Research Paper

Impact of Ozone Dose on the Removal of Total Solids from Pharmaceutical Wastewater

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Abstract: Advanced treatment technologies are used to remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes. Ozone treatment is one such advanced treatment technique carried out to enhance oxidation of unstable organic matter present in the wastewater. Ozone treatment also affects the removal of solids which still remain in wastewater post primary and secondary treatment. Present study deals with the determination of impact of ozone dose on the removal of total solids from pharmaceutical wastewater during ozonation. For the purpose, pharmaceutical wastewater sample was treated under varying conditions of pH. It was observed that highest ozone dose of 32.73 mg/L resulted in greatest reduction of 32.81% in total solids in acidic medium (at pH = 4). It was investigated that change of pH did not greatly affect the removal of suspended and dissolved solids and hence total solids too showed similar removal tendency. It can be said that even if the ozone treatment is intended for the removal of pollutants from pharmaceutical wastewater and not for the removal of total solids, it nonetheless resulted in substantial reduction of the same. It can be concluded that if ozone is used as a primary advanced treatment, higher reduction in total solids can be achieved.

Keywords: Ozonation, pharmaceuticals, pollutants, primary advanced treatment.

Introduction
Pharmaceutical compounds have received attention in the last few decades as potential bioactive chemicals in the environment [1,2]. Consequences of pharmaceuticals on the aquatic environment due to improper disposal and limited effectiveness of conventional wastewater treatments have also been reported [3]. During the last few decades, release of pharmaceuticals into the atmosphere has increased. Frequent occurrence of a vast variety of pharmaceuticals in the aquatic environment may prove to be threatening for the purity of drinking water [4,5]. Presence of pharmaceutical compounds, personal care products and endocrine disrupting compounds affect surface water and may ultimately pose direct or indirect problems to drinking water which may cause serious health problems to human beings especially [6]. Considering the sources of release of pharmaceuticals into aquatic systems and subsequent risks, much better protection strategies are needed to be developed [7]. The available treatment techniques do not completely eliminate the micropollutants, thus, residues of endocrine disrupting compounds and pharmaceuticals & personal care products enter the aquatic system through wastewater.

For ultimate treatment of a variety of organic pollutants in water and wastewater, ozonation and advanced treatment has emerged as important treatment techniques [8,9,10]. Advanced wastewater treatment is the treatment needed to remove suspended, colloidal and dissolved constituents remaining after conventional secondary treatment [11]. Advanced treatment can either eliminate pollutants completely through mineralization or convert them to the products that are less harmful to human health and the aquatic environment. In water or effluent, presence of solids may affect the quality adversely in a number of ways. Solids analyses are important for the control of biological and physical wastewater treatment processes. Generally, waters with high dissolved solids are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. Solids are also important parameter for designing wastewater treatment [12].

Conventionally, solids are removed by primary treatment utilizing physical processes such as screening, equalization, sedimentation, coagulation/flocculation, and pH adjustment/neutralization, to remove a portion of the pollutants that may float, settle or that is too large to pass through simple screening devices. Primary treatment can remove about 60% of the suspended solids and around 35% biochemical oxygen demand [13]. As a consequence of laboratory and field scale experiments wastewater treatment technologies progressed [14,15]. The advanced treatment technique such as ozonation has hardly been studied to determine impact of percentage removal on the...
amount of total solids (combination of both dissolved and suspended solids) from wastewater especially pharmaceutical industry wastewater.

**Material and Methods**

The sample for the research purpose was collected from a nearby pharmaceutical industry. The sample was obtained from a dilute process in formulation division of the pharmaceutical industry. The sample was found as slightly mud green in color, turbid with faint odor, having pH value around neutral, moderate biochemical oxygen demand, high chemical oxygen demand and total dissolved solids. The sample was analyzed for total suspended solids (TSS), total dissolved solids (TDS), total solids (TS), dissolved oxygen (DO), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) under different conditions of pH at Environmental Engineering laboratory of Chemical Engineering Department, Ujjain Engineering College, Ujjain (M.P.), along with the assistance of Regional Laboratory, M.P. Pollution Control Board, Ujjain.

**Experimental set-up and operating conditions:** The ozone generator set-up used for the treatment consisted of ozone generator with in-built voltage regulator, ammeter, oxygen cylinder, two outlet lines bifurcated by a valve. First of the two bubble columns attached in one outlet line was filled with sample for treatment and in the other line; outgoing gas from first column was directed to get dissolved in water. In the other line bubble column was filled with 2% KI solution. Inlet to the ozone generator was pure oxygen from oxygen cylinder. Bubble columns (gas washing bottles) 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. Pure oxygen was supplied through oxygen cylinder; 7 kg in capacity, at a constant flow rate of 0.12 lpm (liter/min) maintained constant by flow regulator mounted on the top of the oxygen cylinder. Before allowing the ozone stream to treat wastewater sample in the bubble column, formation of ozone was confirmed by directing the gas towards the bubble column containing acidified 2% KI solution. The ozone generator assembly is shown in the picture 1.

Concentration of ozone was measured at operating currents between 0.1 and 0.5 ampere and at 230V. Gas flow rate from the oxygen cylinder and gas pressure were maintained constant at around 9.8x10^5 N/m². Care was taken with respect to the pressure of feed oxygen that it is below 14.7x10^5 N/m², as high pressure can damage the electrode. All the samples were treated at room temperature. During ozonation, pH of the sample and ozonator current which directly affects ozone concentration, were altered. Change in total solids was observed at various ozone concentrations. Ozone generator for the purpose of research was provided by AM Ozonics Ltd., Mumbai. All tests were conducted using Standard Methods of Examination of Water & Wastewater, APHA [16] which is suitable for the determination of solids in domestic and industrial wastewaters in the range up to 20,000 mg/L.

