Treatment of a Pharmaceutical Industrial Effluent by a Hybrid Process of Advanced Oxidation and Adsorption

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ABSTRACT: In the present study, a combined approach of ozone-based advanced oxidation and adsorption by activated char was employed for the treatment of a pharmaceutical industrial effluent. Ozone is a selective oxidant, but the addition of H₂O₂ generated in situ hydroxyl radicals, which is a non-selective stronger oxidant than ozone. The effluent obtained from the pharmaceutical industry mainly contained anti-cancer drugs, anti-psychotic drugs, and some pain killers. The peroxone process had 75–88.5% chemical oxygen demand (COD) reduction efficiency at pH 5–11 in 3 h. Adsorption by activated char further reduced the COD to 85.4–92.7% for pH 5–11 in 2.5 h. All other water quality parameters were significantly decreased (>73% removal) during ozonation. The primary operational parameters (system pH and H₂O₂ concentration) were also varied, and their effects were analyzed. The pseudo-first-order rate constants for ozonation were calculated, and they were found to be in the range of 1.42 × 10⁻⁴ to 3.35 × 10⁻⁴ s⁻¹ for pH 5–11. The kinetic parameters for adsorption were calculated for the pseudo-first-order, pseudo-second-order, and Elovich models. The fit of the pseudo-first-order kinetic model to the experimental data was the best.

1. INTRODUCTION

Most of the pharmaceutical industries in India are set up in Ahmedabad, Bangalore, Hyderabad, and Mumbai providing 20% generic medicines of the global market worth $19.14 billion in 2019. However, a rather lenient regulatory for pharmaceutical waste disposal and irresponsible production have significantly affected the aquatic environment. The discharge from the pharmaceutical industries contains non-biodegradable recalcitrant organic substances, which have high toxicity toward the aquatic and human life. 60–80% of the prescribed pharmaceuticals are excreted, and they make their way to the sewage treatment plants and environment. Several researchers have detected pharmaceuticals in the ground and surface water in the range of 15–1200 ng dm⁻³. In recent studies, traces of pharmaceuticals were found in the lakes, rivers, and wells in Hyderabad. Although the amounts of pharmaceuticals were in the range of 90–31,000 μg dm⁻³, the chronic effects of these compounds were caused by their long term exposure. The current situation in USA predicts that the number of deaths (23,000 deaths per year) due to the antimicrobial resistance will surpass the combined number of deaths due to cancer and diabetes. Villages adjacent to the pharmaceutical industries are in alarming condition because of the highly contaminated groundwater, which leads to serious health problems such as cancer, miscarriage, and skin disorders. There are many confirmed cases of fish death in the water bodies and resistance developed in humans toward antibiotics. In 2018, the National Centre for Disease Control (NCDC) of India raised the concern over antibiotic pollution in water and requested the ministry of environment to develop strict laws and to implement them for correct disposal and effective treatment by the antibiotic manufacturers.

The environment ministry of India has classified all pharmaceutical manufacturers in the “red category” because they release toxic and hazardous discharge into the environment. The existing policies are incredibly inefficient for regulating and enforcing the present laws. The conventional wastewater treatment plants have been found to be ineffective for removing the pharmaceuticals discharges due to the presence of refractory and selectively-active organic compounds. It has also been observed that the antibiotics present in the pharmaceutical wastewater show toxicity towards microorganism-embedded wastewater in the treatment plants. Thus, the overall efficiency is reduced.

In the past three decades, the advanced oxidation processes (AOPs) have proven to be a perfect tool for the removal of
refractory organic compounds such as the pharmaceuticals from synthetic wastewater. Most of the AOPs involve the generation of the hydroxyl radical as the main oxidant. The possibility of a high degree of mineralization and the non-selective nature of the AOPs have rendered them attractive. However, the commercial application of the AOPs is still scarce due to their high cost. To overcome the high cost, the AOPs are often integrated with other techniques such as biodegradation, adsorption, electro-coagulation, and membrane separation. AOPs are used in the pretreatment stage for increasing the biodegradability and reducing the cost in the optimized integration for highly contaminated industrial wastewaters.29 Ozone alone has been recognized as a strong oxidant, and it is capable of degrading recalcitrant organic compounds.33–27 Ozone very selectively attacks organic compounds having a high electron density, whereas ·OH is a non-selective oxidant, and the latter reacts with a variety of organic compounds.28

