Ozonation of Common Textile Auxiliaries

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Abstract. The treatability of four different commonly applied textile auxiliary chemicals, namely two tannin formulations (Tannin 1: a condensation product of aryl sulphonate; Tannin 2: natural tannic acid) and two biocidal finishing agents (Biocide 1: 2,4,4'-trichloro-2'-hydroxydiphenyl ether; Biocide 2: a nonionic diphenyl alkane derivative) with ozone was investigated. Increasing the ozone dose yielded higher COD removals for the natural tannin. Optimum ozone doses of 485 and 662 mg/h were obtained at a pH of 3.5 for natural and synthetic tannin carrying textile bath discharges, respectively. When the reaction pH was increased from 3.5 to 7.0, a slight decrease in COD removal was observed for the natural tannin due to ozone selectivity towards its polyaromatic structure. The same increase in ozonation pH enhanced COD removals for the synthetic tannin as a result of enhanced ozone decomposition rendering free radical chain reactions dominant. Optimum ozone doses of 499 and 563 mg/h were established for Biocide 1 and 2, respectively. With the increase of ozonation, pH exhibited a positive influence on COD removals for both textile tannins. A substantial improvement in terms of TOC removals was observed as the reaction pH was increased from 3.5 to 7.0 for the synthetic tannin, and from 7 to 12 for both textile biocides. Higher AOX removals were evident at pH 7 than at pH 12 for Biocide 1 as a result of the higher selectivity of the dehalogenation reaction at neutral pH.

1. Introduction

The variety and complex structural nature of auxiliary chemicals (scouring and mercerizing agents, antistatic, surfactants, sequestering agents, complexing agents, carriers, tannins, softeners, wetting agents, lubricants, levelling agents, emulsifiers, etc.) that are frequently being used in different stages of textile preparation, dyeing and finishing processes render the effective treatment of dyehouse effluents a rather challenging task [1, 2]. For example, tannins are used in the nylon dyeing process to enhance the attachment of dyes onto the dye fabrics. Tannins are used in association with anionic acid or direct dyes. By the electrostatic repelling force between the dye and the hydroxyl groups of the tannins, the dye is “pushed” towards the fabric by tannic acids. The increase in wet fastness prevents dyestuff loss due to desorption during fabric rinsing. Tannins also protect fabrics against negative effects of chlorine; they sequester chlorine, thereby decreasing its oxidation power. Tannins form a thin film on the fabric and adsorb on the physically and chemically active sites of the fabric and thereby functioning as dirt repellents and blockers. On the other hand, biocidal products are active substances being applied to destroy or prevent the action of any harmful organism by chemical or biochemical means. Biocides are added during the manufacture of fabrics to protect the finished product against bio
deterioration and thus usually contain halogenated organics, aromatic and aliphatic hydrocarbons, and organometalloids. Both tannins and biocides are recalcitrant, potentially toxic, bio inhibitory and hence may present serious problems in conventional water and wastewater treatment systems [3]. In some cases, chemical oxidation processes such as ozonation are required to enhance a subsequent biological (activated sludge) treatment and/or to detoxify the industrial contaminant [4-6]. Considering the above mentioned facts, textile bath discharges containing four different commonly applied textile auxiliary chemicals, namely two tannin formulations (Tannin 1; a condensation product of aryl sulphonate and Tannin 2; natural tannic acid) as well as two biocidal finishing agents (Biocide 1; 2,4,4’-trichloro-2’-hydroxydiphenyl ether and Biocide 2; a nonionic diphenyl alkane derivative) were subjected to ozonation at varying ozone doses and pH values. The major purpose of ozonation was to pretreat/partially oxidize the above mentioned textile auxiliaries for biodegradability improvement.

2. Experimental

2.1. Ozonation of tannins and biocides

Ozone was generated from pure oxygen by a Sander Model S1000 ozone generator and applied at varying doses in the range of 450-1100 mg/h. The reactor was a 800 mL-capacity semi-batch bubble column made of borosilicate glass. The ozone + pure oxygen gas mixture was introduced from the reactor bottom through a sintered glass plate diffuser at a rate of 1 mL(O3+O2)/min. The inlet and off-gas ozone concentrations were determined via iodometry according to Standard Methods [7] in gas washing bottles. The tannins were ozonated at pH 3.5 and 7.0 in phosphate buffers to mimic textile dyeing pH conditions, whereas the biocides were ozonated at pH 7.0 and 12.0 in phosphate buffers to mimic biocide finishing pH conditions [7].

