Rinsing wastewater from dyeing and bleaching processes in a cotton dyeing facility has been separately characterized to evaluate the suitable treatment processes and reuse options. Alternative treatment processes were proposed based on molecular weight distribution (MWD), ultraviolet absorbance of 254 nm (UV254) and specific ultraviolet absorbance (SUVA). Rinsing wastewater samples were sequentially filtrated to determine the MWD of 5-day biochemical oxygen demand (BOD5), chemical oxygen demand (COD), dissolved organic carbon (DOC), total Keldahl nitrogen (TKN) and ammonium (NH4+). Bleaching rinsing wastewater had higher organic and nitrogen contents than dyeing rinsing wastewater and concentrations of pollutants decreased after each membrane filtration step. During the sequential filtration, BOD5/COD ratio in bleaching rinsing wastewater slightly decreased while it significantly increased in dyeing rinsing wastewater. SUVA values indicated that organic matters in the rinsing wastewaters have hydrophilic characteristics in all conditions. The evaluation of all experimental data indicates that combination of anaerobic treatment and NF membrane filtration could provide high quality water for reuse within the facility and discharge into receiving environments.

1. INTRODUCTION

Wastewater from textile dyeing industry is one of the most problematic industrial streams with its large volume and complex pollutant characteristics. Dyeing of textile materials is accompanied with sequential processes of bleaching, dyeing and rinsing. The amount and characteristics of effluents from these processes differ based on dyeing technology and properties of dyeing chemicals. The effluent from dyeing process is characterized by high color and organic pollutants due to the releasing of unfixed dye molecules and insoluble pigments from textile materials to the liquid phase. The main pollutants in dyeing wastewater are suspended and dissolved solids, un-reacted dye

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stuffs (color), organic matter, nitrogen compounds [1, 2]. Discharge of dyeing wastewater without adequate treatment may pose harmful effects on the ecosystem in the receiving bodies. Various single or hybrid biological, chemical, and physical processes have been studied for the treatment of dyeing wastewaters [3–6]. Due to restrictive discharge limits and the shortage of water supply, the textile industry is under pressure to increase reusing water amount and improve the effluent quality of treatment plants. Researchers reported that considerable amount of water could be recycled and reused if the rinsing wastewater is treated after separation from other process streams [7, 8]. Our previous study indicated that the hybrid process of membrane filtration and anaerobic treatment has provided a higher quality of recycled water and treatment of pollutants [9]. It has been reported that the separation of rinsing water provides a simple operation of treatment processes compared to the complexity of the treatment of mixed effluents [10, 11]. On the other hand, separated rinsing wastewater can be easily treated and reused by using membrane filtration while mixed textile wastewater requires pretreatment steps before membrane filtration [12–14].

Conventional performance evaluation of a treatment plant has been accomplished based on the difference between influent and effluent pollutant concentrations. However, molecular weight distribution (MWD) analysis has gained increasing popularity in recent years since it contributes to comprehensive evaluation on the treatment performance of the separate processes and gives accurate information on the fate of pollutants in treatment plants [15–17]. MWD analysis on various treatment processes has revealed that pollutants with low molecular weight (<1 kDa) could be easily degraded in biological treatment processes [15, 18]. On the one hand, chemical treatment and filtration processes are more efficient in removing relatively high-molecular-weight (>5 kDa) pollutants [19, 20]. Moreover, Yaman et al. [17] reported that TKN < 1 kDa is efficiently removed during the anaerobic treatment of cotton-dyeing mill wastewater [9]. In this study, MWD analysis was conducted for the pollutants from dyeing and bleach rinsing wastewaters by sequential filtration. Aromatic compounds were identified by UV absorbance analyses at 254 nm and hydrophobicity of organics were defined by calculating SUVA values. MWD, UV254 absorbance and SUVA values were used to propose alternative treatment processes for the removal of pollutants and water reuse.

