digested samples were left to cool down at room temperature, then analysed in a photometer (MD 200 COD VARIO Photometer). The percentage of COD efficiency removal from the treated solution by the oxidation process was evaluated from the following equation:

\[
\text{COD Removal eff.\%} = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \times 100
\]

Where COD\(_0\) is the initial value of COD concentration (in mg/l) at t= zero time, COD\(_f\) is the value of COD concentration (in mg/l) after t time ozonation.

3. Results

The examined samples showed a wide variety of results as illustrated in figures below. Ozonation process was carried out on different wastewater samples having almost the same COD value, although the results were also different. Figure 2. Illustrate ozonation of industrial wastewater having initial concentration of 53 ppm COD, it shows that the best removal efficiency at 20 min was when solution pH is 9, to have 43%. while 41%, 35% and 30% were the removal efficiencies conducted at pH11, pH7 and pH5 respectively. With further oxidation reactions for the whole 80 min showed the maximum reduction of COD was 52% for pH9, followed by 49%, 47% and 41% at pH11, pH7 and pH5 respectively.

In meanwhile Figure 3. Represent removal efficiencies for synthetic wastewater having initial concentration of 50 ppm COD. pH7 was more susceptible to oxidation reactions to a removal of 38%. While 32%, 28% and 24% were removal efficiencies for pH9, pH11 and pH5 respectively. Ozonation continue with a steady response of condition for the whole 80 min to maintain removal efficiencies of 40%, 56%, 50% and 46% for pH5, pH7, pH9 and pH11 respectively, which means synthetic had a greater removal efficiency than industrial wastewater.
Figure 2. COD removal efficiencies of industrial wastewater with initial COD of 53 ppm.

Figure 3. COD removal efficiencies of synthetic wastewater with initial COD of 50 ppm.

Now it’s clear to say there is a difference in response for wastewater ozonation having the same chemical oxygen demand but different qualities, which assimilate that the action of ozone in industrial wastewaters is variable and depends on the quality of organics present as well as the treatment conditions depending on the source of the carried wastewater. In industrial wastewater the response to the solution pH condition was not as stable as synthetic
wastewater at the end of 80 min, on the other hand synthetic wastewater response took almost a straight line with solution pH, this variation refers to the different types of pollutant present in each wastewater and its behaviour toward oxidation. Not to forget that the best removal efficiency for industrial wastewater was found to be 52%, which is less than the efficiency estimated from synthetic wastewater of 56%. As a result, it is found that much higher doses of ozone are required for oxidation of industrial wastewater having the same COD number of synthetic wastewater, due to the higher $\bullet\text{OH}$ scavenger capacity by the water matrix in industrial wastewater, Which was formed by ozonation by products as a result of reactions between chemical disinfectants, organic and inorganic matter (NOM and IOM respectively) during water disinfection process (Wert, 2007; Muller et al., 2012).

Figure 4. COD removal efficiencies of industrial wastewater with initial COD of 53 ppm, (ozone/UV) method.

Figure 4. shows COD removal efficiencies with the present of UV, not to forget the variance was clearly indicated due to the presence of different kinds of pollutant in industrial wastewater as listed in table above.

At 20 min pH9 tend to have 52% efficiency removal, while pH11, pH7 and pH5 have efficiency of 49%, 45% and 43% respectively. At the end of 80 min pH9 remain dominated on the best removal efficiency with a slight difference between pH11 and the earlies, which were 62% and 60%. In meanwhile, pH7 and pH5 indicates 56% and 52% At the end of 80 min respectively.
Figure 5. COD removal efficiencies of synthetic wastewater with initial COD of 50 ppm, (ozone/UV) method.

Figure 5. shows COD removal efficiency of concentration of 50 ppm synthetic solution with the presence of UV. pH7 was also indicated to have the optimum efficiency of 52%, followed by 46%, 40% and 28% removal efficiency of pH11, pH9 and pH5 at 20 min. oxidation continues to reach 70%, 62%, 58% and 56% removal efficiency at the end of 80 min respectively.

the results show a better response than using ozone alone. The photo-activated reactions are characterised by free radical mechanism. These radicals are initiated by the interaction of molecules of chemical species with photons of adequate energy levels, therefor its more easily to produce (Bhatkhand et al., 2002; mazzarino and Piccinni, 1999). As a result the amount of oxidized pollutants were maximized.

UV light penetration into the source water can be adversely affected by turbidity. There are also many interference compounds that absorb UV light (e.g., nitrate and iron) and, thus, reduce process efficiency. A well designed AOP can overcome some of these problems by first dealing with contaminants such as iron or suspended solids prior to the radical formation step. For example, pre-treatment with filtration as explained earlier, which found to be 19.3 and 1.4 NTU for industrial and synthetic wastewater respectively.
4. Conclusion

The degradation behaviour of pollutant in wastewater during ozonation is a function of the type of organic and inorganic matters in wastewater. Solution pH showed a significant effect on pollutant degradation, the optimum values were indicated to have the best efficiency for pH 7 when synthetic wastewater was used. While industrial wastewater were more susceptible to pH condition of > 7 due to the variety types of pollutant present. The optimal contact time is 80 min. The results of the tested samples clearly show the hybrid methods of AOPs is an effective way to reduce the COD through industrial wastewater treatment since COD compounds could not be completely oxidized by conventional ozonation due to the OH scavenging rates of wastewater. UV light improved the removal efficiency through maximizing the formation of hydroxyl radicals.

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