Comparison of coagulation, ozone and ferrate treatment processes for color, COD and toxicity removal from complex textile wastewater
Sameena N. Malik, Prakash C. Ghosh, Atul N. Vaidya, Vishal Waindeskar, Sera Das and Sandeep N. Mudliar

ABSTRACT
In this study, the comparative performance of coagulation, ozone, coagulation + ozone + coagulation and potassium ferrate processes to remove chemical oxygen demand (COD), color, and toxicity from a highly polluted textile wastewater were evaluated. Experimental results showed that ferrate alone had no effect on COD, color and toxicity removal. Whereas, in combination with FeSO₄, it has shown the highest removal efficiency of 96.5%, 83% and 75% for respective parameters at the optimal dose of 40 mL L⁻¹ + 3 mL FeSO₄ (1 M) in comparison with other processes. A seed germination test using seeds of Spinach (Spinacia oleracea) also indicated that ferrate was more effective in removing toxicity from contaminated textile wastewater. Potassium ferrate also produces less sludge with maximum contaminant removal, thereby making the process more economically feasible. Fourier transform infrared spectroscopy (FTIR) analysis also shows the cleavage of the chromophore group and degradation of textile wastewater during chemical and oxidation treatment processes.

Key words | coagulation, ferrate treatment, ozone, textile wastewater

INTRODUCTION
The textile industry produces large quantities of wastewater, varying significantly in composition (Correia et al. 1994). Textile wastewater is highly colored, toxic and non-biodegradable as it has a biochemical oxygen demand (BOD) to chemical oxygen demand (COD) ratio of less than 0.1, and color removal efficiency of only 10–20% (Correia et al. 1994). Biological methods alone are not efficient in treating such types of wastewaters, as their degradation products can be of a toxic nature (Petrick et al. 2014). Considering the hazardous impact of textile wastewater on the environment, it is of great concern to find an effective method of wastewater treatment for the removal of color and toxic organic/inorganic compounds from textile wastewater. Currently, many textile industries are using an activated sludge process followed by a chemical coagulation process for wastewater treatment. However, sludge generation is a big problem, as further sludge treatment is required. The other commonly used physicochemical methods such as membrane filtration or activated carbon adsorption are expensive and commercially not feasible, as these processes transform the pollutant rather than eliminating them from the wastewater domain. Therefore, advanced treatment processes need to be developed for effective treatment to further reduce color and toxicity to meet the stringent discharge standards. These limitations can be addressed by using the advanced oxidation processes (AOPs), which have been extensively studied for the treatment of reactive dyes in aqueous solutions (Blanco et al. 2012; Módenes et al. 2012; Byberg et al. 2013; Nidheesh et al. 2015). AOPs particularly involve the generation of the hydroxyl radical (OH⁻), a highly powerful and non-selective oxidizing agent, for the degradation of refractory and hazardous contaminants present in groundwater, surface water and industrial wastewater (Oller et al. 2011). Hydroxyl radicals produced in AOPs attack the organic molecules by abstracting the hydrogen atom from the molecule through a common pathway as reported by...
The process is described as follows:

