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Application of Advanced Oxidation Processes for the Treatment of Color and Chemical Oxygen Demand of Pulp and Paper Wastewater

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Abstract: The present study was conducted in order to investigate the efficiency of different advanced oxidation processes both individually and in combination with the biological method for the removal of color and chemical oxygen demand (COD) from wastewater in the pulp and paper industry. Advanced oxidation processes include ozone, Fenton, hydrogen peroxide, and photo-Fenton. Biologically treated wastewater was successively subjected to advanced oxidation processes (AOPs). The optimum conditions for the ozone treatment of raw wastewater were found to be a contact time of 9 min and a pH of 5 at a fixed dose of ozone for a removal efficiency of 41.22% for color and 88.53% for COD. Similar optimum conditions for the ozone treatment of biologically treated wastewater showed a removal efficiency of 46.36% for color and 95.92% for COD. The photo-Fenton process also showed an efficiency comparable to the ozone treatment for both raw wastewater and biologically treated wastewater, resulting in a removal efficiency of 39.85% (color) and 90.13% (COD) for raw wastewater, and of 41.34% (color) and 94.29% (COD) for biologically treated wastewater. Each had a contact time of 12 h. The Fenton oxidation of raw wastewater showed a removal efficiency of more than 26.30% for color and 86.33% for COD. Fenton oxidation, however, showed an efficiency of 26.62% for color and 84.49% for COD removal from biologically treated wastewater. Hydrogen peroxide showed an efficiency of 28.45% for color and 85.13% for COD removal from raw wastewater, and 39.48% for color and 86.53% for COD removal from biologically treated wastewater. The results for the raw wastewater treatments indicated that higher removal efficiencies can be achieved when they are used as pre-treatments. Biological treatment is a cost-effective method but it has less efficiency for color removal. In combination with one of the AOPs, either as a pre- or post-treatment under a controlled time and dose, biological treatment increased the efficiency, making treatment feasible at larger scales.

Keywords: industrial wastewater; pollution control; wastewater treatment; chemical oxygen demand; environmental management

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1. Introduction

The paper industry is the world's sixth largest polluting industry and the tenth largest industry in Pakistan; per capita, paper consumption in the country is 3.5 kg/year. Most paper industries are located in the Punjab province of Pakistan [1–3]. One of the major contributors to water pollution is the pulp and paper industry. The effluent of the paper and pulp industry has high concentrations of salts, total suspended solids, chemical oxygen demand (COD), color, nutrients, and toxic compounds (e.g., chlorinated organic compounds, surfactants, and metals). Therefore, wastewater from such industries has severe impacts on the receiving water bodies. Furthermore, the discharge of colored effluents (due to black liquor) into the aquatic environment causes visual pollution that affects aquatic life. Since each industry is exclusive in its production methods, technology, and use of chemicals, it is difficult to measure the characteristics of pulp and paper wastewater [4–6].

Massive amounts of chemicals and water are used in the paper and pulp industry. For the production of one ton of paper, approximately 5–80 m^3 of fresh water is used [7]. The usage of chemicals ranges from 10% to above 35% of the weight of the paper. After digesting, bleaching is used to process unbleached pulp, which then transforms pulp into white fiber. The coloration of pulp fiber can be performed during the process and operation. Pulp and paper processing can be categorized into four steps: the preparation of raw material (straw plant), the digestion of raw material in the presence of steam, water and chemicals (pulping) [8], the washing and bleaching section, and the paper machine process. During manufacturing, a huge amount of water is utilized for different operations, including the flushing steps, cleaning the raw materials, coating material preparation, etc. The characteristics of wastewater depends on the nature of the processing. Various types of raw materials (i.e., recycled and virgin fibers), organic compounds (e.g., biocide dispersing agents, wet strength additives, starches pigments), and inorganic chemicals (e.g., water-based dyes, caustic, alum, soap, stone, etc.) are used in the paper-making process. All of these materials and chemicals become part of the effluent [9]. Effluents of the pulp and paper industry are of a very complex nature, containing lignosulfonate (complex structure) enzymes, alkali residues, reducing and oxidizing agents, remaining black liquor, silica, and different additives, all of which make their treatment economically difficult [10]. Therefore, the characterization of pulp and paper wastewater can be achieved by measuring the extreme fluctuations in different parameters, such as pH, conductivity, color, biochemical oxygen demand (BOD), and COD. Due to the complexity of pulp and paper effluents, one of the most serious challenges is in the pursuit of an effective treatment [11–13]. The dyes are known as the substances in which, upon application to another substrate (cellulose fibrous material), provide color by altering the crystal structure of the colored substances [14].

Anaerobic–aerobic treatment units manage the majority of the wastewater treatment process. Microorganisms are cultivated in activated sludge during this method of treatment, soaking up contaminants and oxygen [15,16]. When cleaning industrial wastewater, in particular, ozonation is good at eliminating color and oxidizing refractory organics. It is also useful for disinfecting effluents. While OH radicals react non-selectively with inorganic and organic dissolved substances, as well as the aqueous matrix, the ozone specifically targets organic molecules. The ozone has the ability to eliminate micropollutants and destroy microorganisms without changing the toxicity of the treated effluent [17,18]. To ensure safe and efficient wastewater treatment, the absorbability of bacteria must be maintained at a certain level [19,20]. AOPs rely on the in-situ synthesis of strong oxidants for the oxidation of organic compounds in wastewater. Different techniques have been investigated for the treatment of wastewater, including oxidation processes [21,22], the use of nanomaterials (e.g., nano sorbents, nano catalysts, molecular polymers, nanostructured catalytic membranes, bioactive nanoparticles, and biomimetic membranes) [23–26], the use of plant extract, etc. [27].

The present study focuses on an aerobic treatment of paper wastewater that is integrated with advanced oxidation processes (AOPs). Due to the oxidation of a variety of total organic compounds, the implementation of AOPs offers a practical and efficient attenuation alternative [28–30]. Considering the above-mentioned impacts of pulp and paper industry-induced wastewater, the present study was conducted to evaluate different advanced oxidation processes at different contact times, as well as the pH level for color and COD removal from raw, biologically, and chemically treated wastewater from the pulp and paper industry in order to make it reusable or recyclable.

2. Materials and Methods

2.1. Sampling of Wastewater

Samples of wastewater were collected from the biological treatment plant of x paper and pulp factory, located in Lahore. Samples were collected using the grab sampling technique from various points, including from the receiving tank, septic tank, aerobic treatment tank, and the final outlet, prior to the discharge. Samples were also collected from the inlet and outlet of the chemical treatment plant to compare its working efficiency with the biological treatment plant. Standard protocols were followed carefully during the collection and transportation of samples [31]. Wastewater samples were stored at 4 °C in an incubator in the laboratory of the industry.

2.2. Chemicals and Reagents

Different chemicals and reagents were used in the study. These include sodium hydroxide (NaOH), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2, 35%), iron sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), distilled water, and ozone. All the chemicals used were of analytical quality, and the experiment was carried out on a laboratory scale.

2.3. Characterization of Wastewater Samples

Wastewater samples were analyzed for the selected physico-chemical parameters using standard methods. The results of all the parameters were compared with National Environmental Quality Standards (NEQS), as given in Table 1.

Table 1. Physico-chemical parameters of wastewater used for the present study.

Paper and Pulp Wastewater				
Parameters	**NEQS**	**Preliminary Treated**	**Biologically Treated**	**Chemically Treated**
Absorbance (at 282 nm)	-	1.441	1.236	1.165
pH	6.5–8.5	7.1	7.5	6.8
COD (mg/L)	Up to 150	1500	245	775
DO (mg/L)	6	4.85	3.45	2.65
TDS (mg/L)	Up to 3500	2375	745	975
Turbidity (NTU)	-	565	14.65	185
EC (mS/cm)	400	308	12.4	116

2.3.1. Color Removal Efficiency

Wastewater from the paper and pulp industry has a yellowish brown color due to the presence of lignin derivatives (e.g., humic and fulvic acids, colored compounds, etc.) in it. The color removal efficiency was estimated by measuring the Lambda maximum on the UV/VISIBLE spectrophotometer (Single Beam Model; SP-UV1100, Scilogex, Rocky Hill, CT, USA) and then by scanning the sample of wastewater in the range of the wavelength, 200–780 nm. The wavelength with the maximum absorbance using the wastewater sample was found to be 282 nm. The absorbance gives the color of the wastewater sample. The percent of the color removal from the wastewater samples was measured using the following equation [32];

$$\text{Color Removal } (\%) = \frac{Co - Ct}{Co} \times 100 \tag{1}$$

where "*Co*" is the initial color concentration (mg/L), and "*Ct*" is the concentration (mg/L) of color after treatment for any contact time (min).

2.3.2. COD Removal Efficiency

COD is the amount of dissolved oxygen required for the decomposition of organic matter present in the wastewater. COD was measured following the procedure that is described in the 10th edition of Standard Methods for the Examination of Water and Wastewater [33]. The following equation(s) were used for the determination of COD in wastewater samples:

$$\text{COD} = \frac{B - A}{\text{Vol. of Sample}} \times 8000 \tag{2}$$

where "A" is the volume (mL) of FAS used in the blank, "B" is the ml of FAS used in the sample.

The percent removal efficiency for COD was calculated using the following equation:

$$\text{COD Reduction } (\%) = \frac{CODi - CODf}{CODi} \times 100 \tag{3}$$

where "*CODi*" is the initial COD of effluents and "*CODf*" is the final COD of effluents.

