Mineralization of some natural refractory organic compounds by biodegradation and ozonation

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Abstract

The objective of this study was to explore the extent of mineralization, reduction in color and reduction of COD of gallic acid, tannin and lignin by ozonation and a combination of aerobic biodegradation and ozonation. Ozonation of pure aliquots (phase I experiments) resulted in the decline in TOC, COD, COD/TOC ratio, UV absorbance at 280 nm and color of the three model compounds investigated, with COD removals of greater than 80% and high removals (>90%) of UV absorbance at 280 nm and color observed in all cases at an ozone dose of 6 mg ozone/mg initial TOC or higher. Aerobic biodegradation of pure gallic acid, tannin and lignin aliquots resulted in COD decline of approximately 36–38%. Subsequent ozonation (phase II experiments) resulted in further decline in TOC, COD, COD/TOC ratio, and increase in UV absorbance at 280 nm and color removals. COD and TOC removals comparable to phase I experiments were obtained with 30–40% lower ozone absorption in phase II experiments. The biodegradation step was quite effective in removing specific UV absorbance at 280 nm, with up to 75% removal observed. Subsequent ozonation increased overall specific UV absorbance at 280 nm to greater than 90%.

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Keywords: Gallic acid; Tannin; Lignin; Ozonation; Biodegradation

1. Introduction

Presence of refractory organic macromolecules such as tannin and lignin in distillery, tannery, pulp and paper wastewaters, etc., imparts color (Kim and Lee, 2004) and renders effective treatment of such wastewaters through biodegradation processes difficult (Beltran et al., 1993). Tannins are water-soluble polyphenolic compounds having wide prevalence in plants and plant residues (Bhat et al., 1998). Tannins have large molecular weights ranging from 500 to 4000 Da (1 Da = 1 atomic mass unit, amu = mass of 1 hydrogen atom), and strong affinity to proteins, alkaloids and heavy metals to form complex molecules (Yoshida et al., 2004). Hydrolysable and condensed tannins are the two major classes of tannins (Bhat et al., 1998). These compounds have a range of effects on various organisms from toxic effects on animals to growth inhibition of microorganisms (Scalbert, 1991). Hydrolysable tannins are principally multiple esters of D-glucose with gallic acid and its oxidative metabolites, while condensed tannins (proantocyanidins) are composed of flavan-3-ol units linked through C–C bond (Yoshida et al., 2004). Lignin is an integral plant cell wall constituent, which is...
Win et al. (2000) reported an increase in biodegradability of effluent with high and persistent COD concentrations. Elimination efficiencies in the tertiary treatment of textile wastewater containing tannin and lignin were high (Perkowski et al., 1996), but the two-stage ozonation with simultaneous biodegradation proved to be a valuable option (Beltran et al., 1997). It is hypothesized that polyphenolic macromolecules like lignin and tannin are prone to attack by electrophilic agents such as ozone (Langlais et al., 1991). Treatment of industrial wastewaters containing tannin and lignin has been studied extensively (Nakamura et al., 2004; Bijan and Mohseni, 2004; Mantzavinos and Psillakis, 2004). Zenaitis et al. (2002) and Zenaitis and Duff (2002) used ozonation as a pretreatment for biological degradation of log yard effluent containing tannin and lignin. In another study (Perkowski et al., 1996), two-stage ozonation with intermediate biodegradation proved to be a valuable tool for obtaining high chemical oxygen demand (COD) elimination efficiencies in the tertiary treatment of textile effluent with high and persistent COD concentrations. Win et al. (2000) reported an increase in biodegradability.

Considerable information is also available regarding ozonation of humic substances, which are also stabilized polyphenolic compounds of plant origin, produced on partial microbial degradation of plant residues, and hence similar to tannin and lignin in many ways, as far as interaction with ozone is concerned. Killops (1986) and Gilbert (1987) reported that ozonation products of hydrophobic organic molecules are often more polar and more bio-available than the original contaminants. Ozonation was recommended as a method to treat debittering table olive wastewaters, containing tannin and lignin before an aerobic biological oxidation step since compounds toxic to microorganisms, e.g., polyphenols are removed and biodegradability is also improved by ozonation (Beltran et al., 1998).