2. MATERIALS AND METHODS

Wastewater collection and analyses. Rinsing wastewater samples were obtained from a full-scale cotton dyeing facility in Istanbul, Turkey. Fabrics were colored in subsequent bleaching and dyeing processes. Reactive and direct dye chemicals were applied in dyeing process while sodium hydroxide and hydrosulfite were used in the bleaching process. In coloring process, textile materials were washed once after bleaching and four times after dyeing.
For filtration tests, a total of five rinsing wastewater samples, one from bleaching rinsing (BR) and four from subsequent dyeing washing (DR1, DR2, DR3, and DR4), were collected and stored at 4 °C. All analyses were performed by using analytical-grade chemicals and by following the instructions of standard methods (SM). Organic content of wastewater samples was determined by the analyses of COD, BOD₅ and dissolved organic carbon (DOC). The particulate and the DOC of the organic matter were determined after filtration of samples by using a 100 kDa membrane [21–23]. COD, BOD₅, TKN/NH₄⁺-N were measured according to SMs as SM-5220D, SM-5210B and SM-4500-A, respectively. DOC was measured by using a IL-550 TOC-TN analyzer, Hach Lange. UV₂₅₄ absorbance was measured by using a double-beam UV 1800 (Shimadzu) with 1 nm resolution. Hydrophobic characteristics of organics were determined by specific ultraviolet absorption (SUVA) through dividing UV₂₅₄ absorbance to DOC values.

![Flow chart of sequential filtration for MWD analysis](image)

**Molecular weight distribution (MWD) analysis.** MWD analyses were performed using a stirred membrane cell (Amicon, Model 8400) which has a diameter of 76 mm and an effective membrane area of 41.8 cm². MWD analyses were conducted as described in our previous study [24]. Rinsing wastewater samples were sequentially filtrated by using ultrafiltration membranes (UF) as shown in Fig. 1.

3. RESULTS

3.1. RINSING WASTEWATERS

The characteristics of the raw and rinsing wastewater samples are given in Table 1. COD in raw bleaching wastewater was 4075 mg O₂/dm³ and it decreased to 3500 mg O₂/dm³.
in the bleaching rinsing wastewater. Similar decreasing trend was observed in each washing step of dyeing. COD was 1250 mg O₂/dm³ in raw dyeing wastewater and it gradually decreased to 576 mg O₂/dm³ in the first rinsing and to 171 mg O₂/dm³ in the last washing step.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw bleaching</th>
<th>Raw dyeing</th>
<th>Rinsing process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COD, mg O₂/dm³</td>
<td>4075</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td>BOD₅, mg O₂/dm³</td>
<td>888</td>
<td>204</td>
</tr>
<tr>
<td></td>
<td>BOD₅/COD</td>
<td>0.22</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>DOC, mg C/dm³</td>
<td>1165</td>
<td>234</td>
</tr>
<tr>
<td></td>
<td>TKN, mg N/dm³</td>
<td>112</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>NH₄⁺-N, mg NH₄/dm³</td>
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<td>28</td>
</tr>
<tr>
<td></td>
<td>UV₂₅₄ absorbance</td>
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<td>4</td>
</tr>
<tr>
<td></td>
<td>SUVA, m³/(g·cm)</td>
<td>0.34</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Controversial changes were monitored in the values of BOD₅/COD ratios of bleaching and dyeing wastewaters. BOD₅/COD slightly decreased from 0.22 to 0.20 in wastewater after washing of bleached fabrics, however the ratio increased almost twice from 0.16 in raw dyeing sample to 0.31 in the DR2 sample. It steadily decreased until 0.23 during the following rinsing steps. It seems that aerobic treatment is not suitable for all wastewaters due to the low biodegradability with the BOD₅/COD ratios less than 0.5 [25]. On the other hand, anaerobic processes have been successfully applied in the treatment of low-biodegradable organics [25, 26]. Analysis of nitrogen compounds showed that raw bleaching wastewater was richer in TKN and organic nitrogen than raw dyeing wastewater. Although TKN values decreased in the rinsing both bleaching and dyeing wastewater, NH₄⁺-N amount significantly increased after rinsing of the bleached fabrics, as well as for the first two rinsing steps of dyed fabrics rinsing. However, NH₄⁺-N decreased from 34 to 11.2 mg NH₄⁺/dm³ when dyeing rinsing was completed. Evaluation of COD and NH₄⁺-N values together indicates that nitrogen content of all rinsing wastewaters might be sufficient when the wastewaters are treated in anaerobic conditions.

UV₂₅₄ absorbance and SUVA values had similar trends after each rinsing steps. UV₂₅₄ absorbance gradually decreased from 4 to 0.23 in dyeing rinsing wastewater and to 0.18 in bleaching rinsing wastewater. SUVA decreased from 1.71 m³/(g·cm) in raw dyeing wastewater to 1.45 m³/(g·cm) in the first rinsing bath while it significantly decreased after each rinsing and the final value was 0.25 m³/(g·cm) in the DR4 sample. All raw and rinsing wastewaters from bleaching and dyeing were of hydrophilic nature with SUVA values less than 2 m³/(g·cm), which indicates that conventional coagulation/flocculation is not appropriate treatment process. On the other hand, filtration with
UF and NF membranes is recommended for the treatment of wastewater with low SUVA values.