2.4. Treatments Processes

After initial characterization, wastewater was treated by different methods. These treatment methods are described as follows:

2.4.1. Biological Treatment

In this treatment, wastewater containing disperse dyes and other chemicals was treated in the aerobic tanks with different species of aerobic and facultative microbes, including microbial strains of *Sphingomonas paucimobilis*, *Bacillus* sp., and filamentous bacteria. These strains were cultured in a wastewater plant. Similar microbes were cultured in the other two tanks and were also provided with aerators to ensure oxygen circulation in the tank. These aerobic tanks had a retention time of 6–8 h. After treatment in the chain of aerobic tanks, the treated wastewater was discharged. Samples of treated wastewater were collected and analyzed for their color, COD, and other physical and chemical parameters.

2.4.2. Chemical Treatment

The chemicals used in the chemical treatment plant included ferric chloride, lime, polymers, and decolorization agents. After their mixing for several hours, wastewater was sent to the settling tank and then moved to the sand multimedia for its discharge. Samples of wastewater were collected and analyzed to measure changes in the target parameters after treatment. The efficiency of the chemical treatment plant was compared with that of the biological treatment. The drawback of chemical treatment is the usage of considerable amounts of chemicals and sludge formation.

2.4.3. Ozone Treatment

A bubble column reactor (3 cm diameter) was used for the ozonation of the wastewater samples, which used an ozone generator with a power requirement of 178 W. An ozone generator was used for the generation of ozone at a gas flow rate of 5–7 L/min, ozone concentration of 5–10 g/m^3, and an ozone output of 3 g/h. The ozonated column was filled with 1 L of sample for its treatment. The ozonated column was filled with 1 L of raw wastewater and ozone was bubbled in the sample via diffusers at a contact time of 3, 6, 9, 12, and a standard 15 min. A sample of 50 mL was withdrawn every time at the completion of each prescribed contact time. For the pH parameter, the ozonated column was filled with 1 L of raw wastewater sample and its pH was measured using the pH meter. The pH values selected for its treatment were 5, 6, 7, 9 and 10. Before bubbling the ozone to the sample, its pH was adjusted to 5 using diluted hydrochloric acid. The ozone treatment was performed in three phases.

In the first phase, the ozone treatment of raw wastewater was performed at varying contact times and wastewater pH levels. Meanwhile, in the second phase, the wastewater sample that was collected from the biological treatment plant after its biological treatment was further subjected to ozone treatment, in order to compare the efficiencies of the treatment methods when applied alone and in combination. In the third phase, the chemically pre-treated wastewater sample was treated with ozone by filling the ozone column with a 1 L sample, and then the ozone was bubbled in it at 5–7 L/min. The final sample was collected after its treatment with ozone. Absorbance measurements and COD analyses were also performed for each wastewater sample.

2.4.4. Fenton Oxidation

In Fenton oxidation, the pulp and paper wastewater was treated with hydrogen peroxide and $FeSO_4$. The optimization of the dose of $FeSO_4$ and H_2O_2 was required. For the dose optimization of $FeSO_4$, four beakers containing 1000 mL of wastewater solution were extracted and the already optimized dose of hydrogen peroxide (0.25 mL) was added to it. Then, varied doses of $FeSO_4$ were added in each beaker, constituting 10, 20, 30 and 40 mg. These samples were then stirred for 15–20 min with the help of a magnetic stirrer. After their standing time, the samples were analyzed for the target parameters. Their color and COD removal efficiencies using Fenton oxidation were measured using standard methods.

3. Results

The results obtained after the treatment of wastewater effluent with the advanced oxidation process, in combination with aerobic pre-treatments, are given in the following sections.

3.1. Lambda Max

A UV–Vis spectrophotometer was used to determine the Lambda maximum value of all the wastewater samples. In the current investigation, the optimal wavelength for the maximal color removal was found to be 282 nm. Figure 1 also shows the highest absorbance removal value of 1.41 a.u along the y-axis. This optimum and precise wavelength was used in the present study for the measurement of absorbance and, ultimately, the color removal efficiency.

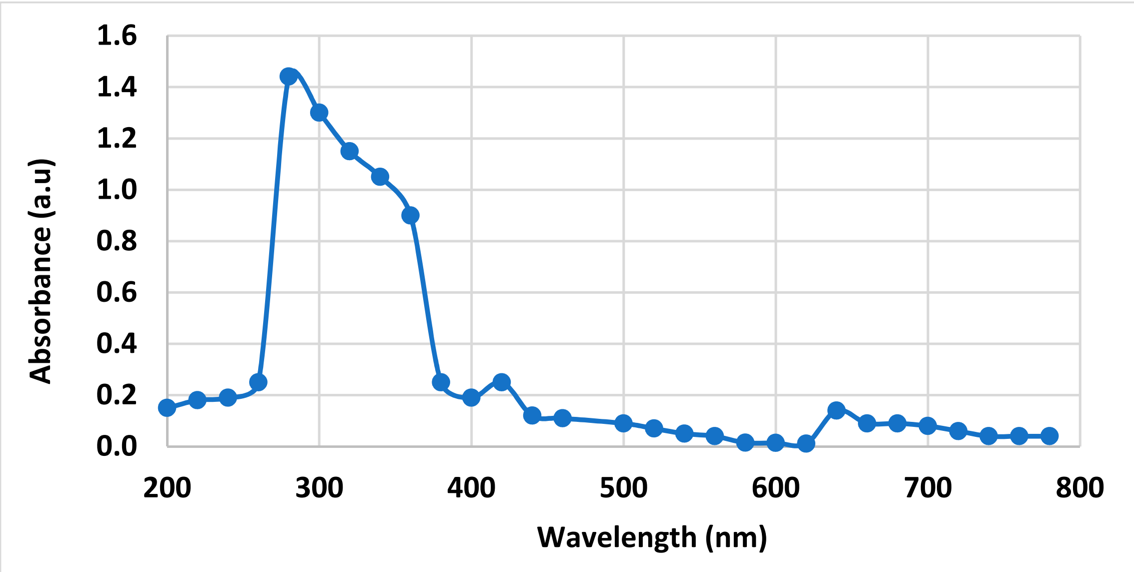

Figure 1. Absorption spectrum of raw wastewater from paper industry in the UV/Vis range.

3.2. Performance of Biological and Chemical Treatment of Wastewater

3.2.1. Biological Treatment

Wastewater from the pulp and paper industry was treated in aerobic tanks that had a retention time of about 6, 8 and 12 h. Results showed that aerobic treatment reduced the COD and turbidity levels of wastewater up to 83.65% and 97.41%, respectively. This treatment was found to be less efficient in terms of color removal, i.e., about 14.25%, as shown in Figure 2. However, aerobic treatment has been given increasing attention by researches as an innovative method in the domain of the biological treatment of paper industrial wastewater [34].

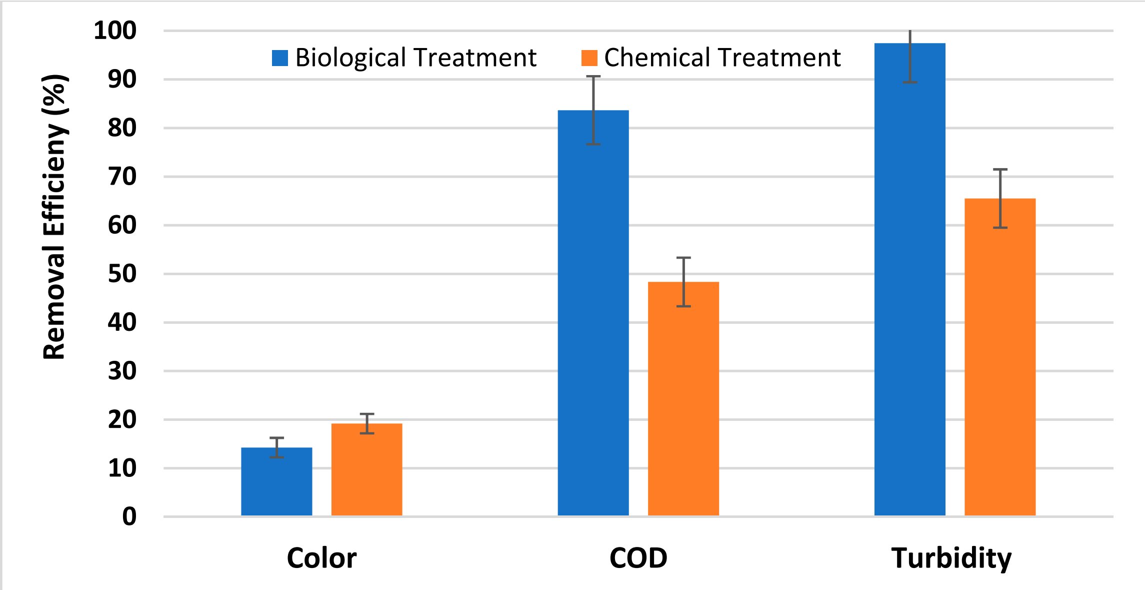

Figure 2. Removal efficiencies of biological treatment and chemical treatment of wastewater from pulp and paper industry for color, COD and turbidity. Mean values of percent removal of pollutant are presented with standard deviation.