This work deals with a real effluent collected from a pharmaceutical-manufacturing industry in India. Although a vast variety of literature is present for pharmaceutical treatment by AOPs from synthetic wastewater, a very few studies are reported for treatment of real pharmaceutical industrial wastewater. The treatment of synthetic wastewater containing pharmaceuticals was a lesser complex process than real pharmaceutical wastewater in spite of high concentration of pharmaceutical present. Treatment of multiple complex compounds at the same time was a difficult task to achieve. The present study includes the complexities encountered for real wastewater treatment, that is, the presence of matrices and interference of other organic compounds. The present study can benefit the treatment of real industrial pharmaceutical wastewater. The pharmaceuticals present in the effluent were identified and classified. The presence of anti-cancer, anti-psychotic, anti-depressant, and anti-biotic drugs was confirmed in the effluent. The effluent was treated with ozone in the presence of H2O2. The pretreated wastewater was passed through a bed of granular activated carbon (GAC) for further reduction of the chemical oxygen demand (COD). The effects of pH, the concentration of H2O2, and ozone feed rate were studied. The water quality parameters of the raw and treated wastewater were analyzed and discussed.

2. RESULTS AND DISCUSSION

2.1. Peroxone Treatment. The experiments were carried out at different pH (i.e., 5, 7.5, 9, and 11) for the ozone supply rate of 0.78 mg s⁻¹. The removal of COD, color, ammonia, chloride, and phenol was recorded with time for different pH. Figure 1a,b shows the reduction in COD with time and COD removal efficiency at different pH, respectively.

The COD removal was 75% (total COD removal = 1950 mg dm⁻³) at pH 5, 85.3% (total COD removal = 2220 mg dm⁻³) at pH 7.5, 86.5% (total COD removal = 2250 mg dm⁻³) at pH 9, and 88.4% (total COD removal = 2300 mg dm⁻³) at pH 11. At neutral and acidic conditions, molecular ozone reacts with the chemical compounds present in the wastewater. As the pH increases, the high rate of ozone decomposition leads to the generation of hydroxyl radicals; vide eq 1.29 The non-selective hydroxyl radical had been found to be a better oxidant than ozone alone.30 The initiation reactions for ozone decomposition in aqueous medium are expressed by the following equations31

\[ \text{O}_3 + \text{OH}^- \rightarrow \text{O}_2^{*^-} + \text{HO}_2^* \]  

(1)

\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{HO}^* + \text{O}_2 \]  

(2)

\[ \text{O}_3 + \text{HO}^* \rightarrow \text{HO}_2^* + \text{O}_2 \]  

(3)

As the organic compounds present in the aqueous medium degrade, the concentration of carbonates and bicarbonates increases. The scavenging nature of these ions for the hydroxyl radicals has been established in the previous studies.31,32 Carbonates and bicarbonates not only obstruct the generation of the accelerating agents for O₃ decomposition such as O₂⁺, HO₂⁺, and O₃⁻ but also scavenge the ·OH rapidly. The presence of these inhibitors also increases the stability of ozone and its exposure. After 100 min of reaction, the increase in the concentration of these scavengers slows down the reaction considerably. Beyond that, the dosage of ozone supply does not affect the mineralization efficiency significantly. It is therefore concluded that the alkaline medium favors the mineralization, but the concentration of ozone or its exposure for a longer duration does not accelerate the mineralization appreciably.

The reaction rate equation can be written in terms of COD and ozone concentrations present in the solution as follows.
The reaction kinetics can be considered as pseudo-first-order,\textsuperscript{33} in as much as the ozone supply was constant throughout the process for the first 120 min [eq 5] as

$$\frac{d[\text{COD}]}{dt} = k[\text{COD}][\text{O}_3]$$

(4)

As the processing time increased, the ozone concentration began to increase because of the lower ozone decomposition rate. Therefore, after 120 min of reaction, the ozone concentration cannot be considered to remain constant.

Integrating eq 5, we get

$$\ln \frac{[\text{COD}]_0}{[\text{COD}]_t} = kt$$

(6)

where $k$ is the pseudo-first-order rate constant, which is calculated by plotting $\ln \frac{[\text{COD}]_0}{[\text{COD}]_t}$ versus $t$. The effect of pH on $k$ is shown in Figure 2, as it can be seen from the value of $k$ which is increasing with increasing pH as higher pH enhance the hydroxyl radical generation.\textsuperscript{34}

