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Eco-Friendly Approach to Remove COD, TSS and Colour from the Effluent Originating from the Pharmaceutical Industry

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Abstract: The aim of this research work was to assess the feasibility of ozone based treatment method for the removal of key pollutants, such as COD, TSS, conductivity and colour, from the wastewater generated during the operations of a pharmaceutical plant. This investigation evaluated the effectiveness of ozone treatment at varied process parameters like pH, ozone exposure timings and ozone doses in order to find optimized conditions for maximum elimination of water pollutants. The study concluded that adequate results were achieved at higher pH values (10-11), extended ozonation exposures (60-90 min) and maximum ozone concentrations (400-500 ppm). This study suggested that ozonation was an efficient method for the treatment of wastewater from pharmaceutical industry. Since all the experiments were conducted at ambient temperature without using any heat or additional chemicals and thus this method proved to be an environmental friendly technique to reduce pollution load in pharmaceutical wastewaters.

Key words: Pharmaceutical wastewater, Ozone, chemical oxygen demand, TSS, colour

INTRODUCTION

The modern lifestyle coupled with increased accessibility and affordability of medical and hospital treatments have resulted to an increased production and consumption of variety of prescribed and over the counter pharmaceuticals (Albrecht, 2012). Recently, several pharmaceuticals have been reported to be potentially contaminated and toxic substances usually found in our environment (Lubick, 2010; Al-Odaini *et al*., 2010; Singh *et al*., 2011).

Thousands of pharmaceutical residues from different therapeutic classes along with their metabolic by-products have been detected in different environmental matrices, such as air, waster and soil (Fick *et al*., 2010; Fram and Belitz, 2011; Fatta-Kassinos *et al*., 2011), posing a serious threat to the wellbeing and health of various living organisms including human beings (Filby *et al*., 2007; Pomati *et al*., 2008; Albrecht, 2012).

The key sources of pharmaceuticals contaminations include aqueous discharges from households and hospitals and from effluents originating from pharmaceutical producers (Kolpin *et al*., 2002; Albrecht, 2012). Unfortunately, these pharmaceuticals which are usually called emerging pollutants, are not regulated yet in terms of their occurrence in water streams and wastewater discharges (Bell *et al*., 2011).

Since wastewater from a pharmaceutical plant is characterized by high organic content such as chemical oxygen demand (COD), toxicity, total suspended solids (TSS), very dark colour (usually black or brown) and high level of salt contents (Xinyu *et al*., 2010), the treatment of such effluents becomes a great challenge to the researchers. Because of such pollution loads in pharmaceutical wastewater, several studies have reported that conventional biological treatments are not efficient enough to completely remove pharmaceutical residuals from the wastewater (Kimura *et al*., 2005; Hollender *et al*., 2009).

The application of ozone gas (O_3) in wastewater treatments is a very efficient method due to very high oxidation power of O_3 molecule. Once dissolved in water, ozone can react with great number of organic and inorganic contaminants in two different pathways: either by direct oxidation as molecular O_3, or by indirect reaction through the generation of secondary oxidants particularly hydroxyl (OH) radicals (Byung *et al*., 2007). The use of ozone in wastewater treatment has a potential to reduce chemical oxygen demand (COD), toxicity, total suspended solids (TSS) and colour (Benitez *et al*., 2008).

The present investigation evaluated the use of ozone for the treatment of a real complex pharmaceutical wastewater in order to assess its suitability for the treatment of such type of water pollution.

MATERIALS AND METHODS

Sampling, analysis and testing techniques: An effluent sample (10 litres) was collected from the final discharge

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of a reputable local pharmaceutical company situated in Multan Road, Lahore, Pakistan. The sample was taken from the real pharmaceutical wastewater and the plant had intermittent and fluctuating wastewater flow with variable wastewater composition depending on the production stage. The chemical analysis including pH, chemical oxygen demand (COD), total suspended solids (TSS), biochemicaloxygen demand (BOD), conductivity and colour were performed in accordance with the standard methods (APHA, 2005). To mix and sample wastewater, a peristaltic pump was used. The pH values of the aqueous solutions were determined using a pH meter (HI 9126). The colour of the effluent was monitored employing platinum-cobalt method using a spectrophotometer (455 nm wavelength) by Datacolor (SF 600).