Literature review indicates that no direct information is available on the specific impact of ozonation carried out either before or after aerobic biodegradation, on mineralization, color reduction, or COD reduction of pure tannin and lignin solutions, despite the desirability.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( M_{O_3} )</td>
<td>Rate of ozone mass transfer, ( \text{mg L}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( [O_3]^i )</td>
<td>Saturated aqueous phase ozone concentration, ( \text{mg L}^{-1} )</td>
</tr>
<tr>
<td>( [O_3]_g )</td>
<td>Gas phase ozone concentration effluent from the reactor, ( \text{mg L}^{-1} )</td>
</tr>
<tr>
<td>( [O_3]_g^i )</td>
<td>Influent gaseous ozone concentration, ( \text{mg L}^{-1} )</td>
</tr>
<tr>
<td>( Q_g )</td>
<td>Gas flow rate, ( \text{L min}^{-1} )</td>
</tr>
<tr>
<td>( k_w )</td>
<td>Specific ozone utilization rate constant, ( \text{s}^{-1} )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>Local mass transfer coefficient, ( \text{ms}^{-1} )</td>
</tr>
<tr>
<td>( D )</td>
<td>Diffusion constant of ozone, ( \text{m}^2 \text{s}^{-1} )</td>
</tr>
<tr>
<td>( [O_3]_l )</td>
<td>Aqueous phase ozone concentration inside the reactor, ( \text{mg L}^{-1} )</td>
</tr>
<tr>
<td>( E )</td>
<td>Enhancement factor, —</td>
</tr>
<tr>
<td>( K_{La} )</td>
<td>Mass transfer coefficient, ( \text{s}^{-1} )</td>
</tr>
<tr>
<td>( M )</td>
<td>Squared Hatta number, ( m = Dk_w/k_L ), —</td>
</tr>
<tr>
<td>( S )</td>
<td>Solubility ratio, ( \text{M}^{-1} )</td>
</tr>
<tr>
<td>( V_L )</td>
<td>Liquid phase volume in the reactor, ( \text{L} )</td>
</tr>
</tbody>
</table>
of having such information to gain better insight into use of ozonation or ozonation in conjunction with biodegradation for removal of natural refractory substances from wastewater. Hence, the objective of this research was to explore the extent of mineralization, reduction in color and reduction of COD of tannin and lignin by ozonation. Gallic acid, which is often considered to be the building blocks of tannin and lignin macromolecules, was also investigated in a similar fashion.

2. Materials and methods

Ozonation experiments were carried out with pure solution of the model compounds, and also with the effluents obtained after an initial biodegradation of these pure compounds.

2.1. Model compounds

The three model compounds used were, Gallic acid, AR Grade (3, 4, 5-Trihydroxybenzoic acid; Molecular formula: C7H6O5; Molecular weight: 170; Minimum assay: 98.0%; Supplier: Fine-Chem. Ltd., Mumbai); Tannin, AR Grade (Gallotannic acid; Molecular formula: C76H52O46; Molecular weight: 1701.23; Minimum assay: 90.0%; Supplier: Fine-Chem. Ltd., Mumbai); and Lignin, LR Grade (Supplier: National Chemicals, India). Carbon, hydrogen, nitrogen and oxygen content of these compounds were estimated using elemental analyzer (CHNOS analyzer, Model CE 440, Leemans Lab. Inc., USA), and the results obtained are presented in Table 1.

2.2. Experimental protocol

Experiments were carried out in two phases. Phase I experiments involved ozonation of aliquots of pure model compounds, i.e., gallic acid, tannin and lignin. Phase II experiments consisted of an initial biodegradation step for each model compound, followed by ozonation of the effluents from the aerobic bioreactors. The parameters monitored in both cases were, ozone consumption, pH, color, UV absorbance at 280 nm, COD and TOC.