The raw wastewater has a pale-yellow color. On the application of peroxone, decolorization took place rapidly. The variation in pH favored decolorization in the same way as the COD removal. Although molecular ozone also decolorizes the wastewater effectively despite its selective attacking nature, at alkaline pH, the color removal rate was found to be higher than that in the acidic pH. Figure 3 shows the effect of pH on color removal. The effect of the concentration of $\text{H}_2\text{O}_2$ in the peroxone process is well known.\textsuperscript{35}

It is observed that the water was initially dark yellow initially. After the peroxone treatment, the water started to decolorize rapidly, and after 180 min, the water turned into a clear liquid, as shown in Figure 4. Initially the color disappears rapidly and after the final stage of reaction, the removal rate for color was found slower. This behavior was observed probably due to nature of product formed during reaction. For example, during ozonation, initially aromatic compounds are converted into phenols and aromatic acids rapidly and then further reaction leads to aldehydes and acids which have slower reactivity towards ozonation.\textsuperscript{36}

The concentration of the phenolic compounds present in the effluent was found to decrease with time, as shown in Figure 5. The degradation of phenolic compounds followed the same trend as the COD and color.

The alkaline pH favored the removal due to the presence of the hydroxyl radicals generated in-situ. At acidic pH, the removal was found to be 87.5\% and at pH 7.5–11, the phenol was not detected after treatment. It was observed the decrease in the removal rate was not commensurate with the COD removal. From Figure 5, the values of phenol concentration at pH 7.5 and 9 are very close to each other, whereas the slow ozone decomposition at neutral pH is already known.\textsuperscript{37} It has been also reported that the presence of the phenolate ions promotes the generation of hydroxyl radical which is in agreement of present behavior.\textsuperscript{37} However, the degradation increased with the system pH, and the phenolic compounds were found to be below the detectable range after treatment. The possibilities to degrade recalcitrant phenolic pollutant by AOP were previously suggested.\textsuperscript{10}

The removal of ammonia by the peroxone process was also studied (see Figure 6). The ammonia present in the effluent leads to aldehydes and acids which have slower reactivity towards ozonation.\textsuperscript{36}
was converted into nitrate by ozone and hydroxyl radical as follows:38,39

$$\begin{align*}
\text{NH}_3 + 4\text{O}_3 & \rightarrow \text{NO}_3^- + 4\text{O}_2 + \text{H}_2\text{O} + \text{H}^+ \quad (7) \\
\text{NH}_4^+ + \cdot\text{OH} & \rightarrow \text{NH}_2\cdot + \text{H}_2\text{O} \quad (8) \\
\text{NH}_2\cdot + 2\text{O}_3 & \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + \text{O}_2 \quad (9)
\end{align*}$$

The removal of ammonia was found to be dependent on pH. Negligible removal of ammonia was observed at acidic pH due to conversion of ammonia into ammonium, which is recalcitrant toward oxidants.40 At pH < 9, very less availability of free ammonia and predominance of ozone as oxidant slow down the ammonia removal. Generation of bicarbonate ions may increase the removal by suppressing the radical reaction and accelerating the ozone decomposition.41 At pH > 9, the hydroxyl radicals take over the removal process and react with free ammonia. Further increase in pH did not accelerate the removal significantly, although the removal (>96%) by the peroxone process was found to be effective than ozone alone.40

The concentration of the chloride ions was found to decrease by the peroxone process, as shown in Figure 7.

It was mentioned in Section 2.1, that at acidic pH, molecular ozone dominates as the oxidant; however, at alkaline pH, the hydroxyl radical plays the role of the dominant oxidant.41 The reactions between the chloride ion and molecular ozone are as follows:

$$\begin{align*}
\text{Cl}^- + \text{O}_3 & \rightarrow \text{ClO}^- + \text{O}_2 \quad (10) \\
\text{ClO}^- + \text{O}_3 & \rightarrow \text{ClO}_2^- + \text{O}_2 \quad (11) \\
\text{ClO}_2^- + \text{O}_3 & \rightarrow \text{ClO}_2^- + \text{O}_3^- \quad (12) \\
\text{ClO}_2^- + \text{O}_3^- & \rightarrow \text{ClO}_3^- + \text{O}_3^- \quad (13)
\end{align*}$$

Chloride ions are well known for their hydroxyl radical scavenging property.42 The reactions between the chloride ion and the hydroxyl radical are as follows:

$$\begin{align*}
\cdot\text{OH} + \text{Cl}^- & \rightarrow \text{HOCl}^- \quad (14) \\
\text{HOCl}^- + \text{H}^+ & \rightarrow \text{Cl}^+ + \text{H}_2\text{O} \quad (15) \\
\text{Cl}^+ + \text{OH}^- & \rightarrow \text{HOCl}^- \quad (16) \\
\text{Cl}^+ + \text{Cl}^- & \rightarrow \text{Cl}_2^- \quad (17) \\
\text{Cl}_2^- + \text{Cl}_2^- & \rightarrow \text{Cl}_2 + 2\text{Cl}^- \quad (18)
\end{align*}$$

It can be concluded that at alkaline pH, chlorine gas would be formed during the reaction, but at acidic pH, chlorate ions are formed. The chloride ion removal efficiency was found to have a moderate pH dependency.

