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RESEARCH ARTICLE

Effect of pH on the abatement of biochemical oxygen demand of pharmaceutical industry wastewater treated by ozone

*Ashish Gome and Kanjan Upadhyay

Chemical Engineering Department, Ujjain Engineering College, Ujjain (M.P.) India.

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Abstract

In the last few decades, research advancements in the medical field have given rise to manufacturing of pharmaceuticals of different varieties including first and second generation drugs. This has proliferated pharmaceutical industries, which in turn are releasing huge amount of wastewater into water bodies after production of pharmaceuticals. The continuous release of pharmaceuticals from such industries in the aquatic environment is getting alarming day by day, despite several environmental regulations. The biochemical oxygen demand of such pharmaceuticals is very high, which is an indication of pollution level and affects the aquatic life also. The present study deals with the ozone treatment of pharmaceutical wastewater for the assessment of reduction in biochemical oxygen demand under varying pH conditions. Ozonation time of 2 min at 30 mg/L ozone resulted in around 75% BOD (biochemical oxygen demand) reduction of the wastewater sample. Out of all the investigations carried out at actual i.e. unchanged, acidic and alkaline pH of the collected sample, alkaline medium produced tremendous results in terms of percentage BOD removal. It can be concluded that ozonation at elevated pH is favorable for reduction in biochemical oxygen demand of pharmaceutical industry wastewater.

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Introduction

In India, surface water sources are getting contaminated due to the release of vast quantity of wastewater from a number of industries including pharmaceutical. These sources have been rendered unsafe for human consumption as well as for other irrigation and industrial activities. Continuous degradation in water quality can contribute to scarcity of water due to limited availability for both human use and for the ecosystem (Murty and Kumar, 2011). The effect of pharmaceutical wastewater on water bodies was reported between 1960 and 1980 (Stumm-Zollinger and Fair, 1965; Snyder et al., 2006). Some studies reported human drugs in the environment in the mid 1970 (Garrison et al., 1976).

Since the first reports of human drugs in the environment, release of pharmaceuticals has been increasing, especially in the form of liquid and giving rise to frequent occurrence of a variety of pharmaceuticals in the aquatic environment in ample

quantity and numbers (Ternes et al., 1998; Kolpin et al., 2002). Pharmaceuticals enter the environment from a number of sources including pharmaceutical production plants, wastewater treatment plants, hospitals, landfills etc., (Khetan and Collins, 2007; Lillenberg et al., 2010). Occurrence of trace pharmaceuticals (mainly antibiotics) in aquatic environments worldwide have been reported in a number of studies (Hamscher et al., 2006; Batt et al., 2006; Lin et al., 2009).

Some studies reported the presence of pharmaceuticals, personal care products and endocrine disrupting compounds in the aquatic environment (Daughton et al., 1999). Some reports emphasized on the risk involved with the use of pharmaceutical compounds on surface water directly or indirectly (Schaar et al., 2010). For the last two decades, pharmaceuticals have been receiving attention as potential bioactive chemicals in the environment (Kümmerer, 2009; Sirés and Brillas,

2012). Dire consequences of pharmaceuticals on the aquatic environment due to improper disposal of pharmaceutical wastes and limited effectiveness of conventional wastewater treatments towards elimination of these compounds have been reported (Hirsch et al., 1999). Considering the sources of release of pharmaceuticals into aquatic systems and intensity of subsequent risks involved, impeccable strategies are required to be developed (Chevre et al., 2013).

Complete removal of the pharmaceuticals, their residue, and micropollutants is hardly achieved in industries with the available treatment techniques. However, some studies suggest that large number of pharmaceuticals can be efficiently removed by physicochemical treatment including screening, chlorination, coagulation/flocculation, sedimentation, adsorption, reverse osmosis, activated sludge process, membrane separation, biological treatments (Huber et al., 2003). Some researches presented biological treatment (both chemical and biological oxidations) of wastewater (Scott et al., 1995). Effects of chemical oxidation as a pre or post-treatment step in biological oxidation of wastewater have also been reported. Advanced wastewater treatment is required to reduce the release of pharmaceuticals into the aquatic environment or to eliminate them from wastewater completely (Huber et al., 2005).