3.2. ORGANIC MATTERS

COD, BOD₅, and DOC analyses were used to determine the concentrations of organic matters and the dissolved organic matter was characterized with the molecules less than 100 kDa. MWD analyses of those parameters were shown in Fig. 2. COD concentration of the bleaching rinsing wastewater was closer to that of the raw bleaching wastewater while both values were considerably higher than those for dye rinsing wastewaters. During the filtration, COD concentrations considerably decreased upon decreasing the membrane size. 82% of COD passed through 0.1 kDa, whereas only 6% was retained by the membrane of 100 kDa of the rinsing wastewater. The particulate COD fractions (>100 kDa) of DR1, DR2, DR3, and DR4 were 17%, 1%, 26%, and 6%, respectively. These values clearly indicate that considerable amount of COD in dyeing rinsing wastewater was in a soluble form. The soluble COD fractions in the range of 100–0.1 kDa were 35%, 13%, 46% and 37%, respectively. Except DR3 (28%), a significant part of MW fractions (48%, 86%, and 48% for DR1, DR2, and DR4) were less than 0.1 kDa.

Similar to COD concentration, BR had significantly higher BOD₅ of values than the dye rinsing wastewaters. Almost all BOD₅ fractions of the dyeing and bleaching rinsing wastewaters were in a soluble form, while BR had only 3% of particulate form. The BOD₅ fractions less than 0.1 kDa were 77%, 95%, 85%, 80%, and 80% for DR1, DR2, DR3, DR4, and BR, respectively. These values indicated that BOD₅ of rinsing wastewaters mainly originated from organic matters with MW < 0.1 kDa and could be easily consumed by microorganisms.

Bleaching rinsing wastewater had considerably higher DOC values than DOC of dyeing rinsing wastewaters. Particulate DOC ratios in the rinsing wastewaters were 3%, 14%, 9%, and 5% for DR1, DR2, DR3, DR4, and BR, respectively. On the other hand, DOC fractions <0.1 kDa were 76%, 74%, 56%, 51%, and 85% for DR1, DR2, DR3, DR4, and BR, respectively. Similar to COD and BOD₅, most of the DOC in the rinsing wastewaters was in soluble form. The values of DOC/COD and BOD₅/COD ratios for each fraction are shown in Fig. 3. The DOC/COD of BR changed between 0.80 and 0.85 while the ratio varied between 0.45 and 0.91 for dyeing rinsing wastewaters. Figure 3 demonstrates that organic carbon content of dyeing rinsing slightly increased for low molecular fraction whereas it almost remained stable for bleaching rinsing wastewater.

The BOD₅/COD ratio in BR did not change during the sequential filtration and it was lower than 0.3 in all molecular fractions. However, BOD₅/COD ratios of dyeing rinsing increased with a decrease in molecular weight and they were between 0.3 and 0.4 for DR1, DR2, and DR4. For DR3, BOD₅/COD ratio increased from 0.28 to 0.47 and 0.85 at the 10 and 0.1 kDa fractions, respectively. It could be concluded that DR3
is suitable for aerobic treatment. The BOD₅/COD ratio also increased from 0.21 and 0.23 to 0.33 and 0.39 after 0.1 kDa fractioning of DR1 and DR4, respectively. Nearly all fractions of the DR1, DR2, DR4 and BR wastewaters had relatively low biodegradability with BOD₅/COD of less than 0.30.

Fig. 2. MWD of organic matter for rinsing wastewater
These low-degradable wastewaters could be effectively treated by anaerobic treatment processes. Anaerobic treatment is effective for the removal of low-molecular organics while the remaining organics in the anaerobic effluent can be efficiently polished by RO and NF membranes. On the other hand, chemical treatment and filtration processes are efficient for the removal of organics with molecular weight higher than 3–5 kDa [18]. Thus, individual application of those treatment processes is not recommended for the removal of organic matters from rinsing wastewater in a textile dyeing facility.