2.2. Effect of H$_2$O$_2$ Concentration. The positive effect of the presence of H$_2$O$_2$ on the ozonation process has been well documented and extensively studied.46,47 The presence of H$_2$O$_2$ triggers the ozone decomposition at a faster rate.38,39 Previous studies have suggested that higher H$_2$O$_2$ concentrations may scavenge hydroxyl radicals.46,47 H$_2$O$_2$ can act as an inhibitor to ozone decomposition by triggering the free radical reactions at elevated concentration, whereas it

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Figure 5. Degradation of phenolic compounds present in wastewater at different pH values (ozone flow rate: 0.78 mg s$^{-1}$, and [H$_2$O$_2$]: 0.176 mol dm$^{-3}$).

Figure 6. Removal of ammonia during the peroxone process at different pH values (ozone flow rate: 0.78 mg s$^{-1}$, and [H$_2$O$_2$]: 0.176 mol dm$^{-3}$).

Figure 7. Concentration of chloride during the peroxone process at different pH values (ozone flow rate: 0.78 mg s$^{-1}$, and [H$_2$O$_2$]: 0.176 mol dm$^{-3}$).
accelerates the hydroxyl radical production at optimum concentration. The present study also suggests the same behavior as COD removal decreases to 75% for 0.264 mol dm$^{-3}$ of H$_2$O$_2$ concentration, whereas for H$_2$O$_2$ concentration of 0.176 mol dm$^{-3}$, the removal recorded was 85%. It is concluded that the COD removal was dropped by 11.8% when H$_2$O$_2$ dose was increase by 50%. However, the generation superoxide ion may prevent the scavenging of hydroxyl radical via eq 19.

$$\text{H}_2\text{O}_2 + \text{O}^{	ext{•}-} \rightarrow \text{O}_2^{	ext{–}} + \text{H}_2\text{O} + \text{H}^+ \quad (19)$$

The optimum concentration of H$_2$O$_2$ was considered at 0.176 mol dm$^{-3}$ as maximum removal was recorded (85%) at this concentration. Figure 8 shows the enhancement in the COD removal efficiency with increasing H$_2$O$_2$ concentration.

Figure 8. Effect of concentration of H$_2$O$_2$ on COD removal at pH 7.5 for the ozone flow rate of 0.78 mg s$^{-1}$.

For the H$_2$O$_2$ concentrations of 0, 0.088, 0.176, and 0.264 mol dm$^{-3}$, the COD removal efficiencies were 61.5, 73.8, 85.4, and 75%, respectively, for same initial pH. Hence, the COD removal efficiency was found to increase with the increasing H$_2$O$_2$ concentration till optimum H$_2$O$_2$ concentration, which corroborated the results reported.$^{26,49}$

Figure 9 shows the low biodegradability (biological oxygen demand (BOD)$_5$/COD = 0.1) of effluent was enhanced after treatment to 0.55 for 0.176 mol dm$^{-3}$ H$_2$O$_2$. Biodegradability is considered as an important factor for the wastewater treatment. Several previous studies also reported that the ozone based processes lead to generate more biodegradable products on degradation hence enhanced biodegradability can be achieved.$^{36,50–53}$ Ozone-based treatment techniques reduce aromaticity which results improved biodegradability.$^{34,55}$ The presence of H$_2$O$_2$ accelerates the hydroxyl radical production which produces the more biodegradable metabolites than ozone alone due to its non-selective nature. At optimum H$_2$O$_2$ concentration, the BOD$_5$/COD was increased by 5.5 folds, whereas at 0.264 mol dm$^{-3}$ H$_2$O$_2$, it is increased by three folds due to less availability of hydroxyl radical. It can be concluded that the perozone treatment increases the biodegradability and H$_2$O$_2$ concentration plays an important role.