Present study deals with the ozone treatment of pharmaceutical industry wastewater and assessment of biochemical oxygen demand reduction, post ozonation. BOD measures the pollution level in wastewater and gives the amount of biodegradable matter required. BOD gives the additional amount of oxygen needed for microorganisms to biodegrade the matter in water sample. BOD of a particular water/wastewater sample depends on the capacity of microorganisms added or which are already present to digest the matter, aerobically. The biodegradability assessment of industrial wastewater is also significant for better analysis of removal efficiency (Arslan-Alaton, 2002). Thus, for the determination of biodegradability of wastewater i.e., BOD/COD ratio, measurement of BOD is important.

Methods of Treatment of Pharmaceutical Wastewater

A number of treatment processes are available to handle vast quantity of wastewater produced from pharmaceutical industries, but they are industry and associated wastewater specific (Gupta et al., 2006). Primary treatment can remove about 60% of the suspended solids and around 35% BOD (Masters, 1998). Suspended and colloidal impurities are

removed by coagulation and flocculation by adding coagulants and literature suggests that high doses of coagulants are required to remove small amount of COD (chemical oxygen demand) from pharmaceutical plants producing allopathic medicines (Mayabhate et al., 1988). It has been observed that by physicochemical and biological treatment, higher removal rates can't be achieved.

Traditionally, biological treatments are used to manage pharmaceutical wastewater (Suman Raj and Anjaneyulu, 2005). Although no particular treatment system could be specified for such diversified pharmaceutical industries, nonetheless, in order to achieve higher removal efficiencies advanced oxidation reactions like ozonation have been used. Many researchers have worked on pharmaceutical wastewater treatment by ozone or ozone combined with H₂O₂ and UV. Most of the published research is related to the mechanism of direct or indirect reactions of ozone and their kinetics (Hoigne & Badar, 1978). Although the degree of removal and mineralization of pharmaceuticals in water/synthetic industrial effluent/pharmaceutical wastewater has been reported, little or no literature exists on the ozone treatment of pharmaceuticals in actual pharmaceutical wastewater (Cokgor et al., 2004).

Material and Methods

For the research purpose, the sample collected from the industry was slightly mud green in color, turbid with faint odor, having pH value around neutral, containing high amount of total dissolved solids and chemical oxygen demand but moderate biochemical oxygen demand. During the treatment period, sample was preserved in the cold storage unit at the Environmental Engineering laboratory of Chemical Engineering Department at Ujjain Engineering College, Ujjain (M.P.). Sample was analyzed for TSS, TDS, TS, DO, BOD, and COD under different conditions of pH. Analysis of the sample was carried out at above mentioned department along with the assistance of Regional Laboratory, M.P. Pollution Control Board, Ujjain. All tests were conducted using Standard Methods of Examination of Water & Wastewater, APHA (1999).

The ozone generator set-up assembled for the treatment was consisted of ozone generator with in-built voltage regulator, ammeter, oxygen cylinder, two outlet lines bifurcated by a valve. Two bubble columns were attached in one outlet line. First of these columns was filled with sample for treatment and in the other, outlet gas from first column was directed to get dissolved in water. In the other line one bubble column was filled with 2% KI solution.

Inlet line to the ozone generator was pure oxygen from oxygen cylinder. Bubble columns of 1 liter capacity were used. However, during the ozone treatment the column was filled up to 500 ml, as some space is left for the ozone gas to maintain pressure. Bubble columns (Borosil), also known as gas washing bottles, were filled with some liquid through which gas is passed from a sintered disc situated in the bottom. Sintered disc having pore size 15-40 microns is used for filtration of liquid and gases. Pure oxygen was supplied through oxygen cylinder 7 kg in capacity, at a constant flow rate of 0.12 lpm (lit/min). The flow was maintained constant by flow regulator mounted on the top of the oxygen cylinder. The outlet pipe from ozone generator was divided into two lines through a valve. Before allowing the ozone stream to treat wastewater sample in the bubble column, formation of ozone was confirmed. To determine the concentration of ozone, the valve (towards bubble column side) was kept closed and the gas was allowed to flow towards bottle containing acidified, 2% KI solution.

