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Biodegradability Assessment of Pharmaceutical Wastewater Treated by Ozone

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Abstract

Biodegradability improvement of untreated wastewater and chemically and/or biologically pretreated industrial wastewater has become popular recently because of stringent environmental regulations for safety. Biochemical oxygen demand (BOD) measures the biodegradability of wastewater but the extent of pollution can be better presented by considering the magnitude of chemical oxygen demand (COD). Thus, the ratio BOD/COD, which measures biodegradability, is used. The present study deals with the treatment of pharmaceutical industry wastewater by ozone. An attempt has been made to assess the biodegradability of the selected pharmaceutical wastewater sample. It was found that higher treatment time favored the enhancement of biodegradability of selected sample. It can be concluded that ozone treatment can improve biodegradability of pharmaceutical wastewater.

Keywords: Biodegradability, pharmaceutical wastewater, ozonation, ozonation time.

Introduction

Human drugs in the environment were first reported in the mid 1970[1]. Since then release of pharmaceuticals into the atmosphere, especially in the form of liquid, has been increasing and resulting in frequent occurrence of a variety of pharmaceuticals in the aquatic environment in large numbers, which may prove to be threatening for the purity of drinking water[2,3]. Presence of pharmaceuticals, personal care products and endocrine disrupting compounds in the aquatic environment has been reported in the last few decades[4]. These pharmaceuticals affect surface water and eventually may pose a serious problem to drinking water directly or indirectly[5]. The available treatment techniques do not completely eliminate the micropollutants, thus, residues of endocrine disrupting compounds and pharmaceuticals and personal care products enter the aquatic ecosystem through wastewater.

A number of studies of different treatment processes, including ozonation, demonstrated that relatively large number of pharmaceuticals can be efficiently removed by these processes[6]. Biological treatment of wastewater which deals with the combined operation of chemical and biological oxidations has been presented in some researches[7]. Effects of chemical oxidation as a pre or post-treatment step in biological oxidation of wastewater have also been reported. To reduce the release of such pharmaceuticals into the aquatic environment or to completely eliminate them from wastewater, the application of advanced wastewater treatment may be required[8].

Different treatment methods like physicochemical treatment which includes screening, chlorination, coagulation/ flocculation, sedimentation, adsorption, reverse osmosis, activated sludge process, membrane separation, biological treatments (both aerobic and anaerobic), ozonation and ozone-hydrogen peroxide treatment are available[9]. Because of the different mechanisms of reaction associated with use of ozone, it plays a major role in wastewater treatment and thus ozone treatment/ozonation has become a promising technology for treatment of water and wastewater in the last few decades[10].

The research work on the application of ozonation process in wastewater treatment started from the late forties[11]. Large number of applications of ozonation in drinking water treatment, industrial wastewater treatment, biomedical waste treatment, etc., has been reported in literature[12]. A number of these works has also reported treatment of pharmaceutical wastewater. In almost all the reported cases so far, synthetic samples were used and thus when the treatment of actual samples from pharmaceutical industries is carried out, the results deviate[13]. Therefore, description of treatment of any wastewater containing pharmaceuticals or pharmaceutical industry wastewater is complex. Conventional biological treatments are not capable of complete removal of antibiotics[14], thus chemical oxidation technologies are necessary for the removal of the formulation wastewater especially containing antibiotics[15]. For ultimate treatment of a variety of organic pollutants wastewater, ozonation and advanced oxidation treatment has emerged as important treatment technique[16].

In ozonation, the ozone molecules rupture the target molecules and produce byproducts that are easily biodegradable. Ozone treatment usually improves the biodegradability of the wastewater. The improvement of biodegradability is an essential requirement environmentally for pharmaceutical effluents resistant to secondary or biological treatment[17]. At natural pH, ozonation could be used as a pre-treatment step to improve the biodegradability of pharmaceutical wastewater mainly

containing antibiotics[18]. In some cases, ozonation can be used as a sole treatment process or in other cases pre-ozonation or post-ozonation is desirable[19]. When ozonation is used as a pre-treatment, biodegradability of pharmaceutical wastewater improves but a combination of ozonation and conventional biological treatment can enhance mineralization of wastewater containing pharmaceuticals such as sulfamethoxazole and bezafibrate[20]. In case of some of the pharmaceuticals, the level of biodegradability can be determined by proper assessment of ozone dose.