2.3. Treatment of Ozonated Wastewater by adsorption. After ozonation, the wastewater was subjected to adsorption by GAC. The adsorption on GAC was found to be effective for removing the COD further. The samples obtained from the perozone process were directly used for the adsorption studies, without any further modification. The initial CODs considerably varied with pH (as shown in Figure 10).

Figure 9. Effect of concentration of H$_2$O$_2$ on biodegradability at pH 7.5 for the ozone flow rate of 0.78 mg s$^{-1}$.

All adsorption experiments were performed at 297 K. During adsorption, the residual COD decreased with time, and after a specific time, the residual COD was found to be constant. It was assumed that the amounts of adsorption and desorption of the metabolites were in a dynamic equilibrium at this point. The residual COD and time were termed as equilibrium COD and equilibrium time, respectively.

The kinetic data for adsorption were analyzed using pseudo-first-order, pseudo-second-order, and Elovich models at pH 5, 7.5, 9, and 11. The linearized forms of the pseudo-first-order and pseudo-second-order models can be expressed as

Figure 10. Removal of COD during the adsorption on GAC (adsorbent dose: 4 g, temperature: 297 K).
\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  
(20)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^t} + \frac{t}{q_e}
\]  
(21)

where \(q_e\) and \(q_t\) are the residual COD values at equilibrium and at time \(t\), respectively. Both these quantities are expressed in mg g\(^{-1}\). The pseudo-first-order and pseudo-second-order rate constants, that is, \(k_1\) (min\(^{-1}\)) and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)), respectively, were obtained from the linear plots of \(\ln(q_e - q_t)\) versus \(t\), and \(t/q_t\) versus \(t\), respectively. These plots are shown in Figure 11a,b. The chemisorption process is best described by the Elovich model,

\[
q_t = \frac{1}{b_e} \ln(a_e b_e) + \frac{1}{b_e} \ln t
\]  
(22)

where \(a_e\) and \(b_e\) are the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)) and extent of surface utilization or required activation energy (g mg\(^{-1}\)), respectively. The values of these two kinetic parameters can be obtained from the plot of \(q_t\) versus ln \(t\) (see Figure 11c).

The deviation of the values obtained from the model and experimental data were calculated in terms of average relative error (ARE) as follows

\[
\text{ARE(\%)} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_i^{\text{cal}} - q_i^{\text{exp}}}{q_i^{\text{exp}}} \right|
\]  
(23)

where \(q_i^{\text{cal}}\) and \(q_i^{\text{exp}}\) (mg g\(^{-1}\)) denote the calculated and experimental adsorption capacities, respectively, and \(N\) represents the number of data points. The kinetics parameters calculated from the models are given in Table 1.

The pseudo-second-order model exhibits the correlation factor close to unity and lower AREs as compared to the pseudo-first-order model for all pH. The point of zero charges (pHpzc) of activated char was found to be in the range of 7.22–8.57. pHpzc plays an important role in the adsorption trend at different pH. In the present study, the adsorption rate was higher in the acidic medium than the alkaline medium. At pH < pHpzc, the surface was positively charged, but at pH > pHpzc, the surface was negatively charged. At pH < pHpzc (i.e., pH = 5), the removal of COD by adsorption was maximum (i.e., 85%). At pH > pHpzc, the adsorption efficiency ranged from 65–71%. The good fit of the pseudo-second-order kinetics to the experimental data indicates that the rate-limiting step was chemisorption or ion exchange.\(^{60-62}\) The values of \(k_2\) ranged from 0.0222 to 0.0274 g mg\(^{-1}\) min\(^{-1}\) for the pH range 5–11. At pH 5, the value of \(k_2\) was minimum that is, 0.0222, which indicates that low pH favored the adsorption.

### 2.4. Cost Analysis and Energy Consumption

Most of the previous studies dealing with real wastewater lack the evaluation of operating and fixed cost, which plays an important role during large scale implication at industries. In real scenario, there are various expenses related to the complete treatment process, which should be taken into account. The fixed cost of the process includes the cost of the reactor and ozone generator mainly. The operating cost includes reagent, chemicals, and electricity consumption. The cost of electricity was calculated for the ozonation process. The operational cost due to energy consumption is given by\(^{63}\)

\[
\text{operational cost} = b \times E_{\text{energy}}
\]  
(24)

\[
E_{\text{energy}} = \frac{b \times V \times I \times t}{V_{\text{eff}}}
\]  
(25)

where \(b\), \(V\), \(I\), and \(V_{\text{eff}}\) represent the rate of electricity, voltage (V), current (A), and volume of effluent treated (dm\(^3\)).
respectively. The state rate of electricity in India was 0.09 USD per kWh in 2019. All the experiments were conducted at an ozone generation rate of 0.78 mg s$^{-1}$ at which the estimated power consumption was 57.93 W. For cost analysis, a different set of experiments were conducted with reaction 180 min and reaction volume 1 dm$^3$. Hence, the total power consumption for ozone generation rate of 0.78 mg s$^{-1}$ and reaction time 180 min was 173.79 Wh.