3.2.2. Chemical Treatment

Wastewater from the pulp and paper industry was also treated chemically in the chemical treatment plant. After being treated with the ferric chloride, lime, polymers and de-colorization agents for several hours in the treatment plant, samples were collected and analyzed for their color, COD and turbidity removal. Results showed that the percent of the removal of color, COD and turbidity was found to be 19.18, 48.33, and 65.49%, respectively, as shown in Figure 2. The chemical treatment showed better results for color removal compared to COD removal. However, their levels were still higher than the National Environmental Quality Standards (NEQS) for effluents. Thus, further treatment is required for the effluent before it is discharged into the environment. Kumar et al. [35] also reported that the colored effluent that is discharged from pulp and paper industrial units remains contaminated with lignin or other constituents even after secondary treatment. However, a lower concentration of chemicals gave adequate results for COD removal in the chemical treatment process [36].

3.3. Ozone Treatment

3.3.1. Ozone Treatment of Raw Wastewater

Ozone treatment is a versatile technology for the treatment of pulp and paper effluent for the removal of COD and color. Ozone is an effective oxidant and is used for mineralization and the degradation of organic pollutants [37]. In the present study, the ozone treatment was applied to the pulp and paper wastewater, and then the samples of treated wastewater were analyzed for the maximum removal of COD and color in relation to two factors, i.e., contact time and pH. Experiments were performed in order to find the optimized contact time for the removal of color and COD from the paper and pulp effluent. For this purpose, a sample of one liter of effluent was ozonized at varying contact times, i.e., for 3, 6, 9, 12 and 15 min. The results showed that the percent of color removal was approximately 37.14, 39.29, 41.22, 39.15 and 36.98%, respectively. It showed that increasing the contact time did not result in a substantial change in the COD removal efficiency.

Maximum treatment efficiencies for all three parameters were achieved when the contact time was 9 min. The COD removal percent at 3, 6, 9, 12 and 15 min was found to be 79.11, 80.2, 88.53, 80.43 and 78.75%, respectively. In ozonation, it has been reported that all the organochlorides found in wastewater are broken down in 60 min of retention time [38,39]. It is clear that the maximum COD and color removal efficiencies after 9 min were 88.53% and 41.22%, respectively. With an increase in the contact time, there was no further increase in the removal efficiencies for color and COD. Turbidity was also analyzed and its removal was at its maximum (81.42%) at the contact time of 9 min, as presented in Figure 3a.

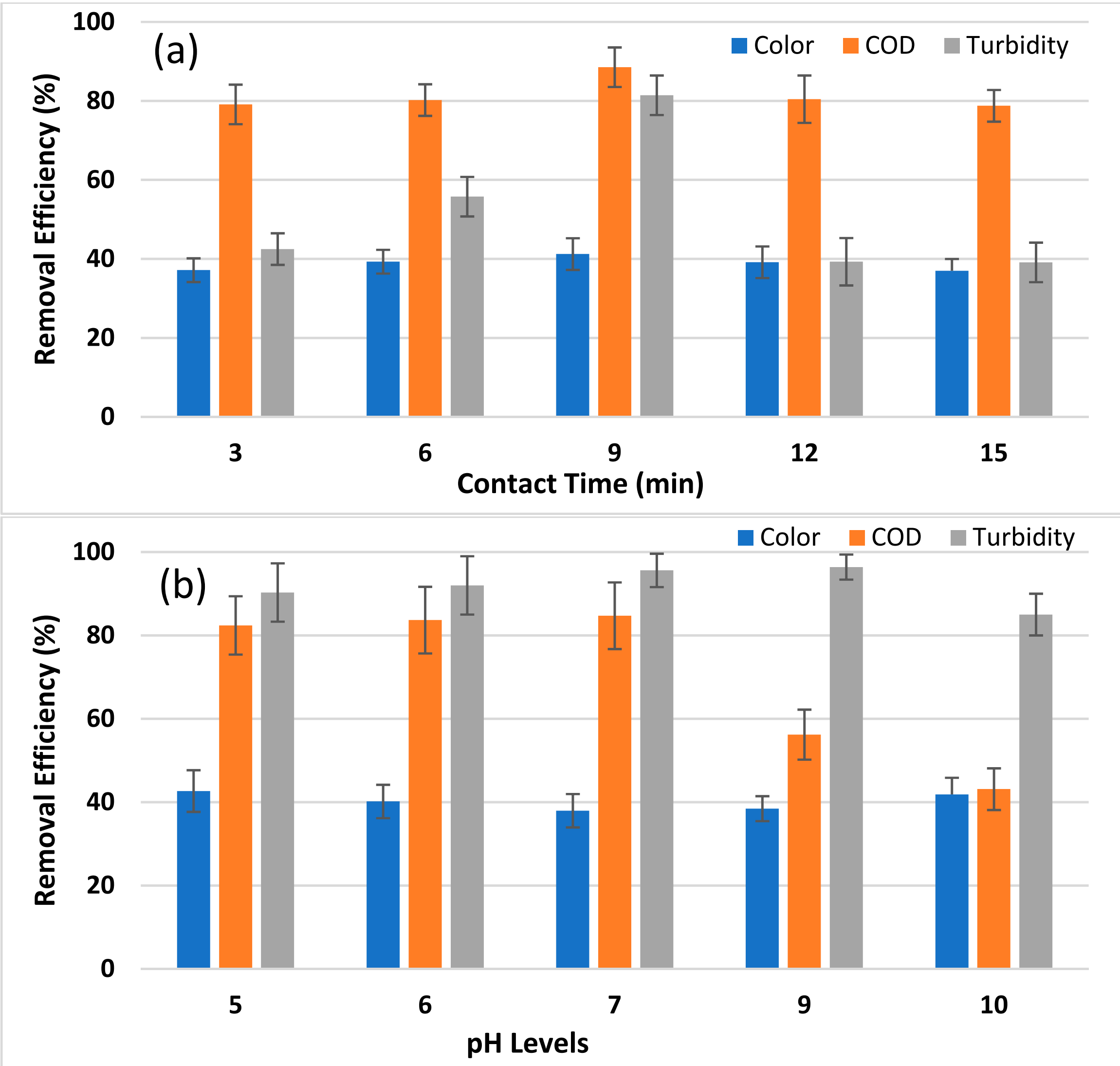

Figure 3. (**a**) Ozone treatment of raw wastewater and removal efficiencies (%) for color, COD and turbidity at varying contact times of 3, 6, 9, 12 and 15 min. (**b**) Ozone treatment of raw wastewater and removal efficiencies (%) for color, COD and turbidity at varying pH values (5, 6, 7, 9 and 10). Means values are presented in graphs with standard deviation.

The ozone treatment of raw pulp and paper wastewater was carried out also at different pH values. Figure 3b shows the ozone treatment of raw wastewater and the removal efficiencies (%) for color, COD and turbidity at varying pH values. The results showed that the color removal was at its maximum (42.67%) at pH 5. However, the COD removal efficiency increased with an increase in the pH value and reached its maximum (84.73%) at a pH of 7. The removal efficiency for turbidity reached its maximum (96.4%) at a pH of 9.

However, COD removal efficiency increased with an increase in the pH value, reaching a maximum removal efficiency of 84.73% at pH 7. The removal effectiveness for turbidity was highest (96.4%) at pH 9. It was found that the turbidity of all the wastewater samples was reduced at higher pH levels. Furthermore, this pattern corresponds to the impact of the contact duration, i.e., a higher contact time corresponds to a maximum color, COD, and turbidity removal from the wastewater. Turbidity is caused by a huge number of individual particles, which causes haziness. Turbid water is always difficult to drink. According to different research studies, coupled hybrid techniques, particularly ozonation, are successful solutions for removing turbidity from industrial effluent. Catalytic ozonation has shown to be greatly advantageous towards the removal of organic materials and has been proven to be highly efficient in water treatment [40,41].

3.3.2. Ozone Treatment of Biologically Treated Wastewater

Biologically pre-treated paper and pulp effluent was treated with ozone under various contact times, i.e., 3, 6, 9, 12 and 15 min. After treatment, these samples were analyzed for their color and COD removal, as presented in Figure 4. It was found that the removal efficiencies for color and COD increased with an increase in the ozonation time. For a contact time of 3 min, the removal efficiencies for color and COD were about 41.42 and 78.67%, respectively. For a contact time of 9 min, the removal efficiencies for color and COD reached their maximums of 46.36% and 95.92%, respectively. After 9 min, there was no significant increase in the color and COD removal efficiency. This higher efficiency for COD removal can be attributed to a lower initial COD concentration as a result of the biological treatment. A decrease in the turbidity level was observed after the ozone treatment, and turbidity removal during the biological treatment further decreased the turbidity during ozonation, which helped to attain more clear treated water [42]. The results showed that the combination of ozonation and performing the biological treatment beforehand achieved a maximum COD removal of 46% compared to the result obtained on processed wastewater.

Biologically pre-treated effluent was also exposed to ozone treatment at different pH values, ranging from acidic to basic (5, 6, 7, 9 and 10). The results obtained for the efficiency of color removal were very much consistent throughout the pH range, at a fixed contact time of 9 min. However, a slight decrease from 39.97% to 37.14% was found in the color removal efficiency at a neutral pH of 7. In the acidic conditions at pH 5, color removal reached its maximum (39.97%); however, an increased pH decreased the color removal efficiency. An increase in the pH towards alkalinity slightly dropped the level of color removal to 35.03%.