$$\text{OH}^* + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^*$$

$$\text{R}^* + \text{H}_2\text{O}_2 \rightarrow \text{ROH} + \text{OH}^*$$

$$\text{R}^* + \text{O}_2 \rightarrow \text{ROO}^*$$

$$\text{ROO}^* + \text{RH} \rightarrow \text{ROOH} + \text{R}^*$$

AOPs are considered to be the potential technologies for complete removal of pollutants from wastewater. However, these processes are only effective for wastewater with low concentrations of organic dyes, and also the dilution of wastewater is required. Further, these processes are too expensive and complex for textile wastewater treatment at the present level of their development (Sanja et al. 2004). In recent years, a higher valent tetraoxy iron (VI) \([\text{FeVIO}_4^{2-}, \text{Fe(VI)}]\), commonly termed as ferrate, is being used for water and wastewater treatment. It is a very strong oxidant with a reduction potential of 2.20 V and 0.70 V in acidic and alkaline solutions, respectively (Wood 1958). In addition, Fe(VI) upon decomposition in water gives molecular oxygen and Fe(III), thus making Fe(VI) as an alternative anion for coagulation, disinfection, and oxidation for treatment of water and wastewater (Jiang & Lloyd 2002; Sharma 2002, 2004). These unique characteristics of ferrate (VI) have attracted many researchers to evaluate its performance for wastewater treatment in comparison with commonly used oxidants and coagulants, e.g. chlorine, chlorine dioxide, permanganate, ferric sulphate, hydrogen peroxide, and ozone. AOPs (which involve \(\text{H}_2\text{O}_2/\text{Fe}^{2+}\), ozone, Fenton, \(\text{H}_2\text{O}_2/\text{UV}\) etc.) have been thoroughly and comparatively investigated. These processes are also demonstrated for effective removal of color and/or organic content of the textile wastewater (Schrank et al. 2007; Karthikeyan et al. 2011). This study evaluates the removal of raw textile dye house wastewater toxicity using ferrate treatment and ozone (O\(_3\)) oxidation with a conventionally used coagulation process. The effectiveness of the processes was measured by color, COD and toxicity removal.

### Materials and Methods

#### Raw wastewater

Raw textile wastewater was collected from a mercerization unit of a textile industry located in Saoner, Nagpur, India, manufacturing cotton fabric. Mercerization is performed most exclusively on pure cotton fabrics, which are treated with a concentrated caustic soda bath and a final acid wash in order to neutralize them. The wastewater collected was stored at 4°C and brought to room temperature prior to each experiment. The detailed characteristics of textile wastewater are presented in Table 1.

#### Potassium ferrate preparation and characterization

Ferrate salts are generally produced using three methods via wet chemical, electrochemical and thermal processes. In this study, ferrate was prepared by the wet chemical method. Ferric chloride is oxidized by hypochlorite in a highly alkaline solution (prepared by using NaOH) to give a highly soluble Na\(_2\)FeO\(_4\). Potassium ferrate salt with high Fe(VI) purity of 99% is precipitated from the Na\(_2\)FeO\(_4\) solution after adding KOH. The resulting ferrate was then dried, and the solid ferrate thus produced was characterized. The ferrate concentration was measured using the chromate titration method based on the oxidation of Cr(III) salt by the ferrate and back titration of Cr(VI) with the ferrous solution (Vicenteperez et al. 1988). Potassium ferrate was also characterized in the wavelength range of 200–1,100 nm; ferrate salt has absorption at 500 nm and 800 nm (Wood 1958).

#### Ozone setup

Ozone gas was generated using an ozone generator (PCI Ozone Corporation-Model INDO2-7, Ozone Research & Applications India Pvt. Ltd, Nagpur, India) by the Corona Discharge Method with water cooling. Oxygen used as feed gas was supplied from an oxygen cylinder at a uniform flow rate of 1 L/min. The experimental setup used for the ozonation experiments is shown in Figure 1. Ozone flow

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
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<tbody>
<tr>
<td>pH</td>
<td>9</td>
</tr>
<tr>
<td>Color</td>
<td>8,000 PCU</td>
</tr>
<tr>
<td>COD</td>
<td>6,980 mg L(^{-1})</td>
</tr>
<tr>
<td>BOD</td>
<td>1,400 mg L(^{-1})</td>
</tr>
<tr>
<td>TOC</td>
<td>2,950 mg L(^{-1})</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>400–550 mg L(^{-1})</td>
</tr>
<tr>
<td>Total solids</td>
<td>1,150–1,200 mg L(^{-1})</td>
</tr>
</tbody>
</table>

Average of 3 sets of data with SD < 5%.
was regulated by monitoring the gas flow rate. Ozonation was carried out in a semi-continuous mode by sparging the ozone into the wastewater. The ozone gas inlet and outlet concentration was measured every 20 min during the oxidation process using a UV analyzer (BMT 964, Berlin). All the ozonation experiments were conducted at room temperature in a well-ventilated laboratory to avoid ozone toxicity.