2.3. Aerobic biodegradation

Reagent bottles of 1000 mL capacity were used as aerobic reactors. An air compressor (Model: Comair NF264, India) was employed for continuous supply of air to the reactors using aquarium diffusers. All reactors were kept at temperatures between 30 and 35 °C, and operated at a hydraulic retention time of 2 days. Three aerobic reactors were operated, with pure gallic acid, tannin and lignin, prepared in BOD dilution water (as described in Method No. 5210 B, APHA, 1995), as feed. All reactors were initially started with sewage from IIT Kanpur oxidation pond, and operated in the semi-batch mode. Continuous and sufficient air bubbling was provided in order to keep microbial population in suspension, and to ensure that oxygen was not rate limiting in the reactors. Aeration was stopped for 30 min each day, and biomass in the reactor was settled. From each reactor, 500 mL of the supernatant was then extracted and replaced with an equal volume of the desired feed. This ensured negligible washout of biomass and very high Biological Solids Retention Time (θc) in the reactor. For the first 15 days after start of reactor operation, reactors were fed only with sewage to ensure rapid biomass growth. From the 16th day onwards, 25% of COD influent to the reactor was replaced with model compound. This proportion was increased to 50%, 75% and 100% from 21st, 26th and 31st day onwards. From 31st day onwards, feed solutions of model compounds were prepared in BOD dilution water, which contained essential macro- and micro-nutrients required for biological growth. This was required because pure gallic acid, tannin or lignin was deficient in these nutrients. Effluent COD from each reactor was monitored until achievement of steady state.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental analysis of model compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>% by weight</td>
<td>%C</td>
</tr>
<tr>
<td><strong>Elemental analysis of gallic acid</strong></td>
<td></td>
</tr>
<tr>
<td>Theoretical</td>
<td>49.412</td>
</tr>
<tr>
<td>Measured</td>
<td>50.805±2.325</td>
</tr>
<tr>
<td><strong>Elemental analysis of tannin</strong></td>
<td></td>
</tr>
<tr>
<td>Theoretical</td>
<td>53.647</td>
</tr>
<tr>
<td>Measured</td>
<td>50.097±0.410</td>
</tr>
<tr>
<td><strong>Elemental analysis of lignin</strong></td>
<td></td>
</tr>
<tr>
<td>Measured</td>
<td>34.870±0.640</td>
</tr>
</tbody>
</table>

*In case of tannin and lignin, the values do not add up to 100 due to the presence of inorganic residues in the samples.*
followed by gradual stepwise increase in influent COD concentration to the desired value. Reactors were operated at these final influent COD concentrations for more than 2 months and steady-state COD removal in each reactor recorded. Effluents collected from the reactors subsequently were stored for phase II ozonation experiments.

2.4. Ozonation setup

The experimental setup used for ozonation consisted of a bubble contactor operated in the semi-batch mode (Fig. 1A). Ozone was generated in gas phase by passing pure dry oxygen through the ozone generator (INDIZONE, CDS/4C/AF, India). Arrangements were made for applying this gas mixture to the bottom of the reactor, where it bubbled through a porous ceramic plate and moved upwards through the reactor. The gas flow into the reactor was controlled using an online mass flow controller (AAL-BORG, GFC171S, USA). Ozone concentration in the gas influent to and effluent from the reactor was measured using an online ozone monitor (ANSEROS, Ozomat GM-6000-OEM) (see Fig. 1B). All components of the experimental setup and the reactor were made of glass, teflon or stainless steel to ensure that ozone consumption due to corrosion of components by ozone leading the erroneous experimental results is fully eliminated.

2.5. Ozonation procedure

For phase I experiments, several aliquots, 250–100 mL in volume, of the model compounds, i.e., gallic acid,
tannin and lignin were prepared by adding model compounds in BOD dilution water, buffered by orthophosphate addition to pH 7, and ozonated for various time periods. For phase II experiments, model compounds prepared as before were first aerobically biodegraded. Several 250–1000 mL aliquots of the effluents from biodegradation reactors were ozonated for various time periods. Influent and effluent gaseous ozone concentrations to the reactor were recorded at 5 min intervals during all such ozonation for determination of adsorbed ozone dose.

### 2.6. Analytical methods

pH was measured using a combination pH electrode (Toshiwal CL-51, India) connected to a digital pH meter (Toshiwal CL-54, India). COD of the samples were analyzed by using closed reflux method as described in Standard Methods (Method No. 5220 C, APHA, 1995). Color of the samples was analyzed by visual examination as described in Standard Methods (Method No. 2120 B, APHA, 1995). Samples were analyzed for inorganic carbon and total carbon as per Standard Methods (APHA, 1995). For TOC determination, samples were analyzed using a TOC analyzer (Model TOC-VCPN, Shimadzu, Japan). Absorbance measurements were done as described in Standard Methods (Method No. 5910 B., APHA, 1995) by using UV–Visible Spectrophotometer (Varian CARY 50 Conc, Australia), and 1 cm quartz cells. The samples were suitably diluted when absorbance values of samples were greater than one.