**Results and Discussion**

Solids refer to matter suspended or dissolved in water or wastewater. Total solids are the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature (either 103 or 180°C). Total solids include total suspended solids, the portion of total solids retained by a filter and total dissolved solids are the portion that passes through the filter. For the present research the amount of total solids were measured under different pH conditions. The results obtained for actual sample (which is untreated sample at its original pH 6.9), acidic sample (at pH = 4) and alkaline sample (at pH = 10) have been discussed below:

**Total Solids - actual sample:** Data obtained for actual sample are given in table 1 below:

In general, appreciable reduction in total solids was reported at all ozone concentrations. At very low ozone dose of 18.46 mg/L, TS started to decrease and continued decreasing till later period of ozonation and resulted in around 15% reduction. During first treatment interval of 0-2 min at 21.18 mg/L ozone dose, sudden decline in total solids was reported. A continuous decrease in TS was reported in all the cases, without any alteration in pH. When ozone dose was increased to 32 mg/L, around 20% reduction (compared to initial) was found. Highest percentage reduction of around 25% in TS was observed at ozone dose of 32.73 mg/L. When the ozonator was operated at highest current of 0.5 ampere, no improvement above 20% could be observed. It can be concluded that at all ozone doses from low to high, an immediate decrease in total solids was observed.
Table 1
Total Solids of actual sample at pH 6.9

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Sample at 0.1 ampere current (18.46 mg/L O₃)</th>
<th>Sample at 0.2 ampere current (21.18 mg/L O₃)</th>
<th>Sample at 0.3 ampere current (30.0 mg/L O₃)</th>
<th>Sample at 0.4 ampere current (32.73 mg/L O₃)</th>
<th>Sample at 0.5 ampere current (32.0 mg/L O₃)</th>
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<td>1950</td>
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Table 2
Total Solids of acidic sample at pH 4.0

<table>
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<th>Time (min)</th>
<th>Sample at 0.1 ampere current (18.46 mg/L O₃)</th>
<th>Sample at 0.2 ampere current (21.18 mg/L O₃)</th>
<th>Sample at 0.3 ampere current (30.0 mg/L O₃)</th>
<th>Sample at 0.4 ampere current (32.73 mg/L O₃)</th>
<th>Sample at 0.5 ampere current (32.0 mg/L O₃)</th>
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Figure 1: Total Solids of actual sample with ozonation time
It is evident from figure 1, that total solids decrease as soon as ozone is applied to wastewater for treatment. The solids during the first period are removed by direct ozone reactions that usually develop in the fast kinetic regimes of ozonation. In the later period, rate of decrease of solids is lower than the initial period due to the fact after initial period ozone starts to dissolve and reactions develop in slow kinetic regime in accordance with Beltran’s theory of kinetics of ozonation [17].

**Total Solids - Acidic Sample:** In the acidic medium, ozone dose of 18.46 mg/L resulted in around 8.33% total solids removal and kept decreasing till 4<sup>th</sup> min of treatment. When ozone dose was slightly increased, percentage reduction increased marginally. In the last treatment interval of 8-10 minute, TS lowered down and reached around 1690 mg/L. At 32 mg/L ozone, total solids reduced by 15% and decreased continuously. The table 2 shows various values of total solids obtained for acidic sample at pH = 4.0. Further treatment at maximum ozone concentration of 32.73 mg/L, resulted in highest percentage reduction. Operation at this condition resulted in more than double improvement in removing total solids. Ozone treatment at highest current of 0.5 ampere continued the trend of total solids removal like previous operations but no further improvement above previous maximum could be seen as shown in figure 2. In all five cases, total solids were removed by ozone and as ozone dose was increased, substantial reduction in total solids was observed. Both, low as well as high treatment time showed improved results. It can be concluded that at all ozone doses, higher treatment time was observed as favorable.

**Total Solids - Alkaline Sample:** Results of treated alkaline sample (pH = 10.0) are given in table 3. Ozone treatment at very low current in alkaline medium did not show an immediate change. But when the time of treatment was increased, total solids started to decrease. At 32.73 mg/L ozone concentration, greatest percentage reduction of 28.37% was observed. Treatment at highest current of 0.5 ampere did not result in appreciable reduction of TS.

![Figure 2: Total Solids of acidic sample with ozonation time](image_url)
In fact, abrupt changes in total solids were reported at this final current intermittently (see figure 3). As far as total solids removal is concerned, it can be concluded that acidic pH at highest ozone dose of 32.73 mg/L shown greatest percentage TS reduction of 32.81%, while at alkaline pH, the highest reduction was about 28.37% (a little higher than the actual sample in which % reduction was 24.59% highest). Hence, it can be concluded that change of pH did not greatly affect the removal of total solids.

**Conclusion**

From the investigations made, at all ozone doses, higher treatment time was observed to be favorable. Ozonation conducted at ozone concentrations of 30 and 32.73 mg/L shown favorable conditions for the removal of total solids in actual sample. In acidic medium, when the ozone dose was increased, improved rate of ozonation due to high values of rate constants resulted in greater percentage reduction of total solids. Overall, as far as total solids removal is concerned, it was observed that in acidic medium, highest ozone dose of 32.73 mg/L shown greatest reduction of 32.81%, while at alkaline pH the highest value was about 28.37% (a little higher than the actual sample in which reduction was highest as 24.59%). It can be concluded that pH did not greatly affect the removal of suspended and dissolved solids and hence total solids too showed similar removal tendency. It can be said that even if the ozone treatment is intended for the removal of pollutants from pharmaceutical wastewater and not for the removal of total solids from wastewater, it nonetheless resulted in substantial reduction of total solids. Thus, ozonation can be used as an advanced primary treatment after further investigations on its economical feasibility.

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