**Experimental procedure**

The wastewater was brought to room temperature before pretreatment studies. The jar test procedure was used to carry out the coagulation experiments at room temperature. The different combinations of coagulants (FeSO₄ and CaCl₂) along with KMnO₄, as given in Table 2, were added to the flask containing 500 ml of filtered textile wastewater and mixed for 2 min at 200 rpm with a magnetic stirrer. The treated samples were allowed to settle for 30 min and analyzed for COD and color. Also different doses of ozone (0.1–0.5 g/hr) were supplied to the wastewater (500 ml) for different intervals of time (15–60 min). Pretreated samples were collected after every 15 min for COD and color analysis. Further experiments were carried out in the combination of different coagulation doses (as given in Table 2) before and after ozonation at an optimized ozone condition. Ferrate experiments were also carried out in a one liter conical flask with 500 ml wastewater at various ferrate doses (20–200 mg L⁻¹) along with FeSO₄ [1 M] at different concentrations (2–20 ml/litre of wastewater) and mixed using a magnetic stirrer at 200 rpm. All the experiments were carried out at the initial pH without pH adjustment. Samples were collected at regular intervals of time and filtered for color and COD analysis. A seed germination test was conducted for each treated and raw wastewater to determine the toxicity removal of wastewater.

**Analytical methods**

COD was analyzed using the open reflux method as per the standard method (APHA 1998). The pH of the wastewater was monitored using a pH meter (Control Dynamics). For color measurement, the samples were centrifuged at 5,000 rpm for 20 min and the supernatant was diluted 10 times with distilled water. The resulting color of the diluted wastewater and mixed for 2 min at 200 rpm with a magnetic stirrer. The treated samples were allowed to settle for 30 min and analyzed for COD and color. Also different doses of ozone (0.1–0.5 g/hr) were supplied to the wastewater (500 ml) for different intervals of time (15–60 min). Pretreated samples were collected after every 15 min for COD and color analysis. Further experiments were carried out in the combination of different coagulation doses (as given in Table 2) before and after ozonation at an optimized ozone condition. Ferrate experiments were also carried out in a one liter conical flask with 500 ml wastewater at various ferrate doses (20–200 mg L⁻¹) along with FeSO₄ [1 M] at different concentrations (2–20 ml/litre of wastewater) and mixed using a magnetic stirrer at 200 rpm. All the experiments were carried out at the initial pH without pH adjustment. Samples were collected at regular intervals of time and filtered for color and COD analysis. A seed germination test was conducted for each treated and raw wastewater to determine the toxicity removal of wastewater.

**Table 2 | Different doses of coagulants added per 500 ml of wastewater**

<table>
<thead>
<tr>
<th>Doses</th>
<th>(KMnO₄(0.1 M) + FeSO₄(1 M) + CaCl₂(1 M)) in mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose 1</td>
<td>2.5 + 5 + 7.5</td>
</tr>
<tr>
<td>Dose 2</td>
<td>5 + 10 + 15</td>
</tr>
<tr>
<td>Dose 3</td>
<td>7.5 + 15 + 22.5</td>
</tr>
<tr>
<td>Dose 4</td>
<td>10 + 20 + 30</td>
</tr>
<tr>
<td>Dose 5</td>
<td>12.5 + 25 + 37.5</td>
</tr>
</tbody>
</table>

Average of 3 sets of data with SD <5%.
sample was measured using a colorimeter (Hanna Instruments, Model HI83200). The total organic carbon (TOC) of the wastewater was analyzed using a TOC analyzer (Shimadzu). The Fourier transform infrared (FTIR) spectrum of the wastewater was recorded using FTIR (Bruker, Vertex 70) before and after treatment. The FTIR spectra were taken in the range of 400–4,000 cm\(^{-1}\) by making pellets with KBr.