Initially, ozone generator performance was determined by operating it at various currents from 0.1 to 0.5 ampere at 230V. Concentration of ozone was also measured at each operating current between 0.1 and 0.5 ampere. During ozonation, pH of sample and ozonator current which directly affects ozone concentration, were altered. Gas flow rate from the oxygen cylinder and gas pressure were maintained constant at around $9.8 \times 10^4 \text{ N/m}^2$. All the samples were treated at room temperature. Bottled oxygen known as oxygen cylinder was used to feed ozone generator as ozone concentration up to 0.12 kg/m^3 can be achieved using pure oxygen. Care was taken with respect to the pressure of feed oxygen that it is below $14.7 \times 10^4 \text{ N/m}^2$, as high pressure can damage the electrode. Before treatment could be allowed, it was make sure that there are no leakages in the oxygen line as moisture can also enter the electrode and damage it. Ozone generator for the purpose of research was provided by AM Ozonics Ltd., Mumbai.

Results

Batch experiments were conducted for the collected pharmaceutical industry wastewater sample and data were obtained at different pH conditions and analyzed. To elucidate the effect of pH, time of treatment i.e. ozonation period, ozone current and ozone dose, pharmaceutical wastewater was subjected to ozonation at actual (pH 6.9), acidic (pH 4) and alkaline (pH 10) of the sample. According to the observations made, biochemical oxygen demand

of actual, acidic and alkaline samples have been discussed:

Biochemical Oxygen Demand - Actual Sample

Generally, BOD of a pharmaceutical industry wastewater is in the higher range. But as the sample was taken from the dilute process, low BOD values were observed. Curves showing BOD change of actual sample can be divided into two parts: first part is between 0-6 min and second one is between 6-10 min of ozonation time.

Initial BOD of untreated sample was 140 mg/L, which started to decrease even at low ozone doses, as soon as treatment was begun. At 18.46 mg/L ozone, about 43% reduction could be achieved. Treatment at 21.18 mg/L O_3 did not show marked improvement. About 35.71% BOD could be removed and intermittent decline was also reported during entire ozonation period which may be the case due to the refractory compounds present in the wastewater. The data obtained are shown in table 1.

At 32 mg/L ozone, substantial reduction in BOD was noticed which surpassed the previous maximum of 42.86%. Highest BOD reduction of 57.14% was noted at this ozone concentration. When the ozone dose was increased to highest value of 32.73 mg/L, sudden decrease in the very first treatment interval of 2 min was observed indicating initiation of fast ozone reaction. Treatment at higher ozonator current at 0.5 ampere (at the reduced ozone dose of 30 mg/L), did not result in significant BOD reduction.

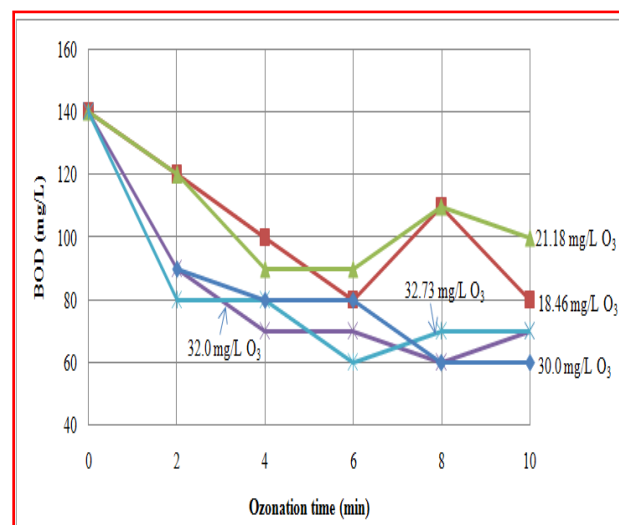


Figure 1 – BOD curves of actual sample

Table 1 – Biochemical oxygen demand of actual sample at pH 6.9

Time (min)	BOD (mg/L)				
	Sample at 0.1 ampere current (18.46 mg/L O ₃)	Sample at 0.2 ampere current (21.18 mg/L O ₃)	Sample at 0.3 ampere current (30.0 mg/L O ₃)	Sample at 0.4 ampere current (32.73 mg/L O ₃)	Sample at 0.5 ampere current (32.0 mg/L O ₃)
0	140	140	140	140	140
2	120	120	90	80	90
4	100	90	70	80	80
6	80	90	70	60	80
8	110	110	60	70	60
10	80	100	70	70	60