3.3. UV$_{254}$ ABSORBANCE AND SUVA

The values of UV$_{254}$ absorbance and SUVA during the filtration of rinsing wastewaters are given in Fig. 4. In all cases, the absorbances UV$_{254}$ constantly decreased upon decreasing molecular weight. After the filtration with 0.1 kDa membrane, UV$_{254}$ absorbance values decreased by 94% for DR1, 97% for DR2, 95% for DR3, 87% for DR4, and 68% for BR. The highest UV$_{254}$ absorbances were obtained with DR1 which indicates the high amount of aromatic organic dyes whereas the concentrations of COD, BOD$_5$, and DOC in BR were higher for BR than for DR1. Particularly in the case of COD, most organic fraction (82%) of BR was less than 0.1 kDa. Experimental results
indicated that filtration with a UF membrane with a MWCO of 1 kDa could provide removal efficiencies of 95%, 93%, 85%, 65% and 65% for DR1, DR2, DR3, DR4 and BR wastewaters, respectively.

Fig. 4. UV254 absorbances and SUVA values of rinsing wastewaters for various molecular fractions of organic matter

SUVA values were lower than 2 m$^3$/(g·cm) for all raw and fractionated rinsing wastewaters (Fig. 4) pointing to the hydrophilic characteristics of organic matters in all cases. Comparison of SUVA values revealed that BR is considerably more hydrophilic than dyeing wastewaters since most of the BR had a MW < 0.1 kDa. Filtration with membrane of 0.1 kDa could reduce SUVA values by about 92% for DR1, 95% for DR2, 91% for DR3, 76% for DR4, and 63% for BR (Fig. 4). Based on these results, it can be concluded that filtration with NF and RO membranes may be effective for reducing SUVA from dyeing rinsing wastewater while membrane filtration is not suitable for bleaching wastewater. Furthermore, conventional coagulation/flocculation processes are not recommended for rinsing wastewaters due to the low treatment efficiency with hydrophilic organics [27, 28].
3.4. TKN AND NH₄⁺

The TKN and NH₄⁺ concentrations in wastewater samples for various fractions of rinsing wastewaters are presented in Fig. 5. In all cases, these concentrations were higher in BR than in the DR1, DR2, DR3 and DR4 fractions. Almost half of TKN in BR was NH₄⁺ however, TKN in dyeing rinsing wastewater was mainly composed of NH₄⁺. Evaluation of the amounts of TKN and NH₄⁺ with organic matter indicates that rinsing wastewaters have sufficient nitrogen content for aerobic and anaerobic treatment processes.

The removal of the TKN from the DR3 and DR4 wastewaters by membrane filtration was very low, 13% and 16%, respectively for 1 kDa membrane. In general, no significant difference was observed in the removal of TKN and NH₄⁺ during the membrane filtration with membranes of MWCO less than 10 kDa. Final filtration with 0.1 kDa membrane reduced TKN and NH₄⁺ concentrations about 26% and 51% for DR1, 37% and 42% for DR2, 17% and 18% for DR3, 13% and 14% for DR4, and 25% and 24% for BR, respectively. These low treatment efficiencies revealed that NF membranes
were not effective to remove TKN and NH$_4^+$+. Similarly, other authors reported that conventional coagulation/flocculation is not effective for removing TKN and NH$_4^+$+. However, Zaho et al. [29] found that a low molecular-weight organic nitrogen could be effectively removed by biological treatment processes. Moreover, UF and NF membranes can be used as a polishing step to remove intermediate parts of the TKN (>1 kDa and <100 kDa) from the effluents of anaerobic treatment [30].

4. CONCLUSIONS

Changes in the molecular weight distribution (MWD) of pollutants in rinsing wastewaters of bleaching and dyeing processes were evaluated based on MWD analysis of pollutants along with hydrophobicity of organic substances. The results are summarized below:

- MWD analysis is useful to separately characterize rinsing processes in a textile dyeing facility and to evaluate the alternative treatment process for reuse purposes.
- Organic content of rinsing wastewaters is mainly composed of fractions less than 0.1 kDa and the low BOD$_5$/COD ratios suggest the application of anaerobic treatment together with membrane filtration for efficient removal of organics.
- Rinsing wastewaters contain hydrophilic organics with SUVA values lower than 2. Conventional coagulation/flocculation is not a proper method for those organics while membrane filtration can be applied for effective treatment.
- Most of TKN is composed of substances with MW less than 1 kDa and it can be effectively removed by the anaerobic treatment process. The amount of nitrogen compounds in bleaching and dyeing rinsing wastewaters is sufficient for the biological treatment processes. By selecting the appropriate treatment method, textile rinsing wastewaters could be reused and amount of water consumption might be reduced.

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