**Seed germination test**

Seed germination tests were carried out to assess the reduction in toxicity of the pretreated effluent as per the protocol reported by Chandra et al. (2014). The pretreated samples were centrifuged and filtered using Whatman filter paper. 10 mL of filtrate was transferred to a Petri dish, and 10 seeds of Spinach (Spinacia oleracea) were placed in each petri dish and incubated at 28 °C. The experiment was conducted for 10 days, and the germinated seeds were counted at the initial appearance of radical formation. The percentage of germination (GP) was calculated using the equation (Zanjani & Asli 2012):

\[
GP = \frac{\text{Number of seeds germinated}}{\text{Number of seeds planted}} \times 100
\]

**RESULTS AND DISCUSSION**

**Effect of coagulation on color and COD removal**

In general, the coagulation process has been extensively used for COD and color removal from textile wastewater, with certain limitations (Lin & Lin 1994; Gohary & Tawfik 2009). In this study, FeSO\(_4\) [1 M] and CaCl\(_2\) [1 M] coagulants along with KMnO\(_4\) [0.1 M], were used in four different combinations with a constant ratio of 1:2:3 at an initial wastewater pH of 9. The experiments were also conducted with different ratios such as 1:1:1, 1:2:1 etc. as well as with a single coagulant (data not shown). However, effective color and COD reduction has been obtained for the reported ratio with varying doses. KMnO\(_4\) has been added with the coagulants, as the use of permanganate along with coagulant lowers the coagulant dose requirement and improves clarification. The COD and color removal of wastewater with different combinations of coagulant doses are shown in Figure 2. It is clear that at low concentrations of coagulant very little COD and color removal was obtained, i.e. 16 and 20%, respectively. Increasing the coagulant doses (up to dose 3) resulted in a sharp increase in color as well as COD removal with the highest color and COD deduction of 52 and 54%, respectively. Since no further increase in COD and color removal was obtained with the increased concentration of coagulant, dose 3 was considered as an optimum coagulant dose. Coagulation in the wastewater is generally defined as the destabilization of dissolved and suspended solids giving rise to aggregation to facilitate its removal by a subsequent sedimentation process. In the present study, higher doses of coagulants resulted in decreased COD and color removal. This may be due to the precise nature of the charge-neutralizing species, charge reversal which can lead to restabilization of colloids in wastewater at high dosages of coagulants. Thus, probably there were no sites vacant on the particle surfaces for the formation of interparticle bridges. The restabilized colloidal particles can become positively charged and instigate electrostatic repulsion amid the suspended solids (Hassan et al. 2012; Chee et al. 2016). In a related study (Süreyya et al. 2005) COD and color removal via coagulation with FeSO\(_4\) was reported to be 56% and 85%, respectively at pH 9 using 1,250 mg L\(^{-1}\) of FeSO\(_4\). Azbar et al. (2004), has reported color removal of 49.2% at a dose of 350 mg L\(^{-1}\) of FeSO\(_4\). It is highly difficult to remove the soluble dyes present in the textile wastewater using coagulation. Therefore, it is important to combine the coagulation process with other processes such as AOP to achieve an acceptable effluent discharge standard specifically with respect to color and COD.

**Effect of ozone pretreatment on color and COD removal**

Ozone is a strong oxidizing agent compared to other oxidizing agents like chlorine, H\(_2\)O\(_2\), Fenton etc. due to its high instability, with an oxidation potential of 2.07. It has a high efficiency of color removal and it is capable of degrading chlorinated hydrocarbons, phenols, and aromatic
hydrocarbons at high pH values due to the higher decomposition of ozone favored by the formation of hydroxyl radicals (Azbar et al. 2004; Souza et al. 2010). The comparative evaluation of ozone for color and COD removal of textile wastewater at different doses (0.1–0.5 g/h) is shown in Figure 3. The COD and color removal efficiency varied from 10–38% and 22–52%, respectively. There was no significant increase in the process efficiency after 45 min of reaction time at an ozone dose of 0.3 g/hr, which resulted in 52% color and 38% COD removal. From these results, it is evident that the ozonation reaction rate for color and COD removal practically becomes mass transfer limited after a threshold ozone input dose for 45 min. In a similar study, 15 min of O₃ (1.4 g L⁻¹ h⁻¹) pretreatment has been reported for 33% COD removal and 91% color removal of textile industry wastewater (Süreyya et al. 2005).