Biochemical Oxygen Demand - Acidic Sample

In the acidic medium of the sample, BOD did not change up to a treatment time of 4 min. After this time, BOD decreased but no significant decrease compared to initial value was seen due to low values of rate constants at lower pH as per literature reported elsewhere. The values obtained are given in table 2. Compared to values of untreated sample, BOD lowered down to 110 mg/L from 140 mg/L when treated up to 6 min. At very low ozone dose of 18.46 mg/L, mere 8.33% BOD reduction was observed. When the ozone dose was increased to 21.18 mg/L, BOD values started to decrease after initial 2 minutes and around threefold increase in % BOD reduction

could be observed. Investigations at 32 mg/L ozone showed improved BOD removal. At this ozone concentration also, initial period was ineffective because of slow oxidation rate but BOD kept on decreasing subsequently till last minute of treatment. Highest % BOD reduction of 41.67 was reported at 32 mg/L O₃. At highest ozone concentration of 32.73 mg/L, BOD values decreased but similar reduction of 25% compared to initial BOD could be reported. Treatment at highest current 0.5 ampere and 30 mg/L ozone, showed identical improvement in terms of % BOD removal and reached previous best of 41.67% at highest current. Higher treatment time produced better results in terms of BOD removal except with highest ozone dose of 32.73 mg/L.

Table 2 - Biochemical oxygen demand of acidic sample at pH 4.0

Time (min)	BOD (mg/L)				
	Sample at 0.1 ampere current (18.46 mg/L O ₃)	Sample at 0.2 ampere current (21.18 mg/L O ₃)	Sample at 0.3 ampere current (30.0 mg/L O ₃)	Sample at 0.4 ampere current (32.73 mg/L O ₃)	Sample at 0.5 ampere current (32.0 mg/L O ₃)
0	120	120	120	120	120
2	120	130	120	110	110
4	120	110	110	100	120
6	110	100	90	90	90
8	120	140	90	90	90
10	110	90	70	120	70

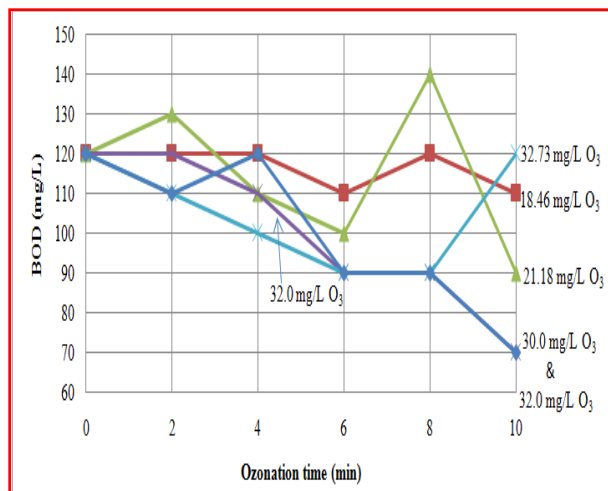


Figure 2 – BOD curves of acidic sample

Biochemical Oxygen Demand - Alkaline sample

A change of BOD was observed soon after changing the pH of the sample to 10, compared to BOD of the untreated sample. Treatment at low ozone dose of 18.46 mg/L could not give very high % BOD reduction. Further increase in ozone concentration could not improve than the previous best of 75%. Moreover, ozone treatment at alkaline pH and at this ozone dose reached lowest BOD i.e. at 30 mg/L, compared to 140 mg/L initial BOD of untreated sample.

In terms of initial BOD of alkaline sample, only 12.5% reduction could be achieved. But, if initial BOD of the actual/untreated sample up to a treatment time of 2 min is compared, a drastic reduction of about 50% was noticed. Data obtained are shown in table 3.