At a high value of pH (9 and 10), hydroxyl radicals are generated from ozone decomposition and these radicals possess a higher oxidative potential, which results in an increased color removal. However, they are less selective towards lignosulfonate molecules. Meanwhile, at a lower level of pH (5), the main functioning oxidant is molecular ozone, which selectively attacks chromophore groups and favors decolorization. Therefore, the color removal efficiency of pulp and paper wastewater at an acidic pH is due to ozone molecules.

It was found that the efficiency of COD removal was higher compared to that of color removal at different pH values, ranging from 5 to 10. At pH 5, COD removal was about 88.16% and it decreased towards a neutral pH. Minimal COD removal (40.0%) was found at pH 7. With an increase in pH from 7 to 10, COD removal slightly increased from 40.0% to 66.53%. In other studies [39,43], at pH 9–11, no noteworthy removal efficiency was found; however, when the pH was adjusted to neutral, the treatment efficiency decreased. It is clear that pH has no significant effect on the removal efficiency of lignosulfonate compounds. Further, unbuffered pulp and paper wastewater solutions have shown better COD removal compared to buffered solutions.

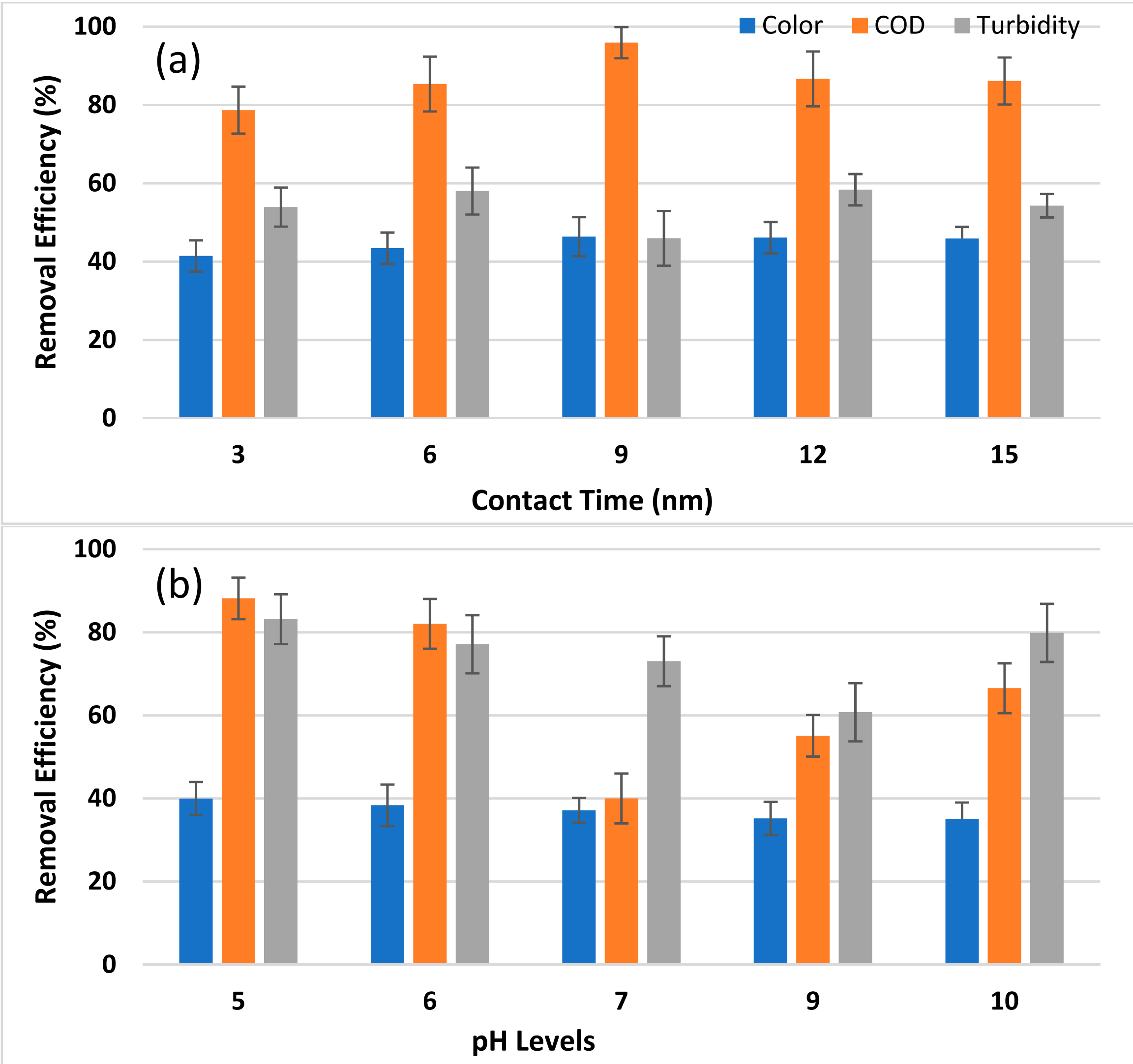

Figure 4. (**a**) Ozone treatment of biologically treated wastewater and removal efficiencies (%) for color, COD and turbidity at varying contact times of 3, 6, 9, 12 and 15 min. (**b**) Ozone treatment of biologically treated wastewater and removal efficiencies (%) for color, COD and turbidity at varying pH values (5, 6, 7, 9 and 10). Means values are presented in graphs with standard deviation.

Turbidity removal from wastewater was also studied after the ozone treatment. Figure 4 shows that the turbidity level decreased at a pH range of 6–9. However, at pH 5 and pH 10, a very high turbidity removal efficiency was attained, with a maximum turbidity removal efficiency of 83.14% at pH 5.

3.3.3. Ozone Treatment of Chemically Treated Wastewater

Chemically pre-treated pulp and paper wastewater was treated with ozone at the optimum conditions of time (9 min) and pH (5). It was found that the removal efficiencies of the ozone treatment for COD, color, and turbidity were 84.77, 41.29, and 35.90%, respectively. High removal efficiencies were achieved with the application of ozone, which can be used as a potential treatment technique for pulp and paper wastewater. Ozonation, when performed in combination with chemical treatment, showed good results for color removal as well as COD removal, as shown in Figure 5.

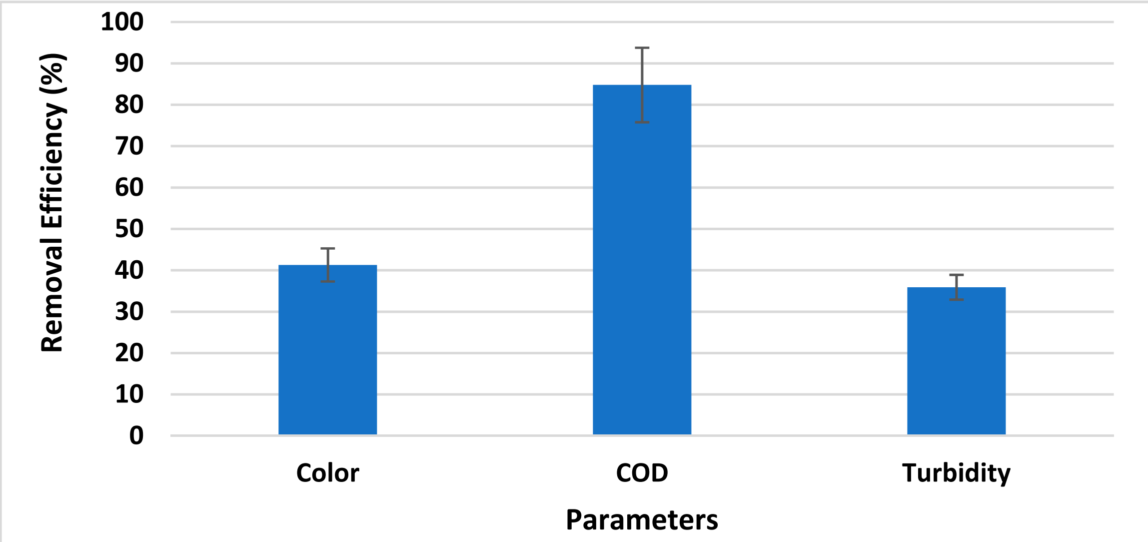

Figure 5. Ozone treatment of chemically treated wastewater and removal efficiencies (%) for color, COD and turbidity. Means values are presented in graphs with standard deviation.

It is clear that the ozone treatment has shown excellent results for the removal of color from the pulp and paper industry's wastewater when used as both a post-treatment and pre-treatment. However, the highest removal efficiency for COD was achieved in the second experiment, in which ozonation was performed on biologically pre-treated wastewater. The maximum COD reduction value in biologically treated wastewater might be due to the lower initial COD concentration; being already biologically treated may have resulted in a prompt degradation during the ozone treatment. Secondly, there was a low absorbance level in the biologically treated wastewater, which added the enhanced removal of COD.

The response of pH controls the rate at which OH radical ions are generated, and it has a substantial impact on how well ozonation, Fenton, and photo-Fenton treatment procedures work overall. Iron and aluminum hydroxides are transformed into the byproducts hydroxy ferrate or hydroxy aluminate by the alkaline pH, respectively. These have the capacity to absorb additional colors, chemicals, and the remnants of electrical conductivity, which ultimately reduce the pH, COD and other chemical parameters of wastewater [44,45].