Material and Methods

Pharmaceutical Wastewater Sample: Wastewater sample was collected from one of the pharmaceutical industries in Dewas (M.P.), India. For the research purpose, wastewater sample was taken from pharmaceutical formulation division which utilizes about 120000 lit per day water for production activities. Actual, rather than synthetic, untreated sample obtained from industry was treated by ozone. During entire treatment period, collected sample was stored in a cold storage unit.

Ozone Treatment of Pharmaceutical Wastewater Sample: Ozone generator performance was first determined by operating the generator at various currents. The currents were varied between 0.1 ampere (amp) and 0.5 ampere and voltage at 230 V was supplied. Ozone generator for the purpose of research was provided by AM Ozonics Ltd., Mumbai. For the treatment purpose, gas washing bottle/bubble columns of 1 liter capacity were used. Pure oxygen, at a uniform flow rate of 0.12 lpm (lit/min), was supplied through oxygen cylinder. The outlet pipe from ozone generator was divided into two lines through a valve.

First, the concentration of ozone was determined by dipping one outlet pipe into bottle containing acidified KI solution. 500 ml sample was then filled in the first of bubble columns connected in series. After confirmation of formation in KI solution bottle, ozone was supplied for 10 minutes. Treated samples were taken after every 2 minutes. In all, five samples were collected. Ozone concentration was determined by Iodometric titration and by using the formula recommended by International Ozone Association (IO_3A) given below:

$$O_3(\text{gm/lit}) = \frac{\text{Volume of hypo (ml) x Normality of hypo x 24}}{\text{Volume of gas sampled (lit) x 1000}}$$

In wastewater, the actual pollution concentration is not exactly known and parameters like COD and total organic carbon (TOC) are used to express the pollution concentration[21]. Another parameter employed to measure the degree of pollution is BOD (biological oxygen demand). Each sample was analyzed BOD and COD under different conditions of pH. All tests were conducted using standard methods of examination of water and wastewater[22].

Biodegradability: BOD measures the pollution in wastewater and gives the amount of biodegradable matter required. BOD gives the additional amount of oxygen needed for micro-organisms to biodegrade the matter in water sample. BOD of a particular water/wastewater sample depends on the capacity of micro-organisms added or which are already present to digest the matter, aerobically. Hence, BOD does not give absolute measurement of the biodegradability of wastewater. The biodegradability assessment of industrial wastewater is significant for better analysis of removal efficiency[23]. Therefore, the ratio BOD/COD, known as biodegradability, is determined. The ratio is used to measure the degree of biodegradation in a wastewater sample.

Results and Discussion

All samples were analyzed for various pollution load parameters like pH, total dissolved solids (TDS), total suspended solids (TSS), total solids (TS), BOD, COD and biodegradability (ratio of BOD to COD). The results obtained are plotted in the graphs and discussed.

Table-1
Characteristics of untreated sample (actual sample)

Parameter	Value of the parameter
pH	6.9
TSS (mg/lit)	680
TDS (mg/lit)	1760
TS (mg/lit)	2440
BOD_5 (mg/lit)	140
COD (mg/lit)	540
BOD_5/COD	0.259

Biodegradability of Actual Sample: Biodegradability of actual sample reduced to 0.18 compared to initial value of 0.259 up to 6^{th} min of ozonation at very low O_3 dose of 18.46 mg/lit. No further decrease in biodegradability was observed at this concentration even for higher treatment time, indicating that the biodegradability of sample actually increased. At 21.18 mg/lit O_3 nothing significant could be observed as far as biodegradability concerned. After increasing the ozone dose, no improvement in biodegradability could be noticed at 0.3 ampere current. At highest O_3 dose of 32.73 mg/lit, biodegradability improved after initial treatment period of 2 min. At highest current of 0.5 ampere and lowered O_3 dose of 30 mg/lit, abrupt change in biodegradability occurred intermittently.