- Total power consumption for ozonation process = 173.79 Wh
- Total COD removal = 2450 mg dm$^{-3}$. COD removal was 88.5% for pH 5–11. All other parameters (i.e., color, and the concentration phenolic compounds, chloride, and ammonia) also decreased significantly. The high pH and high ozone supply rate accelerate the degradation process. The increasing concentration of H$_2$O$_2$ was also effective. The COD removal was increased by 50.4% when H$_2$O$_2$ concentration was varied from 0 to 0.264 mol dm$^{-3}$. BOD$_5$/COD was also improved from 0.1 to 0.55 at 0.176 mol dm$^{-3}$ H$_2$O$_2$. The ozonation followed the pseudo-first-order kinetics, and the rate constants were in the range of $1.42 \times 10^{-4}–3.35 \times 10^{-4}$ s$^{-1}$.

Application of adsorption by activated char as a post-treatment after the peroxone treatment was effective. After adsorption, the COD value was further decreased by 34.5–41.2%. The minimum COD achieved from the hybrid process was 190 mg dm$^{-3}$ at pH 11, the ozone flow rate of 0.78 mg s$^{-1}$, H$_2$O$_2$ concentration of 0.176 mol dm$^{-3}$, and an adsorbent dose of 4 g. The parameters for the adsorption kinetics for the pseudo-first-order, pseudo-second-order, and Elovich models were determined. The fit of the pseudo-second-order model was the best. The kinetic parameters for this model ranged from $2.22 \times 10^{-2}$ to $2.74 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$. Total COD removal by the combination of both processes was in the range of 85.4–92.7%.

The results obtained from the present work demonstrate that a hybrid process of peroxone and adsorption can be applied for the treatment of real industrial pharmaceutical wastewater containing complex organic compounds. A selective oxidant, that is, ozone, was partially effective for treating the complex wastewater, whereas the presence of a non-selective and stronger oxidizing species, that is, ozone, was partially effective. After ozone treatment, the COD value was decreased by about 30%. The COD removal was further increased in the adsorption process. The removal of COD by ozonation followed the pseudo-first-order kinetics, and the rate constants were in the range of $1.42 \times 10^{-4}–3.35 \times 10^{-4}$ s$^{-1}$.

The reagents used for wastewater characterization and quantitative detection of substrates, that is, chloride ion, nitrate ion (i.e., nitrate test), color intensity (i.e., color), ammonia (i.e., ammonia test), alkalinity, and phenolic compound (phenol test) were purchased from Palintest (UK). The reagents for COD measurements were supplied by Hach (USA). Hydrogen peroxide (purity = 30%) was purchased from Merck (India). Sodium hydroxide pellets (purity >97%), manganese dioxide (purity >99%), and hydrochloric acid (purity >35%) were purchased from Merck (India). Granular activated charcoal was purchased from Loba Chemie (India).

### 4. MATERIALS AND METHODS

#### 4.1. Chemicals and Reagents

The reagents used for wastewater characterization and quantitative detection of substrates, that is, chloride ion, nitrate ion (i.e., nitrate test), color intensity (i.e., color), ammonia (i.e., ammonia test), alkalinity, and phenolic compound (phenol test) were purchased from Palintest (UK). The reagents for COD measurements were supplied by Hach (USA). Hydrogen peroxide (purity = 30%) was purchased from Merck (India). Sodium hydroxide pellets (purity >97%), manganese dioxide (purity >99%), and hydrochloric acid (purity >35%) were purchased from Merck (India). Granular activated charcoal was purchased from Loba Chemie (India).