Experimental set-up: Experimental set-up was comprised of a batch reactor made out of Pyrex glass. The reactor internal diameter was 3.30 cm. Similar reactors can be found in other research articles (Fanchiang and Tseng, 2009; Oguz *et al*., 2006). Ozone (O_3) was produced from a pure and dry oxygen (99.99%) in a bench-scaled ozone generator (JQ-6M PURETECH). Ozone gas was bubbled at the bottom of the reactor using a stone diffuser at varied rates between 100 to 500 mg/h. Ozone resistant Teflon tubing was used for connections and the transfer of ozone gas.

RESULTS AND DISCUSSION

Characteristics of pharmaceutical effluent: The sample of wastewater collected from pharmaceutical site was analyzed, characterized and following results were obtained.

Table 1 indicates the presence of very high values of COD, TSS, conductivity and colour. The results clearly showed that COD values of 1160 mg/L were about 8 times elevated than those allowed (150 mg/L) by National Environmental Quality Standards (NEQS). The TSS values (324 mg/L) in the pharmaceutical wastewater were also found to be exceeded the allowable limit of 200 mg/L set by regulating body. The pH of this aqueous discard was observed to be on basic side (9.70). The pollutant loads in pharmaceutical is mainly due to the presence of solvents, process stream washes, product washes, spent acids/caustics and condensed steam (Albrecht, 2012).

Reduction of COD at varied pH values: At a constant dose of ozone, the pharmaceutical wastewater under investigation was exposed to ozone gas at varied pH (5, 7 and 11) for time intervals of 10, 30, 60 and 90 min. At these set conditions, reduction of COD values were calculated and results are presented in Fig. 1. The data clearly showed that an increase in ozone exposure timing was found to be directly proportional to COD reduction because in all cases additional treatment time yielded further COD removal. At acidic pH of 5, an ozone treatment of 10 min achieved 20% reduction of COD, which was increased to 30 and 50% when ozone exposure timings were increased to 30 and 90 min, respectively. The data also indicated that a raise in pH also caused increased COD removal from pharmaceutical wastewater due to generation of highly active hydroxyl radicals (OH). Comparing the results obtained at pH 5 and 11, the COD removal increased from 50 to 72% for similar time (60 min) of ozone exposure. The maximum COD removal (90%) was achieved when pH and treatment timing were increased to 11 and 90 min, respectively.

Table 1: Characteristics of effluent collected from the pharmaceutical company

Parameters	Results
pH	9.7
Chemical oxygen demand (COD)	1160 mg/L
Total suspended solids (TSS)	324 mg/L
Conductivity	1385 µS/cm
Colour	Dark grey
Temperature	26°C