2.2. Textile tannins and biocides

The tannin and biocide formulations were obtained from a local dyehouse and used as received. All other chemicals and reagents used in the analytical and instrumental procedures were of at least analytical grade and purchased from either Fluka or Merck (Germany). Certain physicochemical properties of auxiliaries under investigation are given in Table 1. The synthetic and natural tannins are referred to as “Tannin 1” and “Tannin 2”, respectively. All textile chemicals were of high water solubility and only a negligible pH change occurred in the reaction solutions after their addition.

2.3. Measurements

The TOC of the original and ozonated samples was measured by high temperature catalytic combustion with an Apollo 9000 organic carbon analyser (Tekmahr - Dohrmann Instruments, USA), whereas the COD of the samples was determined according to [8]; the open reflux titrimetric method. AOX measurements during ozonation of the Biocide 1 formulation were carried out on an AOX/EOX/TOX analyser (Analytik Jena AG, Germany).

3. Results and Discussions

3.1. Ozonation of textile tannins and biocides

It is well-known from ozone chemistry that this strong oxidant can react with organic pollutants in two different ways; via direct reactions of molecular ozone (O3, L) with the compound (cyclo-addition and electrophilic reactions) which is pre-dominant under acidic pH conditions; or indirect reaction mechanisms, namely free radical chain reactions involving hydroxyl radical formation due to enhanced ozone decomposition at elevated pH, particularly at pH > 11.0-11.5 [9].

Table 1 presents ozonation results at varying ozone doses for Tannins 1 and 2 while Table 2 shows ozonation results at different pH values for Biocides 1 and 2 in terms of specific performance parameters. The ozonation parameter being more effective of oxidation performance was selected for presentation of obtained results. From Tables 1 and 2, the positive influence of increasing the ozone dose in terms of COD abatement removals/abatement rates is evident.
For Tannin 1 having an initial COD of 465 mg/L, 64% COD removal was obtained after 1 h ozonation (applied ozone dose = 890 mg; 0.9 mg O3/mg CODo) at pH of 7.0 (data not shown). For Tannin 2 bearing effluent at an initial COD of 1100 mg/L, 28% (applied ozone dose = 900 mg; 1.4 mg O3/mg CODo) at the same pH (data not shown). For both examined textile biocides, the highest COD removal efficiency was obtained in the range of 67-72 % after 1 h ozonation (applied ozone dose = 900 mg; 4.2 mg O3/mg CODo) at a pH of 12.0. COD removal efficiencies typically increased with increasing pH and ozone doses.

**Table 1.** Ozonation of the textile tannins: Effect of ozone dose (COD of the synthetic tannin = 460 mg/L; COD of the natural tannin = 1200 mg/L; ozonation pH = 3.5)

| Tannin 1 | Tannin 2 |
|----------|----------|
| O3 Dose (mg/h) | YO3* | YCOD** | COD Removal (%) | kCODx10^3 (min⁻¹) | YO3* | YCOD** | COD Removal (%) | kCODx10^3 (min⁻¹) |
| 464 | 0.33 | 0.67 | 22 | 5.8 | 0.80 | 0.37 | 30 | 1.21 |
| 1085 | 0.79 | 0.37 | 29 | 9.4 | 1.84 | 0.31 | 58 | 5.15 |

*Specific applied ozone dose (mg O3A/mg CODo).
**COD removal yield (mg ΔCOD/mgO3A).

**Table 2.** Ozonation of the textile biocides: Effect of pH (Average COD of the Biocides = 213 mg/L; Average ozone dose = 895 mg/h)

| Biocide 1 | Biocide 2 |
|----------|----------|
| pH | YO3* | YCOD** | COD Removal (%) | kCODx10^3 (min⁻¹) | YO3* | YCOD** | COD Removal (%) | kCODx10^3 (min⁻¹) |
| 7.0 | 3.00 | 0.17 | 49 | 11.9 | 2.79 | 0.15 | 42 | 10.0 |
| 12.0 | 4.12 | 0.16 | 67 | 18.5 | 3.56 | 0.20 | 72 | 24.7 |

*Specific applied ozone dose (mg O3A/mgCODo).
**COD removal yield (mg ΔCOD/mgO3A).

The AOX content of Biocide 1 originally being 45 mg/L was completely eliminated after 20 min ozonation at a rate of 900 mg/h (applied ozone dose = 300 mg; 1.4 mg O3/mg CODo) at both of the studied pH levels of 7 and 12. AOX abatement proceeded faster at pH 7 than at pH 12 revealing that selectivity is important for dehalogenation reactions (data not shown).