Table 3 - Biochemical oxygen demand of alkaline sample at pH 10.0

Time (min)	BOD (mg/L)				
	Sample at 0.1 ampere current (18.46 mg/L O ₃)	Sample at 0.2 ampere current (21.18 mg/L O ₃)	Sample at 0.3 ampere current (30.0 mg/L O ₃)	Sample at 0.4 ampere current (32.73 mg/L O ₃)	Sample at 0.5 ampere current (32.0 mg/L O ₃)
0	80	80	80	80	80
2	80	90	70	70	70
4	80	90	60	60	40
6	70	60	30	40	30
8	90	40	20	50	50
10	70	30	20	30	30

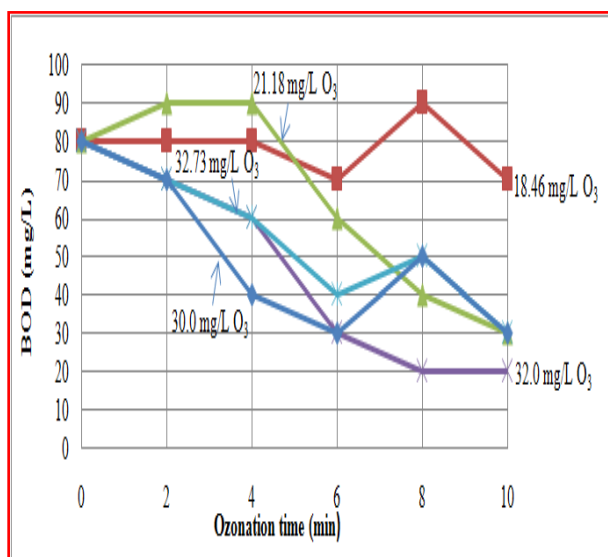


Figure 3 – BOD curves of alkaline sample

Treatment at 21.18 mg/L O₃ resulted in further % BOD reduction. In this case also, BOD values declined after initial treatment interval of 4 min and approximately 62.5% BOD reduction was estimated once ozone dose was further increased.

Discussion

In case of actual sample, it was observed that BOD reduced mostly during the period when direct ozone reactions are dominant over indirect reactions. In the second period ozone BOD is removed by indirect ozone reaction which develops in slow kinetic regime as ozone starts to dissolve or gets dissolved as the ozonation time increases in accordance with the Beltran’s theory of kinetics of ozone reactions (2004). In the second part of the curve, low ozone doses were found insufficient to enhance the rate of ozonation. It can be deduced that the pharmaceutical wastewater initially contained organic

compounds/pollutants resistant to biological oxidation.

From the BOD graph obtained for acidic sample, it is apparent that most of pollutants shown reluctance to degradation in the acidic medium. Rate constants at this pH are lower than that of actual sample pH (around neutral) or higher, thus, ozone reactions proceed in the fast kinetic regime but develop for a very short period (Balcioglu and Ötger, 2003). Hence, it can be stated that the intermediates formed during ozonation showed more resistance to biological degradation as compared to parent compounds in the later stages of ozonation.

The rate of removal of BOD was appreciable at pH = 10 of the sample at around 30 mg/L O₃. When the ozonator was operated at highest current (0.5 ampere), O₃ treatment did not produce results better than the previous conditions. However, a similar percentage BOD reduction of 62.5 % was observed at this ozonator current. At 21.18 mg/L ozone, BOD initially increased or remained unchanged during initial ozonation exposure time up to 4 min and did not change appreciably thereafter until the ozone dose was increased. This action can be explained by the fact that some organic compounds are more susceptible to oxidation than others, while some are only partially oxidized (Camel and Bermond, 1998).

Conclusion

Out of all the investigations carried out at unchanged, acidic and alkaline pH of the sample, alkaline medium shown tremendous results in terms of percentage BOD removal. It was observed that low ozone doses are not sufficient to accomplish conversions of all initially present refractory substances in the pharmaceutical wastewater under chosen conditions of treatment. Conversely, higher ozone doses likely lead to removal of biodegradable compounds formed during the chemical oxidation process. Thus, it is evident that these effects are highly dependent on the nature of the wastewater and treatment conditions. It was concluded that ozonation at elevated pH is recommended for BOD reduction of pharmaceutical industry wastewater which will also improve its biodegradability irrespective of the initial concentration of pollutants present in it. Optimization of ozonation conditions can be the subject of further investigations.

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