### 3. Results and discussion

#### 3.1. Ozonation of model compounds

Phase I of the study involved investigation of the extent of mineralization, oxidation and color removal of the model compounds by ozonation. Data pertaining to ozone consumption by pure aliquots of gallic acid, tannin and lignin is presented in Fig. 2A. For each model compound, several aliquots of different volumes and organic content were ozonated for this purpose. Ozone consumption data in all cases have been normalized by dividing by the initial TOC of the aliquot. This was necessary to account for differences in volume and organic content of various aliquots being ozonated, thus enabling comparison of results obtained under varying conditions. Following conclusions may be drawn from Fig. 2A. First, normalization to account for differences in volume and organic content of various aliquots of a particular organic substance, i.e., gallic acid, tannin or lignin, resulted in coincidence of ozone consumption characteristics, thus validating the normalization process. Second, ozone consumption characteristics were very similar for the three substances tested, i.e., for gallic acid, tannin and lignin. Third, in all cases, ozone absorption efficiency was nearly 100%, i.e., ozone concentration in the gas effluent from the reactor was nearly zero, up to an ozone dose of 2 g ozone absorbed per gram initial TOC. When higher ozone dose of up to 7 g ozone absorbed per gram TOC were applied, the ozone absorption efficiency declined to approximately 80%.

Ozone mass transfer into the liquid phase in above cases can be described using the mass transfer equation (Dankwerts, 1992)

$$M_{O_3} = \frac{Q_x [\text{O}_3]_l [\text{O}_3]_g}{V_L},$$

where

$$M_{O_3} = K_L \alpha \sqrt{1 + m} \left\{ [\text{O}_3]_L - \frac{[\text{O}_3]_g}{1 + m} \right\}. \quad (1)$$

In the above equation, $E = \sqrt{1 + m}$ is known as the mass transfer enhancement factor, which accounts for the fact that in aqueous phases with rapid ozone demand, as is the case when aqueous phase gallic acid, tannin or lignin is ozonated, ozone transferred from the gas phase is partially consumed at the gas–liquid interface itself, i.e., before diffusion to the to the bulk liquid phase. Carrying out experiments involving ozonation of pure water at pH 8.5, i.e., where $E \approx 1$, $K_L \alpha$ of the reactor in question was calculated to be approximately 0.10/s (Kumar and Bose, 2004). In the present case, putting $K_L \alpha = 0.1/s$ in Eq. (1), and noting that $[\text{S}[\text{O}_3]_L - ([\text{O}_3]_L / 1 + m)$ is very small under conditions of nearly 100% ozone transfer efficiency, $E$ is expected to be very large, i.e., almost no ozone diffuses into the bulk liquid phase. In cases where ozone transfer efficiency is less than 100% the decline in ozone mass transfer efficiency is due to a lower value of $E$, which is only partially offset by the consequent increase in $[\text{S}[\text{O}_3]_L - ([\text{O}_3]_L / 1 + m)$.

Alternatively, the enhancement factor, $E = \sqrt{1 + m}$ can be approximately represented as follows, where 'm' is defined as, $m = Dk_w/K_L^2$. Since $D$ and $K_L$ are constant in a particular reactor at constant temperature, change in $E$ may be attributed to decline in $k_w$ at higher ozone doses, i.e., as organic molecules in aqueous phase most susceptible to attack by ozone are progressively consumed, $k_w$ decreases.

Ozone consumption by molecules of gallic acid, tannin and lignin involve attack by ozone on aromatic rings and unsaturated sites on these molecules, leading to oxidation and possible mineralization. The extent of mineralization of gallic acid, tannin and lignin can be represented by the decline in TOC content of aliquots of these compounds on ozonation, as shown in Fig. 2B. The degree of mineralization of all three compounds with degree of ozonation was found to be approximately same, with approximately 25%, 50% and 70% mineralization.
observed at ozone doses of 2, 4 and 6 mg ozone absorbed per milligram initial TOC. For all three compounds, the percentage of mineralization declined linearly with increase in ozone dose at lower ozone doses, before leveling off at higher ozone doses.