3.4. Fenton Oxidation

In the Fenton oxidation process, wastewater is treated with Fenton's reagents, including $FeSO_4$ and H_2O_2. In this experiment, the initial wastewater was treated using the Fenton oxidation process and two parameters were studied, including the optimization of the dose concentration for H_2O_2 and $FeSO_4$. The Fenton process is frequently applied in the treatment of wastewater from the paper industry. This process has both an oxidation and coagulation function, and can omit all organic portions of COD produced in biological treatment [46,47].

3.4.1. Optimization of H_2O_2 and $FeSO_4$ Dose Concentration for Raw Wastewater

A dose of H_2O_2 was optimized for the experiment on the Fenton oxidation treatment. Figure 6 shows that at 0.25 mL of H_2O_2, dose removal efficiencies of 26.30% and 85.13% were found for color and COD, respectively. A further increase in the dose of H_2O_2 did not produce any increase in the removal efficiencies for color and COD. This decrease in COD removal with an increase in the dose might also be due to residual H_2O_2, which consumes potassium dichromate. Hydrogen peroxide is eco-friendly and, with its increased oxidative capacity, can comprehensively mineralize and produce H_2O, O_2 and OH as non-toxic by-products [48].

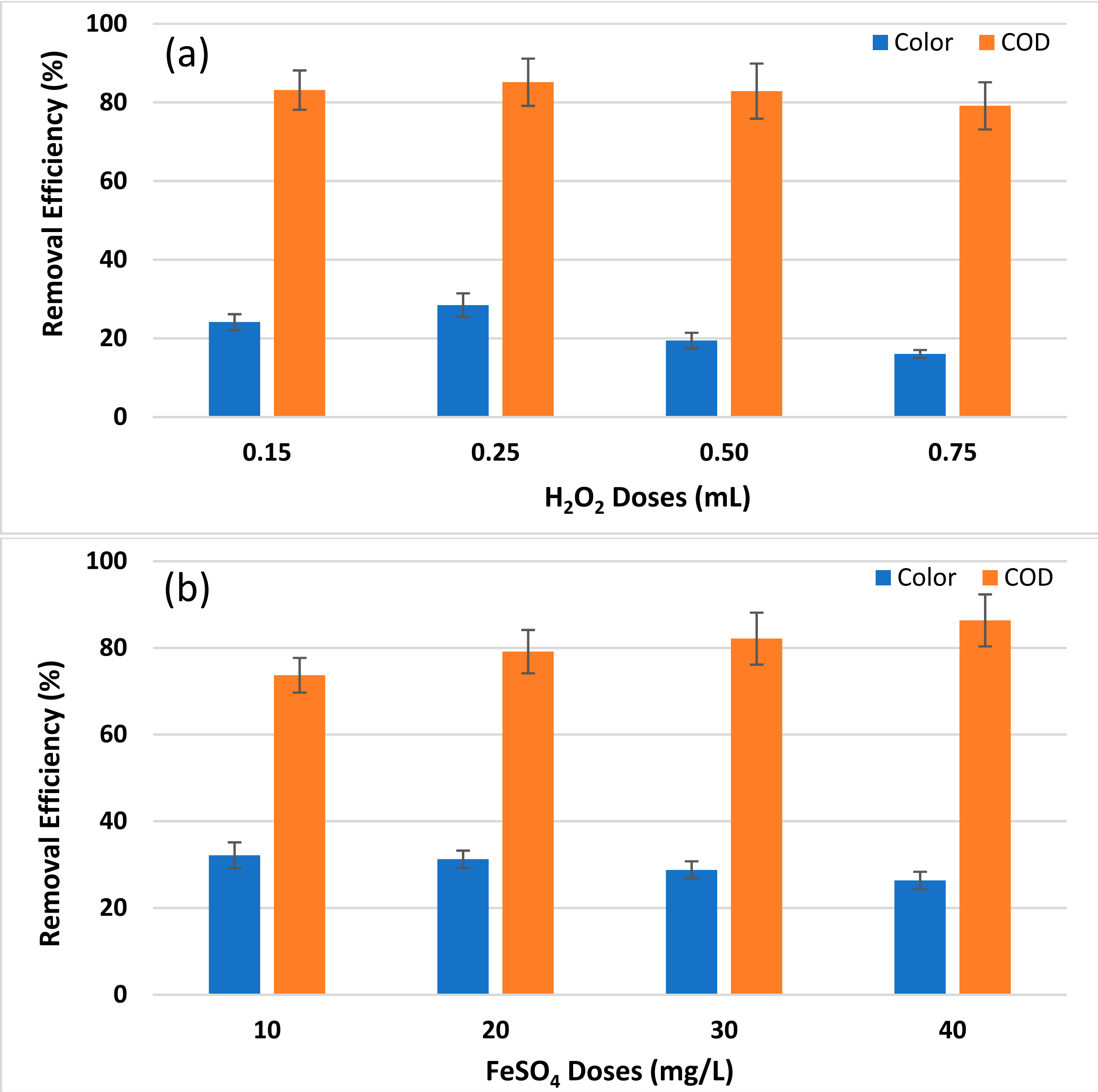

Figure 6. (**a**) Optimization of H_2O_2 dose of raw pulp and paper wastewater for Fenton oxidation at different doses (0.15, 0.25, 0.50 and 0.75 mL). (**b**) Optimization of $FeSO_4$ dose of raw pulp and paper wastewater for Fenton oxidation at different doses (10, 20, 30 and 40 mg/L). Means values are presented with standard deviation.

The impact of $FeSO_4$ concentration in Fenton's reagents on COD and color removal was investigated by varying the $FeSO_4$ salt concentration from 10 to 40 mg/L, while maintaining the H_2O_2 at 0.25 mL and the time at 20 min. The results showed that increasing the $FeSO_4$ concentration from 10 to 40 mg improved the COD removal efficiencies from 73.67 to 86.33%. However, the highest color removal efficiency of 32.13% was achieved at the lowest quantity of $FeSO_4$, 10 mg per 1000 mL of solution. With increasing the dosage concentration, there was no decline in the color removal efficiency, which might be due to the suspension of iron precipitates. The $FeSO_4$ dosage of 40 mg provided the best COD removal efficiency. The increased COD removal efficiency with 40 mg/L $FeSO_4$ concentration may be due to the increased ferrous content, which results in the generation of more hydroxyl radicals and speeds up the redox process. Secondly, Fe^{2+} changes to Fe^{3+}, which acts as a coagulant and improves COD reduction.

3.4.2. Optimization of H_2O_2 and $FeSO_4$ Dose Concentration for Biologically Treated Wastewater

The color removal efficiency was 26.30% for the Fenton-treated effluent and 26.62% for Fenton in combination with the biologically pretreated effluent (Figure 7a,b). However, there is a noticeable variation in the COD removal efficiency, with the Fenton treatment at a 0.25 mL of H_2O_2 concentration removing COD by 86.33%, and the Fenton-treated and biologically treated wastewater removing COD by 84.49%. In all cases, the highest COD and color removal efficiency was found at 0.25 mL of H_2O_2. Based on these findings, it is obvious that the Fenton method is a viable option for the treatment of pulp and paper effluent. It has shown satisfactory results for the use of the Fenton process as a pre-treatment, but has shown better results when performed in combination with the biological method. Treatment of the paper and pulp industry wastewater using Fenton as a post-treatment combined method has not yet been frequently reported. The Fenton oxidation process has been studied in relation to the removal efficiency of pollutants [49]. In another study, the COD removal efficiency increased from 86.9 to 91% using Fenton's treatment after the biological process [50]. Special attention must be paid to the study of the residual contents of H_2O_2 and their potential effects. In addition, guidelines should also be developed for the maximum allowable H_2O_2 concentration used in the treatment of wastewater [51].