During the treatment of actual sample, highest BOD/COD ratio of 0.286 was observed at 0.5 ampere which was not a good indication of biodegradability improvement if compared with initial ratio of 0.259. Thus ozonation conducted under unchanged pH had no significant effect on biodegradability of the pharmaceutical wastewater. After carrying the treatment of actual sample, it can be concluded that biodegradability of the actual sample did not improve significantly either at low or high ozone concentrations. Higher treatment time in ozonation may help achieve improved biodegradability. Literature suggests that extension of ozonation period above 30 minute for a pharmaceutical wastewater containing antibiotics, increases biodegradability[24].

Biodegradability of Acidic Sample: The effect of pH on the biodegradability of selected pharmaceutical wastewater sample was studied by conducting the ozone treatment in acidic medium of the sample. The pH was changed to 4 by adding hydrochloric acid. The characteristics of the acidic sample before ozonation are given in table below:

Table-2
Characteristics of acidic sample (untreated)

Parameter	Value of the parameter
pH	4.0
TSS (mg/lit)	370
TDS (mg/lit)	1550
TS (mg/lit)	1920
BOD_5 (mg/lit)	120
COD (mg/lit)	490
BOD_5/COD	0.245

Data obtained after treatment are plotted and shown below: Soon after pH was brought to 4, biodegradability of the sample decreased to 0.245 from an initial value of 0.259 of the actual sample. At this pH, no further improvement in biodegradability could be noticed during initial treatment intervals at 18.46 and 21.18 mg/lit O_3. Biodegradability seemed improving at later intervals when ozonation was continued at 21.18 mg/lit. When ozonation was carried out at highest concentration of 32.73 mg/lit, biodegradability kept on increasing after 6 min and surpassed previous initial value of 0.245 and reached 0.25. Treatment at highest current did not result in any increase in biodegradability. Under acidic conditions of the sample, not much in biodegradability could be altered on a higher side. It can be concluded that after very first treatment interval, biodegradability increased at highest O_3 dose and initial increment in biodegradability was appreciable. In case of acidic sample, the ratio varied between 0.189 and 0.245. Therefore not much in biodegradability could be improved.

Biodegradability of Alkaline Sample: At pH 10 of the sample, parameters obtained after treatment are as shown:

Table-3
Characteristics of alkaline sample (untreated)

Parameter	Value of the parameter
pH	10
TSS (mg/lit)	140
TDS (mg/lit)	1305
TS (mg/lit)	1445
BOD_5 (mg/lit)	80
COD (mg/lit)	330
BOD_5/COD	0.242

Data obtained after treatment of alkaline sample are plotted and shown below: An immediate improvement in biodegradability was observed at alkaline pH of the sample. At very low ozone concentration of 18.46 mg/lit biodegradability kept on increasing up to a treatment time of 8 min. Ozonation at 21.18 mg/lit concentration also resulted in improved biodegradability up to 4 min and found decreasing afterwards. Treatment at moderate ozonator current did not show any sign of biodegradability improvement but when operation was carried out at maximum ozone dose, a continuous increase after 6 min was reported. Under alkaline medium of the sample, the ratio showed extreme variation from lowest of 0.105 at 32 mg/lit ozone to 0.455 at 0.5 ampere current but slightly lower ozone concentration of 30 mg/lit, indicating that much improved biodegradability can be achieved at pH = 10. Like in acidic medium or at actual pH of the sample, treatment at highest current shown mixed variations in biodegradability at different intervals during treatment.