**Effect of coagulation + ozone + coagulation pretreatment on color and COD removal**

It was reported that ozone in the presence of a catalyst such as H₂O₂ and UV radiation produces a large number of OH⁻ radicals. These radicals are more reactive than the parent compounds and thereby increase the color and COD removal efficiency. In this regard, from the economic point of view, due to the high cost of H₂O₂ and UV radiation compared to coagulants, the ozone (0.3 g/hr for 45 min) treated effluent was pre- and post-coagulated using different combinations of coagulant concentrations (Table 2). As depicted in Figure 4, the combined pretreatment process was found to be effective for COD and color removal, with maximum COD and color removal of 72% and 80% at pretreatment dose 3. Moreover, the COD and color removals obtained at doses 1, 2, and 4 were still higher compared to ozone and coagulant processes used alone. In literature, the effect of the coagulation process in combination with ozone for textile industry wastewater has reported 90% residual color removal and 20–25% COD removal (Tzitzi et al. 1994).

**Effect of ferrate treatment on color and COD removal**

Ferrate exhibits multiple advantages as an oxidant and disinfectant, as it is a strong oxidizing agent with an oxidation potential of 2.2 and 0.7 in acidic and basic media. The doses of ferrate studied ranged from 20 to 200 mg/l of wastewater. In this study, experiments were carried out at alkaline pH, though the ferrate activity is highest at acidic pH. This is due to the fact that at higher pH the oxidizing power of the ferrate (VI) ions is lower, but the oxidation of water is much slower, with the result that ferrate oxidizes the chemical species to be removed rather
than the water. Whereas, when the pH is acidic, such ions oxidize water very quickly and convert them into Fe(III) ions and gaseous oxygen (Ciabatti et al. 2010). It was observed that ferrate alone was not effective for color and COD removal. However, in combination with FeSO\(_4\) (1–10 ml), ferrate has shown the highest color and COD removal efficiency. The ferrate pretreatment effect on color and COD removal of textile wastewater is illustrated in Figure 5. It was found that the removal efficiency increases by increasing the ferrate doses up to 40 mg L\(^{-1}\) with 3 ml FeSO\(_4\) (1 M) (COD and color removal of 83% and 96.5%, respectively); at higher ferrate doses COD and color removal, efficiency decreases. It is plausible when the potassium ferrate dose is greater than 40 mg L\(^{-1}\), more ferric ions are produced, which leads to the increase in color. Studies have already proved that the COD and color removal efficiency decreases when the potassium ferrate dose is greater than some value (Sun et al. 2011; Wu & Lan 2011). The oxidative mechanism of ferrate for maximum efficiency at an optimal dose can be described by means of the kinetics of the ferrate reaction in an aqueous solution. The ferrate ion reacts with water and solute in aqueous solution by two different pathways. The reaction of the ferrate ion with water is of the second order with respect to Fe(VI) concentration.

\[
-d[\text{Fe(VI)}]/dt = k_1[\text{Fe(VI)}][\text{Fe(VI)}]
\]

while the reaction of the ferrate ion with the solute is of the first order, as follows

\[
-d[\text{Fe(VI)}]/dt = k_2[\text{Fe(VI)}][P]
\]

where [P] is the concentration of the compound that reacts with the ferrate. When \(k_2[P] > k_1[\text{Fe(VI)}]\), i.e. \([\text{Fe(VI)}] < (k_2/k_1)[P]\), reaction of ferrate with a compound in aqueous solution predominates the reaction with water. Hence, when the concentration of Fe(VI) is higher than \((k_2/k_1)[P]\), the reaction with water prevails (Ciabatti et al. 2010). The high oxidation efficiency of ferrate for removing COD is attributed to the highest oxidation potential of ferrate compared to the other oxidants applicable to wastewater treatment. The comparative performance of potassium ferrate(VI), ferric sulphate (FS) and aluminum sulphate (AS) for the removal of turbidity, COD, color and bacteria in sewage treatment is reported. Potassium ferrate is reported to remove 50% more color and 30% more COD in comparison to AS and FS at the same or at lower doses (Jia et al. 2006). Similarly, COD removal of 96% at laboratory scale and 40% at pilot scale was reported by using potassium ferrate treatment on dyeing wastewater, indicating the strong capability of ferrate for oxidizing complex organic compounds (Ciabatti et al. 2010).