The extent of oxidation of the model compounds by ozonation can be determined by observing the decline in COD values of aliquots on ozonation, as shown in Fig. 2C. The decline in COD as depicted in this figure may be attributed partially to mineralization, in which case the mineralized portion of carbon will cease to exert COD. Decline in COD may also be partially attributed to partial oxidation, but not full mineralization of organic molecules. In order to further elucidate this point, COD/TOC ratio of all three compounds was plotted against absorbed ozone dose in Fig. 2D. Decline in COD/TOC with increase in absorbed ozone dose was observed in all three cases, suggesting that the organic carbon remaining in solution after ozonation was on an average in a higher oxidation state than before ozonation. Assuming that all COD of these aliquots could be attributed to reduced carbon, theoretical COD/TOC ratios for various average carbon oxidation states were calculated (see Table 2). Comparison of these values with actual COD/TOC ratios before and after ozonation suggests that while before ozonation the average oxidation state of organic carbon in aliquots of tannin and lignin was between −1 and 0, the average oxidation state of remaining organic carbon after ozonation at the highest dose (Fig. 2D) had increased to between +1 and +2. In case of gallic acid, the average carbon oxidation state before ozonation was between 0 and +1, and after
ozonation at the highest dose (Fig. 2D) had increased to between +2 and +3. This observed increase in oxidation state of organic carbon can be explained by literature reports on decline of aromatic structures, and formation aliphatic structures with −COOH, −OH, and −CHO functional groups (Langlais et al., 1991) on ozonation of organic compounds. Aliphatic structures, in general, contain higher oxidation state carbon than carbon atoms in aromatic rings.

Plots of the normalized or ‘specific’ absorbance at 280 nm values versus ozone dose (Fig. 2E) exhibit an exponential decline with increasing ozone dose. Plot of apparent color (Pt−Co units) per unit TOC, or ‘specific color’ at various ozone doses for the model compounds presented in Fig. 3 also show exponential decline with ozone dose. Absorbance spectrum in the wavelength range of 190–450 nm is shown in Figs. 3A–C for gallic acid, tannin and lignin, respectively, both before ozonation and after ozonation at various doses. A decline in absorbance over the entire wavelength range is observed for each model compound with increase in ozone dose. Absorbance spectra of the unozonated ozone dose. Absorbance spectrum in the wavelength of solutions of pure lignin and tannin. Hence COD/TOC ratio of the aliquots after biodegradation of these substances is expected to be lower than the of solutions of pure lignin and tannin.

### 3.3. Ozonation of model compounds after aerobic biodegradation

After the initial biodegradation step, effluent from the aerobic reactors operated with pure gallic acid, tannin and lignin as feed were ozonated. Data pertaining to ozone consumption by these post-biodegradation aliquots of gallic acid, tannin and lignin are presented in Figs. 5A–C, respectively. Ozone consumption pattern by pure aliquots of gallic acid, tannin and lignin, presented earlier in Fig. 2A are also shown for the purpose of comparison. Ozone consumption in all cases have been normalized by dividing by the initial TOC of the aliquot, and plotted against the ozone absorption efficiency in the reactor. In case of gallic acid, the post biodegradation aliquots are seen to consume ozone more efficiently than pure gallic acid, i.e., while 100% ozone absorption efficiency was observed for aliquots of pure gallic acid up to an ozone dose of 2 mg ozone absorbed per milligram initial TOC, 100% ozone absorption efficiency of post-biodegradation gallic acid was observed up to an ozone dose of 5 mg ozone absorbed per milligram initial TOC (see Fig. 5A). This supports the hypothesis regarding formation of condensed by-products on gallic acid biodegradation, as presented in the previous section. Such condensed by-products, by virtue of containing lower oxidation state organic carbon, presumably exhibit more affinity toward ozone than pure gallic acid. Ozone absorption efficiency of post-aerobically biodegraded tannin is observed to be nearly identical to that of pure tannin (see Fig. 5B), while that of post aerobically biodegraded lignin is observed to be less than that of pure lignin (see Fig. 5C). These observations support the hypothesis regarding formation of partially oxidized by-products on tannin and
lignin biodegradation. Such partially oxidized by-products, by virtue of containing higher oxidation state organic carbon, presumably exhibit equivalent or less affinity toward ozone than pure tannin and lignin.