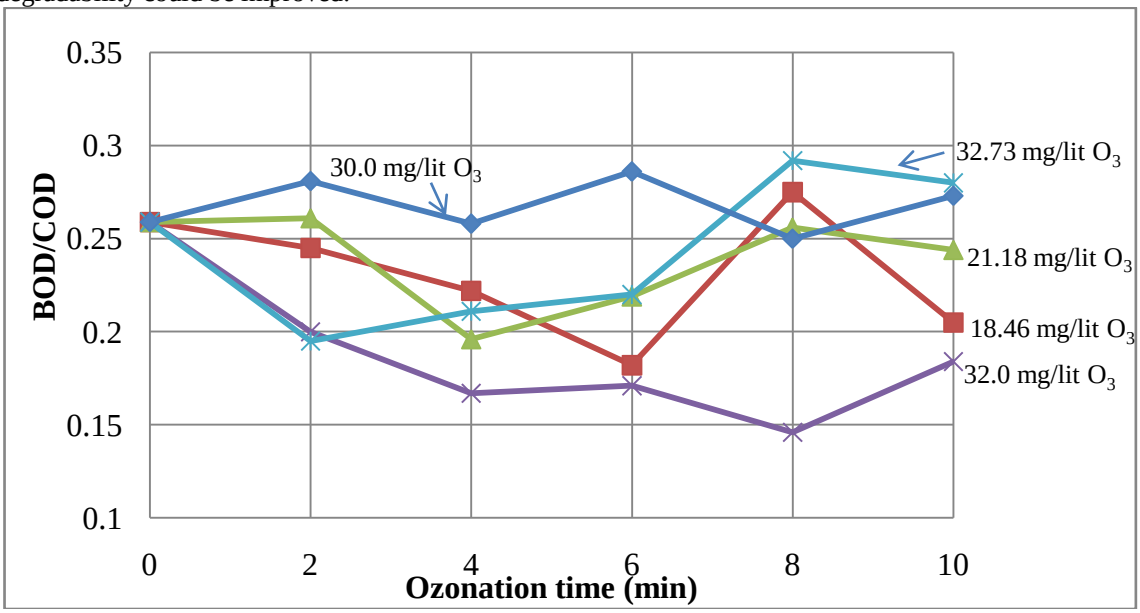

Figure-1
Biodegradability of actual sample at all operating currents of ozonator

Conclusion

For biodegradability improvement of selected pharmaceutical sample, it is suggested that treatment under acidic condition at highest ozone concentration of 32.73 mg/lit for a treatment time of 8 min and for alkaline medium ozonation was found more suitable at highest ozonator current of 0.5 ampere and 30 mg/lit O_3 concentration. Because higher treatment time favored the enhancement of biodegradability of samples, it can be said that due to low treatment time, no significant improvement could be reported. It can be concluded that biodegradability improved at alkaline pH of the sample. However, ozonation was not favored at all concentrations of ozone. If all three selected samples are compared, it can be concluded that ozonation can improve biodegradability from pharmaceutical wastewater.