**FTIR spectroscopic studies**

The FTIR spectra of the control and treated textile wastewaters via different treatment processes are shown in Figure 6. The FTIR spectrum of untreated textile wastewater had the characteristic sharp peaks at 3,476, 2,935, 2,496, 1,774, 1,689, 1,587, 1,449, 1,336, 1,298, 1,156, 824, 724 and 626 cm\(^{-1}\). However, the disappearance of the peaks during different treatment processes can be explained by the degradation of organic compounds and the formation of new compounds as intermediate organic compounds (Raghu et al. 2009). The peak at 1,449 cm\(^{-1}\) represents the azo group (C = N), which is a chromophore group that may give a colored compound (Zhao et al. 2010). The decrease in the intensity of the peak at 1,449 cm\(^{-1}\) in the treated textile wastewater corresponds to color removal during the different treatment processes. The corresponding probable functional groups of untreated and treated textile wastewater are summarized in Table 3.
Toxicity removal

The pretreated effluent via coagulation, ozone and ferrate was further subjected to a seed germination test to evaluate the toxicity removal with spinach seeds. The appearance of radicals in the Petri plate indicated the seed germination. Toxicity test was only carried out for an optimized condition of each pretreatment process. The effluent treated with coagulation showed only 32% toxicity removal, whereas 45 and 58% toxicity of effluent was removed during ozone and combined pretreatment (coagulation + ozone + coagulation) processes respectively (Figure 7). The ferrate treated effluent showed the highest toxicity removal of 75%, and no seed germination was observed with untreated effluent. Toxicity removal observed during various pretreatment experiments may be because of the conversion of recalcitrant or complex organic/inorganic compounds into the less toxic compounds. In a similar way, complete toxicity removal from textile wastewater using the Daphnia magna test was reported using Fenton and ozone oxidation processes (Süreyya et al. 2005).

Sludge production

During pretreatment processes, sludge generation is a major issue as further treatment processes are required to eradicate the sludge. Hence it is necessary to compare the performance of pretreatment processes for sludge production. A cone shaped vessel called an Imhoff cone was used to study sludge production under the optimum operating conditions of various pretreatment processes. About 0.5 L of textile effluent was placed into the Imhoff cone, then the respective optimized doses of different pretreatment processes via coagulation, ozone, coagulation + ozone + coagulation and ferrate were added and mixed rapidly at a speed of 200 rpm for their respective optimized pretreatment time. After mixing properly for an optimized period, the solution was allowed to settle for at least 60 min. The sludge production (dry basis) obtained was measured and is shown in Figure 8. It is observed that very little quantity of sludge was produced during ferrate treatment with the highest COD and color removal efficiency compared to the other pretreatment processes. It has to be emphasized that for a lower COD and color removal with coagulation treatment, a larger amount of sludge is formed. Whereas, the sludge formation during ozone and combined treatment (coagulation + ozone + coagulation) processes is less, but still higher than ferrate treatment, as illustrated in Figure 8. A pretreatment process with good performance and less sludge generation is the basic requirement of most of the water and wastewater industries. Hence ferrate or ozone in combination with a coagulation process is recommended for the complex textile wastewater treatment.
Cost evaluation

The overall costs are characterized by the sum of the capital costs, the operating costs, and maintenance. For a large-scale system, these costs intensely depend on the flow rate of the effluent and the design of the reactor as well as the type of the effluent. In this study, labor cost was excluded and only operating costs such as the costs of reagents (potassium ferrate: 45 $/kg; FeSO₄·7H₂O: 0.08 $/kg; CaCl₂: 0.264 $/kg; KMnO₄: 1.97 $/kg; O₃: 0.36 $/kg) and electricity (0.1 $/kWh) consumption were considered. A comparative cost evaluation is given in Table 4. Although the cost of ferrate treatment among other methods studied was found to be higher, it has shown the best result (83% removal for COD and 96.5% removal of color), and seems to be a more sustainable solution for the cotton dyeing effluent on the basis of lower sludge generation and higher toxicity removal (75%).