Comparison of mineralization of gallic acid, tannin and lignin by phase I and phase II experiments is presented in Figs. 6A–C, respectively. In phase I experiments, entire mineralization was through ozonation, while in phase II experiments, mineralization was partially through the initial biodegradation step, and then through ozonation. Results presented in Fig. 6A indicate that the rate of mineralization of pure gallic acid by ozonation (phase I) is faster than the rate of mineralization of post-biodegradation gallic acid aliquots through ozonation (phase II). However, at an ozone dose of around 6 g ozone absorbed per gram initial TOC, total mineralization by both processes become roughly equal, with approximately 80% of the
starting TOC being mineralized at this ozone dose by both processes. Similar results presented in Fig. 6B indicate that in case of tannin, phase II treatment process is clearly superior as far as mineralization is concerned, with 90% mineralization at an ozone dose of 6 g ozone absorbed per gram initial TOC, as compared to approximately 80% mineralization at the same ozone dose using phase I treatment. In case of mineralization of lignin (Fig. 6C), both phase I and phase II treatment result in 60% mineralization at an ozone dose of 6 g ozone absorbed per gram initial TOC. However, due to partial mineralization of the model compounds by the initial biodegradation step, phase II treatment process consumes less ozone compared to phase I processes for equivalent ozone doses, as lesser amount of organic carbon has to be ozonated in the former case.

Comparison of COD removal of gallic acid, tannin and lignin aliquots by phase I and phase II experiments is presented in Figs. 6D–F, respectively. The COD removal trends are nearly identical to the TOC removal or mineralization trends presented in Figs. 6A–C. Comparison of the decline in specific absorbance at 280 nm for gallic acid, tannin and lignin aliquots by phase I and phase II experiments is presented in Figs. 7A–C, respectively. Comparison of phase I and phase II results at zero ozone dose indicates that the initial aerobic biodegradation step in phase II experiments is quite efficient in partially removing aromaticity of the aliquots. Ozonation removes more aromaticity in all
cases, with progressively lower specific absorbance values observed at higher ozone doses. In all cases, specific absorbance removal by phase II experiments is either equally or more efficient. Comparison of the specific color removal by phase I and phase II experiments is presented in Figs. 7D–F, respectively. In case of phase II experiments involving gallic acid (Fig. 7D) and lignin (Fig. 7F), the initial biodegradation step increases the specific color of the aliquots, suggesting that portions of organic structure not contributing to color are removed selectively by biodegradation, or compounds with more color are formed as by-products of the initial biodegradation step. Ozonation resulted in removal of specific color in all cases, with increased removal observed at higher ozone doses. Phase II experiments resulted in more color removal for tannin and lignin, while color removal more through phase I experiments for gallic acid.

4. Conclusions

The objective was to evaluate the degree of mineralization, reduction in color and reduction of COD of gallic acid, tannin and lignin by ozonation. Two treatment options were evaluated, Direct ozonation (i.e., phase I experiments) and aerobic biodegradation
followed by ozonation (phase II experiments). Main conclusions were

- During ozonation of pure aliquots of gallic acid, tannin and lignin, ozone absorption efficiency was nearly 100% up to an ozone dose of 2 g ozone absorbed per gram initial TOC, after which a decline in ozone absorption efficiency was observed (see Fig. 2A).
- Ozonation during phase I experiments resulted in the decline in TOC, COD, COD/TOC ratio, UV absorbance at 280 nm and color of all aliquots (see Figs. 2B–F). COD removal of greater than 80% and high removals (>90%) of specific UV absorbance at 280 nm and specific color was observed in all cases at an ozone dose of 6 mg ozone absorbed per milligram initial TOC or higher.
- Aerobic biodegradation of pure gallic acid, tannin and lignin solutions resulted in COD decline of approximately 36–38% (see Fig. 4).
- Residual organic matter remaining after aerobic biodegradation of gallic acid showed enhanced reactivity toward ozone (see Fig. 5A). Ozone absorption efficiency of post aerobically biodegraded tannin was observed to be nearly identical to that of pure tannin (see Fig. 5B), while that of post-aerobically biodegraded lignin was observed to be less than that of pure lignin (Fig. 5C).
- Ozonation during phase II experiments resulted in decline in TOC, COD, and COD/TOC ratio with
increase in ozone dose (Figs. 6A–I). When the total decline in either COD or TOC, i.e., through both aerobic biodegradation and ozonation was considered, the decline through phase II experiments were higher than in phase I experiments at lower ozone doses, but became comparable to corresponding results of phase I experiments at ozone doses of 6 mg ozone absorbed per milligram initial TOC or greater.

- The initial biodegradation step was observed to be quite effective in removing specific UV absorbance at 280 nm (see Figs. 7A–C). Subsequent ozonation also reduced this value further. Similar observations can be made about specific color removal also (see Figs. 7D–F).

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