### 3. CONCLUSIONS

The present study has demonstrated a hybrid approach for treating a real industrial effluent obtained from a pharmaceutical manufacturer. The identified pharmaceuticals in the effluent were mainly anti-cancer drugs, anti-psychotics, anesthetics, and mild pain killers. A combination of ozone and H$_2$O$_2$ was effective in treating the wastewater. The COD removal of wastewater during the peroxone process was in the range of 75–88.5% for pH 5–11. All other parameters (i.e., color, and the concentration phenolic compounds, chloride, and ammonia) also decreased significantly. The high pH and high ozone supply rate accelerate the degradation process. The increasing concentration of H$_2$O$_2$ was also effective. The COD removal was increased by 50.4% when H$_2$O$_2$ concentration was varied from 0 to 0.264 mol dm$^{-3}$. BOD$_5$/COD was also improved from 0.1 to 0.55 at 0.176 mol dm$^{-3}$ H$_2$O$_2$. The ozone-based treatment processes at an industrial level to treat real complex effluents are found to be cost effective in present study. The treatment cost for 1 m$^3$ effluent was 6.38 USD m$^{-3}$. In previous studies,$^{64–69}$ various combinations of ozone-based AOPs were found to be cost effective comparative to other treatment techniques.
4.2. Characterization of the Effluent. The effluent was obtained from a leading pharmaceutical industry located in Hyderabad (India). The wastewater was transported and stored at 298 K. All the experiments were performed within 30 d after receiving the wastewater. High resolution-liquid chromatography mass spectrometry (HR-LCMS) (make: Agilent Technologies, model: 6550 iFunnel Q-TOF, country: USA) was used to analyze the wastewater qualitatively. The details of the analytical methodology employed and the pharmaceuticals detected are summarized in Section 4.4.

4.3. Experimental Setup and Procedure. An assembly of an oxygen concentrator (make: Oz-Air, model: HG 03, country: India) and an ozone generator (make: Oz-Air, model: ISM 10 Oxy, country: India, capacity: 0–10 g h⁻¹) were used...
### Table 2. Analytical Methodology and the Pharmaceuticals Detected

| Compound name          | Retention time (min) | Mass (g mol⁻¹) | Formula  | Compound Structure | Type and Use |
|------------------------|----------------------|----------------|----------|--------------------|--------------|
| Hydroxy anastrozole    | 3.86                 | 309.15         | C₃₇H₃₈N₁₀O₆ | ![Image](image1.png) | A metabolite of the anti-cancer drug, which is used for the breast cancer treatment |
| Carboxy Primaquine      | 4.39                 | 274.13         | C₁₂H₁₆N₅O₅ | ![Image](image2.png) | A metabolite of medicine, used for the treatment of malaria and pneumonia |
| Letrozole               | 5.49                 | 285.09         | C₁₃H₁₄N₅ | ![Image](image3.png) | Used for the treatment of breast cancer |
| Meropenem               | 5.89                 | 401.16         | C₁₆H₁₂N₅O₈S | ![Image](image4.png) | An antibiotic, used for the treatment of bacterial infections |
| Butorphanol            | 6.04                 | 219.22         | C₁₉H₂₆NO₃ | ![Image](image5.png) | Used as a painkiller and also used as an anesthetic |
| Dihydroxy streptomycin | 8.97                 | 567.29         | C₂₀H₂₁N₁₀O₁₁ | ![Image](image6.png) | Used for the treatment of bacterial infections in cattle |
| Ketamine               | 8.99                 | 235.08         | C₃H₆ClNO | ![Image](image7.png) | Used in anesthesia and antidepressant |
to supply ozone to the reactor vessel. The oxygen concentrator worked on the pressure swing adsorption method, which isolated the oxygen from air based on its molecular characteristics and affinity toward the adsorbent. It produced pure oxygen and fed it to the ozone generator. The ozone generator worked on the corona discharge method. In this method, the applied voltage generated nascent oxygen, and it combined with the oxygen molecule to generate ozone. The ozone thus generated was supplied through a sparger to a glass reactor of 1 dm$^3$ volume. The excess ozone escaping from the reactor was captured and passed into the ozone destructor (make: Oz-Air, model: Dest 50, country: India), which converted the unreacted ozone to oxygen. The ozonated water was further treated by activated carbon in a glass column (length: 15 cm, diameter: 2 cm). The detailed schematic is shown in Figure 12.

The experiments were performed at different pH (i.e., 5, 7.5, 9, and 11) and different concentrations of H$_2$O$_2$ (i.e., 0.088, 0.176, and 0.264 mol dm$^{-3}$). 200 cm$^3$ of wastewater was taken in the glass reactor for each run. Spillage due to foaming during the initial phase of ozonation was avoided by keeping this volume proportion. H$_2$O$_2$ was added to the reactor just before the experiment. The samples were withdrawn at 30 min interval up to 3 h. Each 10 cm$^3$ sample was quenched with 1 mg MnO$_2$ for removing the residual H$_2$O$_2$ and O$_3$. For adsorption experiments, the treated wastewater samples (pH 5–11) obtained from peroxone treatment at pH 5 (COD = 650 mg dm$^{-3}$) was adjusted to pH 5–11.