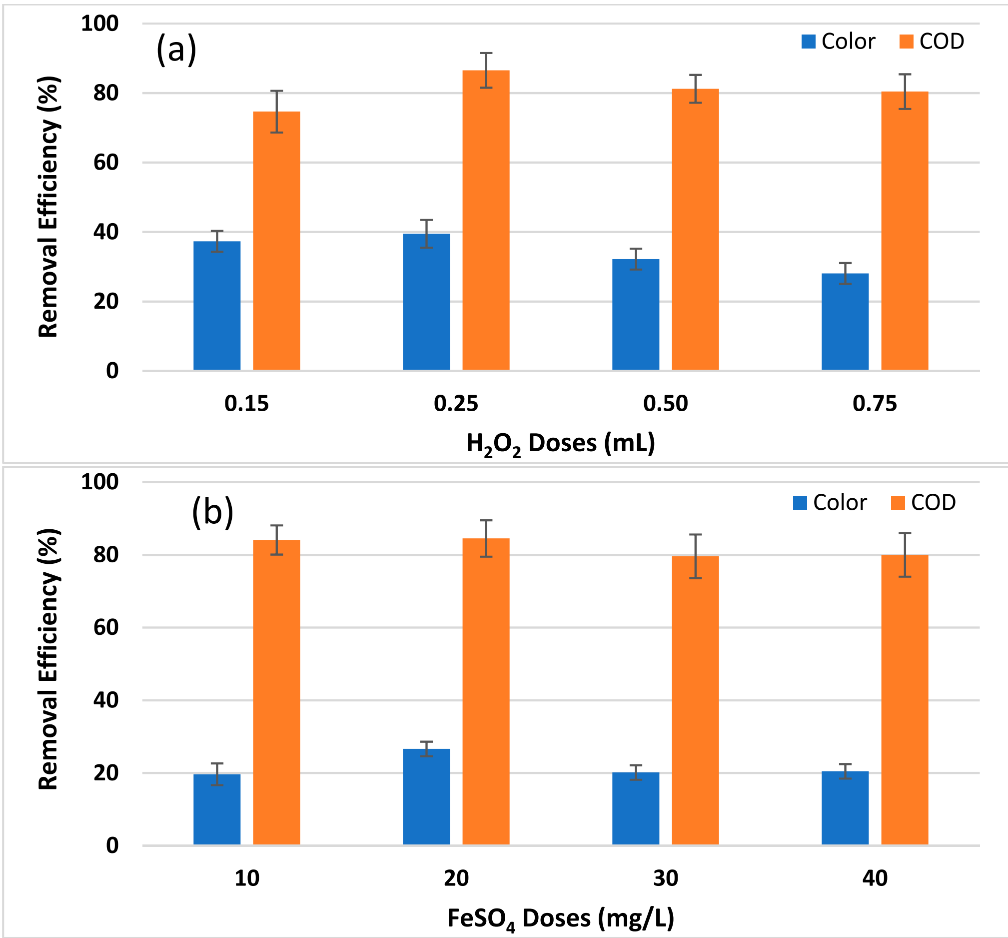

Figure 7. (**a**) Optimization of H_2O_2 dose of treated pulp and paper wastewater for Fenton oxidation at different doses (0.15, 0.25, 0.50 and 0.75 mL) for biologically treated wastewater. (**b**) Optimization of $FeSO_4$ dose of treated pulp and paper wastewater for Fenton oxidation at different doses (10, 20, 30 and 40 mg/L) for biologically treated wastewater. Means values are presented with standard deviation.

3.4.3. Fenton Oxidation of Chemically Treated Wastewater

Fenton oxidation was applied to the chemically treated pulp and paper wastewater as a post-treatment method. The chemically treated pulp and paper wastewater was treated with Fenton's reagents under optimum conditions, which were 40 mg of $FeSO_4$, 0.5 mL of H_2O_2, pH 5 and a stirring time of 15–20 min. From the results (Figure 8), it was found that the efficiency of color and COD removal was 35.48 and 75.68%, respectively. It was also found that turbidity dropped by up to 21.28%. From these results, it is clear that the Fenton oxidation process is useful for removing the COD from the wastewater of the paper and pulp industry.

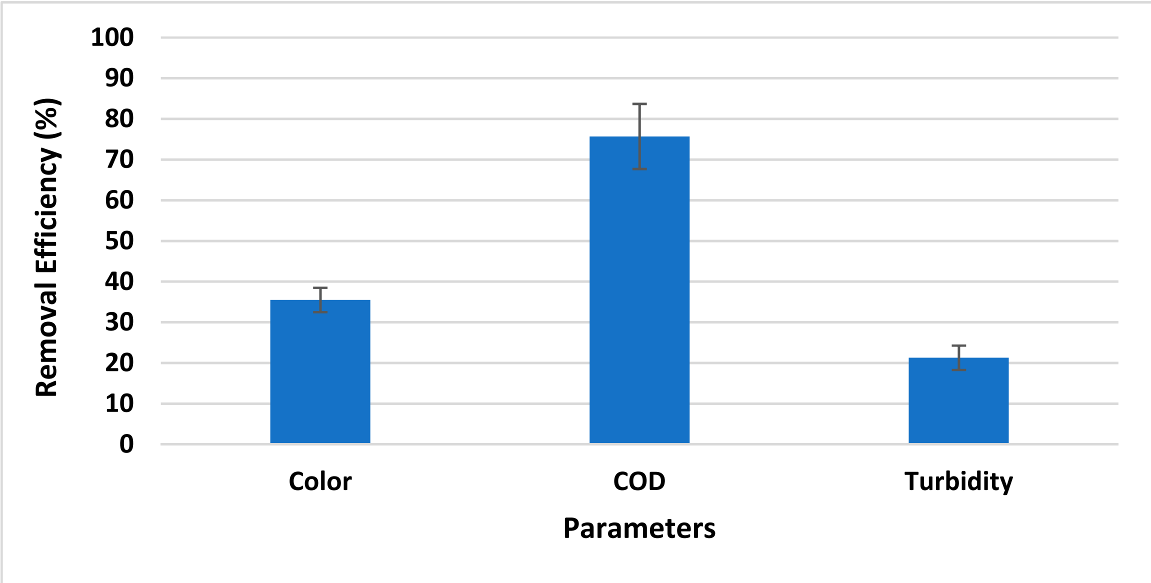

Figure 8. Fenton oxidation of chemically treated wastewater for removal of color, COD and turbidity. Means values are presented with standard deviation.

3.5. Photo-Fenton Oxidation of Raw and Biologically Treated Wastewater

Raw and biologically treated wastewater were also treated with the solar-assisted photo-Fenton process and the removal efficiencies for color and COD were compared (Figure 9). It was found that the photo-Fenton treatment of raw wastewater gave excellent results for color removal. A color removal efficiency of 39.85% was achieved in the photo-Fenton process; meanwhile, the COD removal efficiency was about 90.13% for raw wastewater, which is low compared to the photo-Fenton-treated and biologically treated wastewater.

It was found that the removal efficiencies for color and COD increased with an increase in the contact time. The removal efficiency for COD is slightly higher than the color removal values for biologically treated wastewater compared to raw wastewater. This might be due to the reduced value of the initial COD of wastewater because the biological pre-treatment has a better removal efficiency for pollutants. The efficiencies for COD and color removal at 12 h of contact time were 94.29% and 41.35%, respectively. Oxidation processes are being used in various wastewater treatment projects worldwide [21,22].

3.6. Comparison of Efficiencies of Different Treatment Methods

3.6.1. Comparison of Efficiencies of Different Treatment Methods for Raw Wastewater

Different techniques were used to treat the raw wastewater collected from the pulp and paper industry for the removal of pollutants, particularly COD and color. Figure 10 shows the comparison of the percent removal efficiencies for color and COD using different techniques.

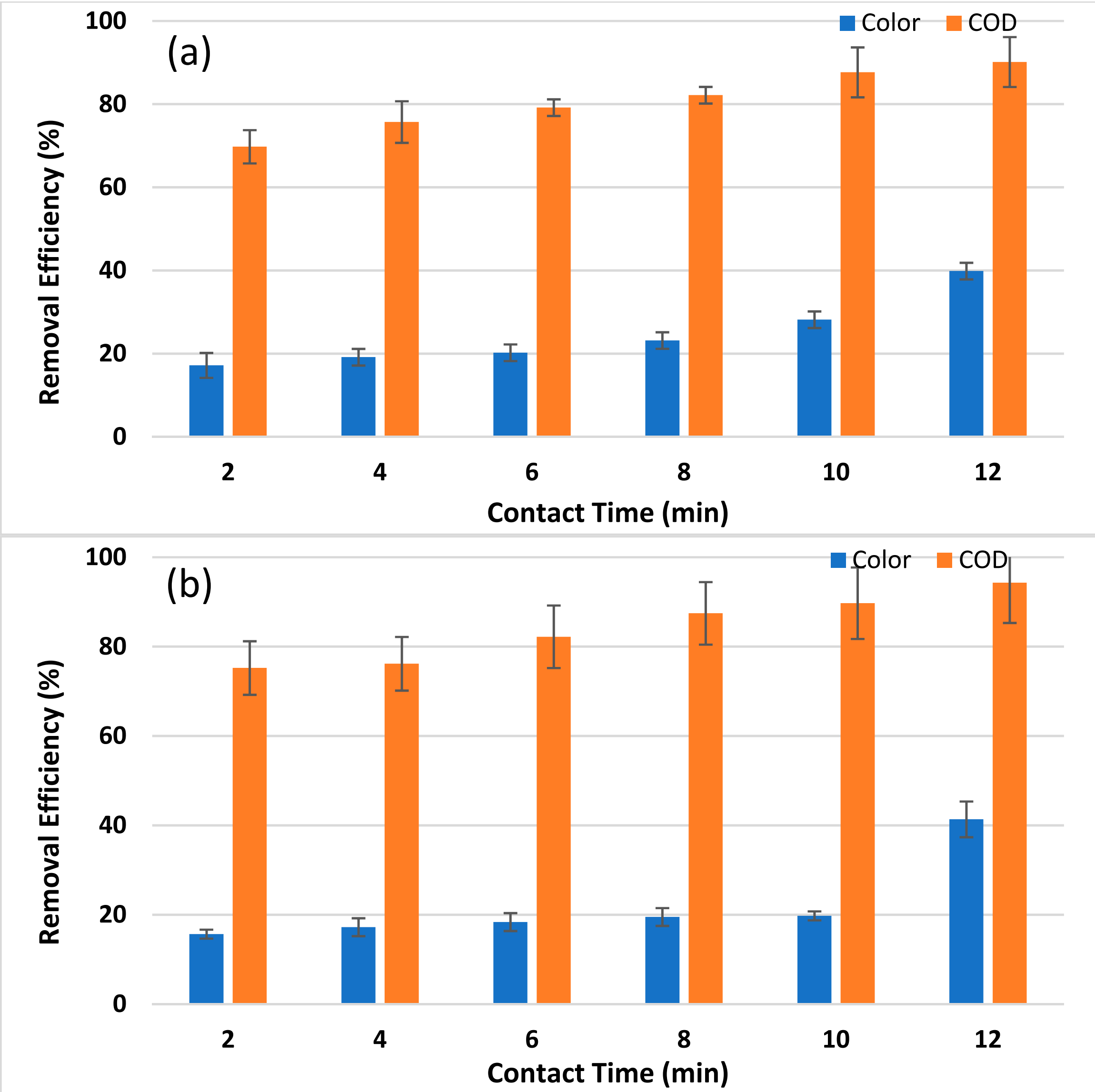

Figure 9. (**a**) Photo-Fenton treatment of raw pulp and paper wastewater and its removal efficiency for color and COD at different contact times of 2, 4, 6, 8, 10 and 12 min. (**b**) Photo-Fenton treatment of biologically treated pulp and paper wastewater and its removal efficiency for color and COD at different contact times of 2, 4, 6, 8, 10 and 12 min. Means values are presented with standard deviation.