Both biocides and the synthetic tannin (Tannin 1) had negligible BOD₅ contents (< 10 mg/L). The BOD₅/COD ratio was observed to increase after 40 min ozonation (applied ozone dose = 667 mg) for both of the biocide bath discharges (from 0.03 to 0.13 for Biocide 1 and from 0.009 to 0.155 for Biocide 2) and Tannin 1 (from 0.0130 to 0.529) containing segregated effluent, whereas a decrease in the aforementioned ratio was obtained for the natural tannin (Tannin 2) bearing effluent. Tables 3 and 4 summarize BOD₅ values and BOD₅/COD ratios for the tannins and biocides obtained after 40 min ozonation, respectively, under optimized reaction conditions.

Tables 3 and 4 indicate that the biodegradabilities of the biocides and the synthetic tannin were appreciably improved after 40 min ozonation (ozone dose per reaction volume after 40 min = 750 mg/L) at the above mentioned reaction conditions.

3.2. Influences on results

Speaking of the TOC parameter, a substantial enhancement was obtained in terms of TOC removals after ozonation for 2 h at a dose of 900 mg/h (applied ozone dose per reaction volume = 2250 mg/L). TOC removals particularly increased for the synthetic tannin and the textile biocides, namely from 19 to 50%, 12 to 35% and 9 to 56% for Tannin 1, Biocide 1 and 2, respectively, at extended ozone feed rates (data not shown). TOC removal was improved but remained poor for the natural tannin formulation (9% at pH 3.5 and 14% at pH 7.0), most probably due to its higher initial TOC content (340-350 mg/L).
and more complex polyaromatic structure, resulting in a variety of organic ozonation intermediates (incomplete oxidation products).

Table 3. Biodegradability parameters after 40 min ozonation of the textile tannins (Avg. ozone dose = 1000 mg/h; COD of the Synthetic Tannin=460 mg/L; COD of the Natural Tannin=1200 mg/L; BOD₅ of the Synthetic Tannin = < 10 mg/L; BOD₅ of the Natural Tannin = 86 mg/L; ozonation pH = 3.5)

| Tannin   | Specific O₃ Dose (mg O₃/CODₒ) | BOD₅ (mg/L) | BOD₅ /COD* (-) |
|----------|-------------------------------|-------------|---------------|
| Synthetic| 1.45                          | 135         | 0.53          |
| Natural  | 0.56                          | 15          | 0.02          |

*Original BOD₅/COD of the natural tannin = 0.07.

Table 4. Biodegradability parameters after 40 min ozonation of the textile biocides (Applied ozone dose = 600 mg/h; COD of Biocide 1 = 200 mg/L; COD of Biocide 2=216 mg/L; BOD₅ of the Biocides = < 10 mg/L; ozonation pH = 12.0).

| Biocide Nr. | Specific O₃ Dose (mg O₃/CODₒ) | BOD₅ (mg/L) | BOD₅ /COD* (-) |
|-------------|-------------------------------|-------------|---------------|
| 1           | 2.00                          | 9           | 0.13          |
| 2           | 1.85                          | 16          | 0.16          |

**original BOD₅/COD of the biocides < 0.05.

4. Conclusions
The main conclusions that could be drawn from the present study are the following:

- Increasing the ozone dose improved COD removals for the natural tannin. 485 mg/h was found to be the optimum ozone dose at pH = 3.5. For the synthetic tannin, 662 mg/h was the optimum ozone dose at the same pH.

- COD removals of natural tannin showed a slight decrease as the pH of the reaction solution was increased from 3.5 to 7.0, which could be explained by the ozone selectivity for the complex polyaromatic structure of the natural tannin formulation. On the other hand, increasing the pH from 3.5 to 7.0 enhanced COD removals for the synthetic tannin, revealing that the free radical pathway was important for its degradation/oxidation.

- For both biocides, optimum ozone doses of 499 mg/h and 563 mg/h were established considering specific COD removal efficiencies, kinetics and ozone absorption rates.

- Increasing the reaction pH from 7 to 12 had a substantial positive effect on COD removals for both textile biocides due to enhanced free radical production at elevated pH.

- On the other hand, for Biocide 1, a haloaromatic substance, higher AOX removals were obtained at pH = 7 than at pH = 12 which could be attributable to the pronounced selectivity of the dehalogenation reaction at neutral pH.

- Higher TOC removals were observed at the higher studied pH values which could be explained by changes in the reactivity and selectivity of ozone towards the mother pollutants and their oxidation products. Mineralization rates were particularly enhanced for the synthetic tannin and both biocides.

- For the originally refractory synthetic tannin, the BOD₅/COD ratio increased to 0.53 after ozonation, which indicates a fair biological degradability. No improvement was achieved for the biodegradability of the natural tannin that was already fair.

- The BOD₅/COD ratios obtained after ozonation of the extremely recalcitrant biocides increased to the range of 0.13-0.16, which are still low for a subsequent biological treatment step.
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