4.4. Analysis Methods. The wastewater was qualitatively analyzed by HR-LCMS at the sophisticated analytical instrument facility of IIT Bombay (India). The chromatogram of wastewater is shown in Figure 13. The organic compounds identified are listed in Table 2.

The separation of the pharmaceuticals was achieved by the HPLC using an analytical C18 column (100 mm × 2.1 mm × 3 $\mu$m) (make: Thermo Fisher Scientific, model: Hypersil, country: USA). The details of the mobile phase composition and the gradient method are given in Table 3. In the mass spectrophotometer, the capillary voltage applied was 3500 V, $\mathrm{H}_2\mathrm{O}$ flow rate was 11 dm$^3$ min$^{-1}$ (at 523 K), the sheath gas flow rate was 11 dm$^3$ min$^{-1}$ (at 573 K), the nebulizer pressure was 2.4 bar, and the nozzle voltage was 1000 V.

The properties of the raw wastewater were measured by a photometer (make: Palintest, model: 7100, country: UK). For the COD analysis, the samples were filtered with Whatman filter paper (grade 1, pore size: 0.45 $\mu$m) and diluted with Milli Q water. The COD reagents were added carefully in the COD vials and digested for 2 h in the COD digester (make: Velp Scientifica, model: ECO 25, country: India) at 423 K. Then, the digested samples were kept at room temperature to cool, and the COD was measured. BOD of effluent was measured by respirometric method. A measured amount of wastewater and inocula were used in 0.3 dm$^3$ bottles. For the chloride test, the samples were acidified to avoid the interference from the reducing and complexing agents. Then, a reagent containing silver nitrate was added, and the chloride present in the sample reacted with it forming a turbid dispersion of silver chloride. The turbidity thus developed was measured in terms of the chloride concentration. For color intensity measurement, the samples were filtered through a glass fiber filter for removing the suspended solids. In the test of ammonia, it reacted with salicylate and gave a green–blue color due to the formation of indophenol in the presence of chlorine. Phenol and phenol substitutes gave red color by reacting with 4-amino-antipyrine. Before analysis, the sample was neutralized to prevent hindrance of the metal ions. The intensity of the red color was measured by a photometer. The properties of the raw effluent are summarized in Table 4.

| Table 4. Water Quality Properties of the Raw Effluent |
|--------------------------------------------------------|
| parameter | Value |
| pH | 7.5 |
| COD (mg dm$^{-3}$) | 2600 ± 20 |
| BOD$_5$ (mg dm$^{-3}$) | 260 ± 5 |
| color (mg dm$^{-3}$ Pt–Co) | 380 ± 5 |
| alkalinity (mg dm$^{-3}$ CaCO$_3$) | 2500 ± 50 |
| chloride (mg dm$^{-3}$) | 1250 ± 50 |
| ammonia (mg dm$^{-3}$ N) | 25 ± 2 |
| nitrate (mg dm$^{-3}$ N) | 80.5 ± 5 |
| phenol (mg dm$^{-3}$ C$_6$H$_5$OH) | 8 ± 0.5 |
| sulfate (mg dm$^{-3}$) | (1.1 ± 0.1) × 10$^3$ |

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Notes
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NOMENCLATURE

- $a_0$: initial rate of adsorption for Elovich model (mg g$^{-1}$ min$^{-1}$)
- $b$: rate of electricity (USD kW$^{-1}$ h$^{-1}$)
- $b_0$: rate constant for chemisorption for Elovich model (g mg$^{-1}$)
- $I$: current (A)
- $N$: number of data points (–)
- $k_1$: rate constant for the pseudo-first-order reaction (min$^{-1}$)
- $k_1'$: rate constant for the second-order reaction (dm$^3$ mol$^{-1}$ s$^{-1}$)
- $k_2$: pseudo-first-order rate constant for the adsorption kinetics (min$^{-1}$)
- $k_2'$: pseudo-second-order rate constant for the adsorption kinetics (g mg$^{-1}$ min$^{-1}$)
- $q_{e0}$: equilibrium values calculated from the kinetic model of adsorption (mg g$^{-1}$)
- $q_e$: equilibrium adsorption capacity (mg g$^{-1}$)
- $t$: time (s)
- $V$: voltage (V)

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