The results showed that the ozone treatment had the highest efficiency, with efficiencies of 41.22% and 88.53% for color and COD removal, respectively. The photo-Fenton technique produced good results, with removal efficiencies of 39.83% for color and 90.13% for COD. Its efficiency for COD removal was somewhat greater than that of the ozone treatment, but when contact time was considered, the ozone treatment produced the best results in the shortest contact time. Another crucial consideration is the generation of sludge, which is low in the ozone treatment. Other treatments, such as the biological and chemical treatments, demonstrated poor efficiency for these parameters. Aside from the chemical and biological treatments, removal efficiencies of 26.30% for color and 86.33% for COD using Fenton oxidation, and 28.45% for color and 85.13% for COD using the hydrogen peroxide treatment, were achieved. Ozone treatment is expensive, and Fenton treatment generates sludge that is difficult to manage.

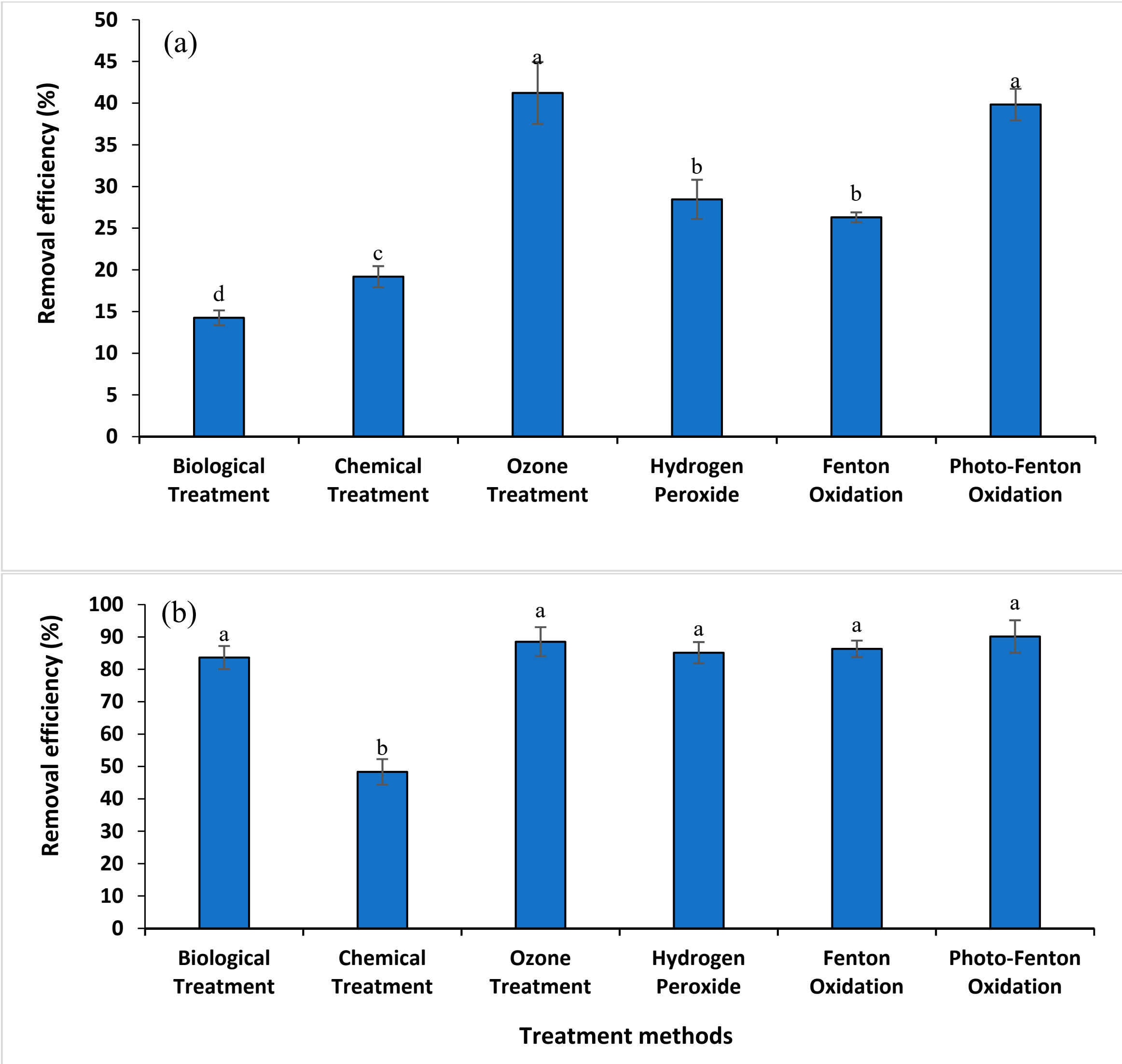

Figure 10. (**a**) Comparison of color removal efficiencies of different treatment methods applied to raw pulp and paper wastewater. (**b**) Comparison of COD removal efficiencies of different treatment methods when applied to raw pulp and paper wastewater. Mean values are presented with standard deviation. Different letters (a–d) show significant differences between treatments methods. Same letters (a, a, a) show that there is no significant difference between treatment methods.

From the results, it is clear that the ozone treatment showed the maximum overall removal efficiency, i.e., 41.22% and 88.53% for color and COD, respectively. The photo-Fenton process also showed good results, i.e., 39.83% and 90.13% removal efficiencies for color and COD, respectively. Its efficiency for COD reduction was a little higher than that of the ozone treatment, but if the contact time is considered, the ozone treatment showed the maximum results in a short time. Another important factor is the production of sludge, which is negligible in the ozone treatment. Other treatments, such as the biological and chemical treatment, showed lower efficiencies for these parameters; in addition, values for other physico-chemical properties (TDS and EC) were also higher than the NEQS. Therefore, after these treatments, the wastewater could not be feasibly discharged and, therefore, further treatment was required in order to meet the NEQS for effluents. According to the preceding explanation, certain tactics are beneficial while others have drawbacks. Therefore, the application of these treatments in combination would be a good strategy in order to overcome cost and maintenance issues in the pulp and paper wastewater treatment plant.

The order of different treatment methods in terms of their color removal efficiency is given below: Ozone Treatment > Photo-Fenton > H_2O_2 Treatment > Fenton Treatment > Chemical Treatment > Biological Treatment.

The order of different treatment methods in terms of their COD removal efficiency is given as follows: Photo-Fenton > Ozone Treatment > Fenton Oxidation > H_2O_2 Treatment > Biological Treatment > Chemical Treatment.

3.6.2. Comparison of Efficiencies of Different Treatment Methods for Biologically Treated Wastewater

Wastewater collected from pulp and paper was biologically treated, but the results showed that removal efficiencies lower and parameter values higher than the NEQS were obtained. The results of the biological treatment indicated that biological treatment alone is not enough and that another treatment is required for the significant removal of pollutants. Therefore, different treatment methods were applied to the biologically treated wastewater and their efficiencies in terms of color and COD removal were compared, as shown in Figure 11. It can be seen that the ozone treatment was found to be the most efficient method in terms of color and COD removal among all the other treatments investigated. It achieved a 46.34% color and 95.92% COD removal from wastewater. Another treatment showing comparable values was the photo-Fenton treatment, which achieved removal values of 41.34% for color and of 94.29% for COD. Treatment with hydrogen peroxide and the Fenton oxidation treatment also showed good results for the removal of color and COD. It is also evident that using the studied treatment methods in combination can be a good strategy for the treatment of pulp and paper wastewater, and the management of environmental quality. Improving the efficiency of these treatments further could help in the treatment and management of wastewater. The order of the efficiency of the post-treatments used in the present study in terms of COD and color removal is as follows: Ozone Treatment > Photo-Fenton Treatment > H_2O_2 Treatment > Fenton Treatment.