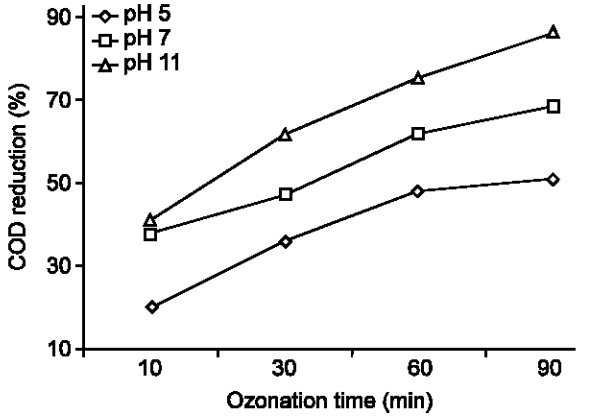

Fig. 1: COD reduction at varied pH values

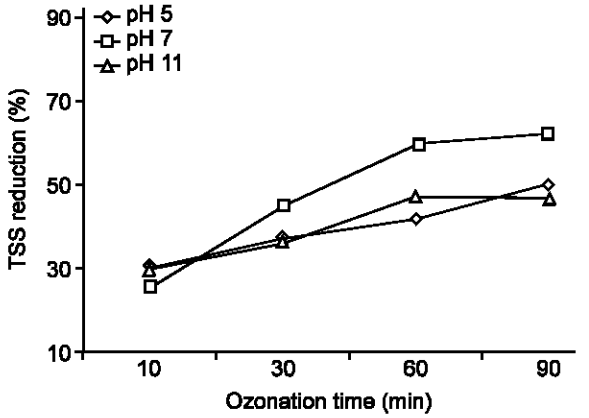

Fig. 2: TSS reduction at varied pH values

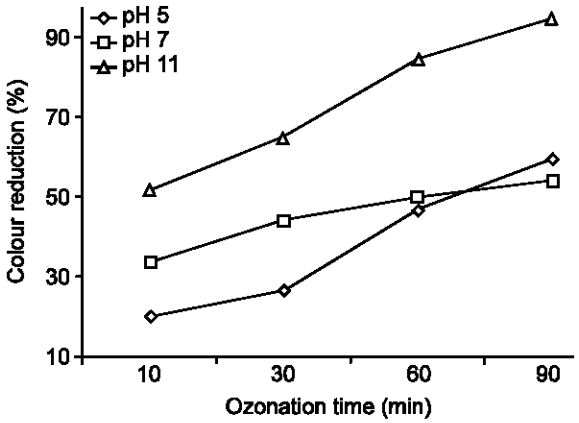

Fig. 3: Colour reduction at varied pH values

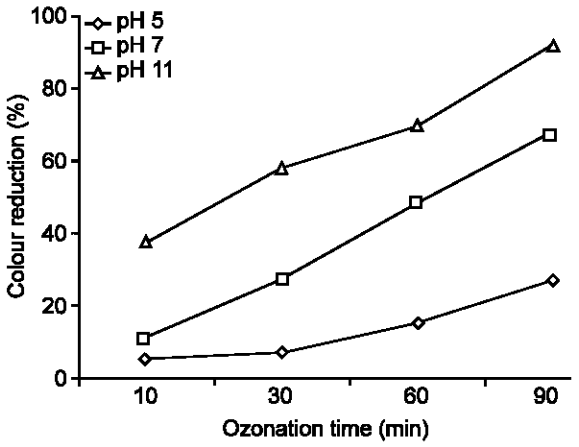

Fig. 4: Colour reduction at varied ozone concentrations

Reduction of TSS at varied conditions: At a constant ozone exposure (300 ppm), pharmaceutical wastewater was treated with ozone gas to reduce TSS from the effluent. The duration of ozone exposure and pH of the wastewater were altered to study their impacts on removal efficiencies and results are shown in Fig. 2. In most cases, reduction in TSS was observed when ozone exposure timings were increased. At pH 7, 30% reduction of TSS was observed at 30 min of ozonation, which was increased to 50% when ozone exposure time was increased to 90 min. The results also suggested that increase or decrease in pH values of wastewater did not affect TSS removal significantly and only marginal changes were noticed. For example, at ozone exposure timings of 60 min, TSS removals of 42, 60, 47% were achieved at pH values of 5, 7 and 11, respectively.

Colour removal VS pH values: The effect of varied pH values of wastewater on the colour removal efficiency of ozone was studied and results were summarized in Fig. 3. The results showed that an increase in pH value yielded superior colour removal from pharmaceutical wastewater. At acidic pH value of 5, a 30 min ozone treatment time only achieved around 30% colour removal; however, this removal efficiency became doubled (60%) when pH was increased to 11. The use of neutral pH value (7.0) in ozonation study also failed to achieve acceptable colour removal efficiencies. The results also showed that the maximum decolourization (above 90%) was achieved when ozone exposure timing and pH of wastewater were set to 90 min and 11, respectively. These results are well correlated with the findings of Fanchiang and Tseng (2009).

Colour removal efficiencies at various O_3 concentrations: At a constant pH of 11, the samples pharmaceutical wastewaters were treated with ozone gas using varied concentrations. The results are displayed in Fig. 4. The data obtained in this study clearly indicated that an increase in ozone concentration was accompanied by high degree of colour removal from pharmaceutical wastewater. In case of treatment using 300 ppm of ozone for 90 min exposure timing, only 30% colour removal achieved, which was increased to almost 99% when ozone concentration was increased to 500 ppm. The results are owing to the fact that more O_3 is available to degrade colour producing matters present in the pharmaceutical wastewater.

Conclusion: This investigation was carried out to assess the effectiveness of ozone treatment for the removal of major pollutants, such as COD, TSS and Colour from the effluents coming from the pharmaceutical industries. Several important process parameters like pH, exposure timings and ozone concentrations were altered to optimize conditions for maximum removal of pollutants. The study concluded that best results were achieved at higher pH values (10-11), extended ozonation timings (60-90 min) and maximum ozone concentrations (400-500 ppm). All the experiments were carried out at ambient temperature without use of external heat or chemicals and thus proved to be a cost-effective and environmental friendly technique to reduce pollution load in pharmaceutical or similar wastewaters.

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