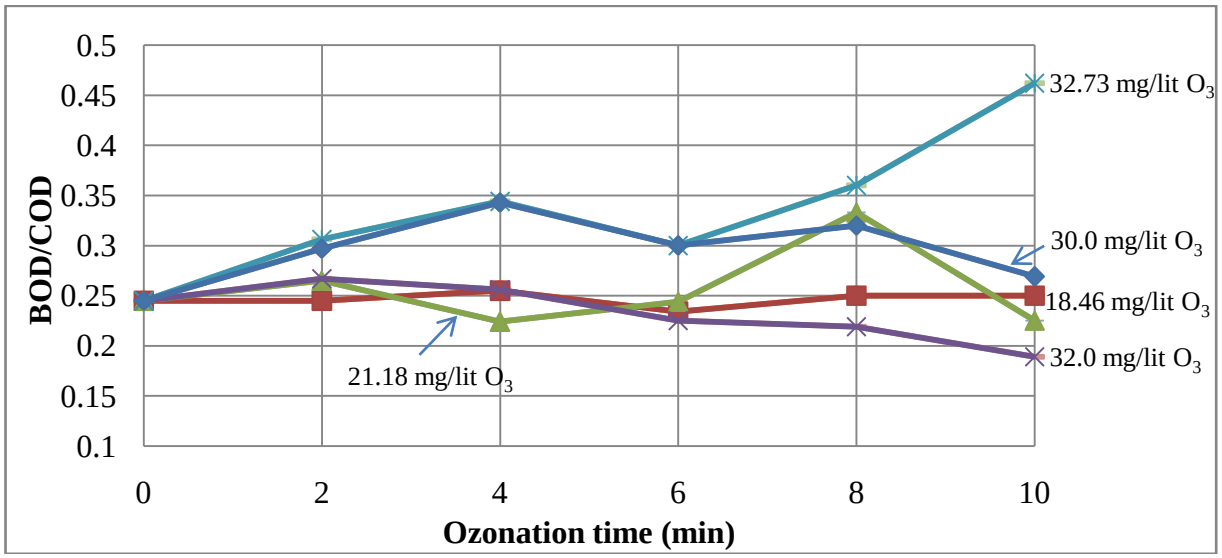

Figure-2
Biodegradability of acidic sample at all operating currents of ozonator

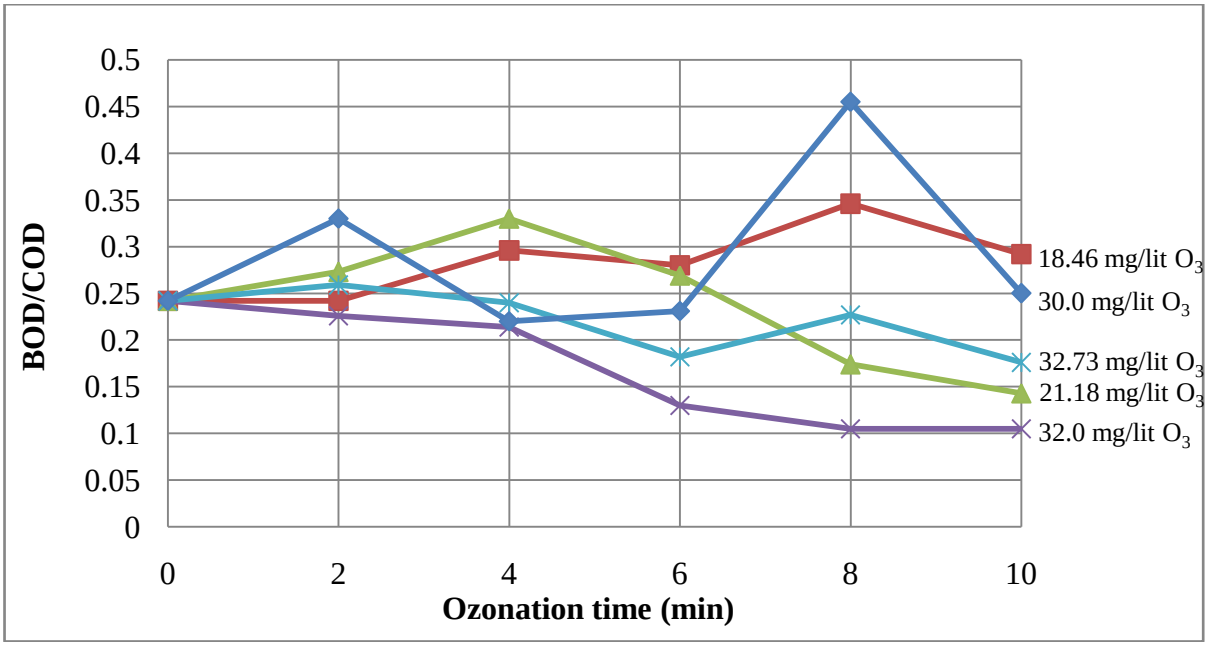

Figure 3
Biodegradability of alkaline sample at all operating currents of ozonator

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