3.7. Effective and Efficient Methods for the Treatment of Wastewater from the Paper and Pulp Industry

Chemical treatments that depend on advanced oxidation processes (AOPs) have been widely employed to treat a wide range of organic contaminants. Removal activity is often carried out by the oxidation of complex substances by non-selective hydroxyl radicals produced by AOPs via a sequence of complicated processes. Such AOPs have been used successfully to treat wastewater with a low biodegradability index. According to Lucas et al., 2012, Fenton reactions may be successfully used for the tertiary treatment of paper and pulp industrial effluent [52]. Coagulation, flocculation, sedimentation, filtration, electrocoagulation, radiation, and adsorption are the most common physicochemical processes that have been employed by various researchers for the treatment of wastewater in different industries [53]. Table 2 shows the most efficient methods for the treatment of such effluents. Contaminants were removed at a high rate using the processes described in Table 2, such as the activated sludge system, which removed around 93% COD and other pollutants [54], the submerged attached bioreactor, which removed 97% COD, TSS, and pH [55], and the combined biological and chemical methods, which also significantly removed pollutants [25–27,56–59]. According to the above results reported by various researchers, biological methods for the treatment of industrial wastewater are efficient and sustainable; as in our previous work, Irshad et al., 2022, found that effluents from the textile industry were treated to the greatest extent by combining *A. indica* leaf extract with $AgNO_3$ solution [27]. Furthermore, this procedure is simple and eco-friendly. Similarly, for the effective wastewater treatment of paint industry effluents, this combined biochemical technique must be used on a large scale. The color removal efficiency is dependent on the pH, type of dye and dosage of coagulant. The mechanism of color removal from wastewater is largely abstract due to the different chemical structures that the different dyes present in wastewater possess [56]. COD is removed from wastewater by AOPs using oxidants (chemical) in order to reduce and remove both organic and inorganic components. AOPs can completely oxidize the chemicals present in wastewater and convert them into carbon dioxide and water [57].

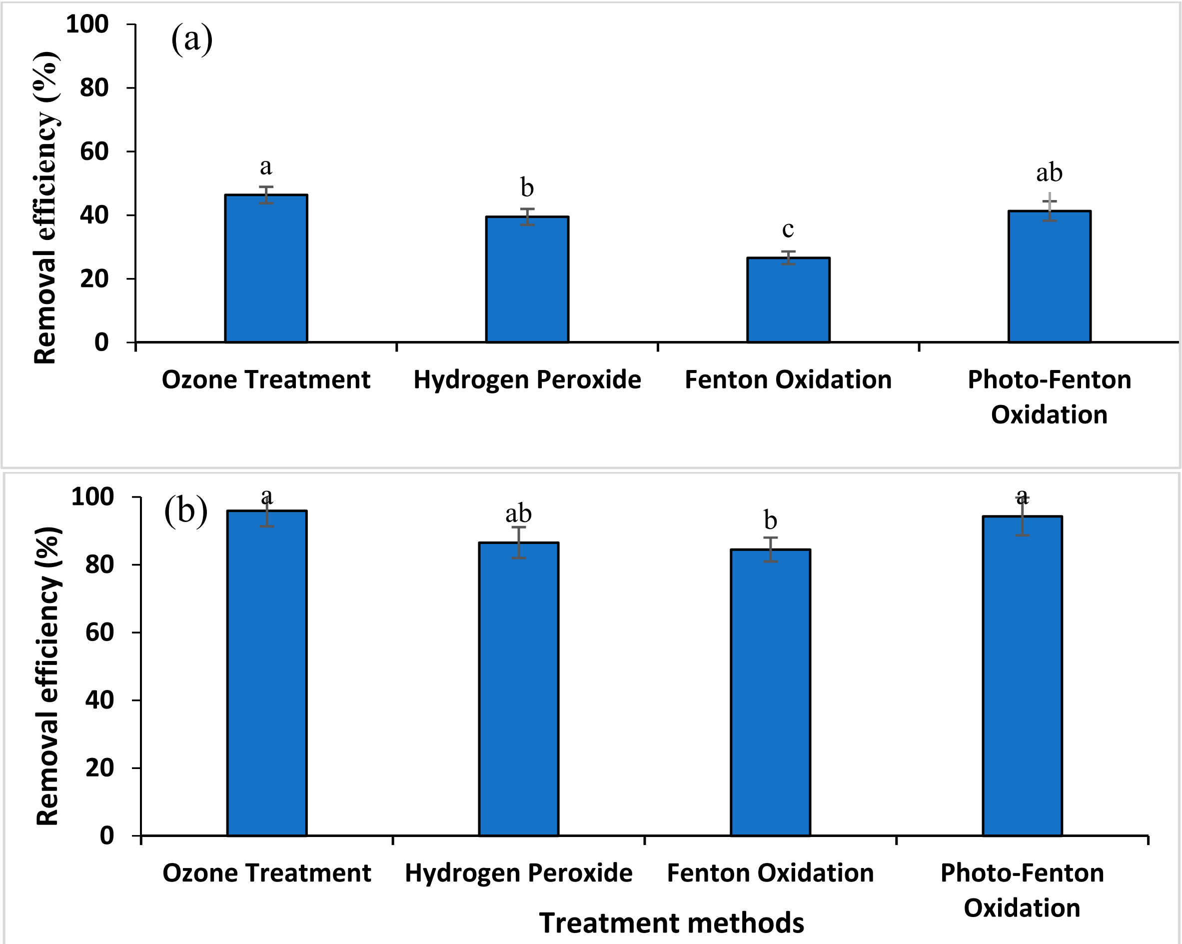

Figure 11. (**a**) Comparison of color removal efficiencies of different treatment methods applied to biologically treated pulp and paper wastewater. (**b**) Comparison of COD removal efficiencies of different treatment methods applied to biologically treated pulp and paper wastewater. Mean values are presented with standard deviation. Different letters (a–c) show significant differences between treatment methods. Same letters (a, a, a) show that there is no significant difference between treatment methods.

Table 2. Various effective wastewater treatment methods for the paper and pulp industries.

S. No	Treatment Method	Results Obtained	Recommendations	References
1	Activated sludge system	A 93% and 99% BOD removal	Treatment is difficult due to the presence of potentially harmful organic and inorganic micro pollutants, as well as a high Chemical Oxygen Demand (COD) content.	[54]
2	Submerged attached bioreactor	A 97% COD removal efficiency	Hazardous organic solvent decomposition is achievable and efficient.	[55]
3	Azadirachta leaf extract combined with $AgNO_3$ solution	pH, COD, BOD, TDS and TSS removal up to permissible limits recommended by PEQs	Combined chemical and biological method is the sustainable solution for pollutants removal from waste industry wastewater	[27]

Table 2. *Cont.*

S. No	Treatment Method	Results Obtained	Recommendations	References
4	Combination of a chemical coagulation/flocculation step with an aerobic biological process	A 96% COD, 97% color and 92.5% BOD removal	Combined biological and chemical method is good for paint industry wastewater	[59]
5	Ozonation + electrolysis	COD, pH and other parameters removed 50%	Combined use of two methods can enhance the removal efficiency	[60]
6	Solar photo-Fenton ($Fe^{2+}/H_2O_2/UV$	COD and DOC removal efficiency is nearly 90%	Photo-Fenton treatment is an efficient technique for large scale treatment	[61]
7	Ozone treatment	A 46% color removal and 96% COD removal for biologically treated pulp and paper wastewater.	Treatment of pulp and paper wastewater with combined process can boost the effectiveness of color and COD removal.	Present study.
8	Photo-Fenton Oxidation	A 41% color removal and 94% COD removal for biologically treated pulp and paper wastewater.	Treatment of pulp and paper wastewater with combined process can boost the effectiveness of color and COD removal.	Present study.

4. Conclusions and Recommendations

4.1. Conclusions

All the advanced oxidation processes investigated for the treatment of wastewater in the present study showed the ability to remove color and COD up to a reasonable level in a short period of contact time. Ozone treatment showed a color removal efficiency of about 41.2% and 46.4% from raw and biologically treated wastewater, respectively. The ozonation process was found to be the most promising in terms of COD and color removal. It showed a removal efficiency of 41.2% for color and 88.5% for COD from raw wastewater at the contact time of 9 min. The efficiency of color and COD removal from biologically treated wastewater at a contact time of 9 min was 46.4% and 95.9%, respectively. The removal efficiency for the aerobic treatment was about 14.25, 83.65 and 64.60% for color, COD and turbidity, respectively. The combined use of the ozone treatment and photo-Fenton oxidation treatment produced the highest effectiveness for color removal; meanwhile, photo-Fenton oxidation, followed by ozone treatment, produced the highest efficiency for COD removal from raw wastewater. In the case of biologically treated wastewater, the ozone treatment was followed by the use of hydrogen peroxide in order to obtain maximal color removal effectiveness. Meanwhile, the ozone treatment, followed by photo-Fenton oxidation, had the highest efficiency for COD removal from raw wastewater. It has been found that combining two treatment procedures is more efficient in removing color and COD from wastewater than either treatment method alone.

It is concluded that a combination of two treatment methods is more efficient in comparison to when a treatment method is applied alone. Biological treatment is a cost-effective method but it has less efficiency in terms of color removal. However, when it is used in combination with one of the advanced oxidation processes, either as a pre-treatment or post-treatment under a controlled time and dose, it reduces the cost of treatment and also increases the efficiency, making treatment feasible at larger scales.

4.2. Recommendations

The treatment of pulp and paper wastewater with an integrated treatment that involves advanced oxidation processes can boost the removal efficiency for color and COD. However, there is a need to improve the efficiency of the biological treatment by increasing its retention time and improving the conditions. Advanced oxidation processes (such as ozone treatment, Fenton treatment and photo-Fenton treatment) can be used for the treatment of paper and pulp industrial wastewater at a low cost in order to minimize the discharge of dangerous pollutants into the environment. A treatment design for their industrial-scale application is required to achieve the best wastewater purification. An engineering management system should be designed and operated on an industrial scale for application in industrial ecology. The manufacturing processes in the pulp and paper industry should be modified, and cleaner production practices should be applied for the protection of the environment.

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