### Table 3 | Peak position and corresponding probable functional group of untreated and treated textile wastewater

<table>
<thead>
<tr>
<th>Peak position</th>
<th>Control</th>
<th>Coagulation</th>
<th>Ozone</th>
<th>Coag + Ozone + Coag</th>
<th>Ferrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,476</td>
<td>3,478</td>
<td>3,438</td>
<td>3,498</td>
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<tr>
<td>2,935</td>
<td>–</td>
<td>2,956</td>
<td>–</td>
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<tr>
<td>2,496</td>
<td>–</td>
<td>–</td>
<td>2,357</td>
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<tr>
<td>1,774</td>
<td>1,766</td>
<td>1,769</td>
<td>–</td>
<td>–</td>
<td>1,771</td>
</tr>
<tr>
<td>1,689</td>
<td>–</td>
<td>–</td>
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<td>724</td>
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<tr>
<td>626</td>
<td>623</td>
<td>663</td>
<td>655</td>
<td>627</td>
<td></td>
</tr>
</tbody>
</table>

Probable functional group

1. N-H₂ asymmetric stretching vibration of free NH₂
2. O-H stretching vibration of single bridged compound
3. C-H asymmetric and symmetric stretching of alkane
4. N-H₂ asymmetric stretching of NH₂ salt
5. N-H stretching of anhydrides
6. O = C-NH bending of amide
7. C-C asymmetric and symmetric stretch (in ring) of aromatics
8. 1 C-C stretch (in ring) of aromatics
9. 2 C-H bending of alkanes
10. N-O symmetric stretch of nitro compounds
11. C-N stretch of aromatic amines
12. 1 C-H stretch of alkyl halides
13. 2 C-N stretch of aliphatic amines
14. 1 N-H strong and broad stretching of primary and secondary amines
15. 2 C-H strong stretching of aromatics
16. 3 C-Cl medium stretching of alkyl halides
17. C-H rock medium stretching of alkanes
18. -C = C-H broad and strong stretch of alkynes

**Figure 7** | Effect of pretreatment processes on toxicity removal of textile wastewater (data are the averages of the values obtained in independent experiments conducted in triplicate).

**Figure 8** | Sludge produced during different pretreatment processes (data are the averages of the values obtained in independent experiments conducted in triplicate on a dry basis).
Table 4 | Operating costs for the studied processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Cost ($/m³)</th>
<th>COD removal (%)</th>
<th>Color removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation</td>
<td>2.64</td>
<td>54</td>
<td>52</td>
</tr>
<tr>
<td>Ozone</td>
<td>1.17</td>
<td>38</td>
<td>52</td>
</tr>
<tr>
<td>Coagulation + ozone + coagulation</td>
<td>6.46</td>
<td>72</td>
<td>80</td>
</tr>
<tr>
<td>Ferrate</td>
<td>4.5</td>
<td>83</td>
<td>96.5</td>
</tr>
</tbody>
</table>

CONCLUSION

In this study, pretreatment of complex textile wastewater with very high color and COD was carried out. Coagulation, ozone, coagulation + ozone + coagulation and ferrate for color, COD, and toxicity removal was investigated. All the pretreatment processes were effective in removing color, COD, and toxicity of wastewater. However, the application of coagulation is still difficult due to the higher volume of sludge production and chemical consumption, whether used alone or in combination with ozone treatment. In this study, ferrate at a very low concentration was more effective in removing color, COD, and toxicity along with a lesser quantity of sludge production.

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