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# Removal of Dye and COD from Textile Wastewater Using AOP ($UV/O_3$, $UV/H_2O_2$, $O_3/H_2O_2$ and $UV/H_2O_2/O_3$)

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**ABSTRACT**

***Introduction:*** Textile industry effluent is a complex sewage with chemical and color materials that is discharged into the environment and can cause serious problems. In this way using advanced oxidation methods and finding the best methods for removing color materials is necessary. An experimental method was done on Kashan textile industry effluent in laboratory scale and batch system.

***Material and Methods:*** Initially, optimal condition was obtained for $O_3$ and $H_2O_2$ and followed by advanced oxidation methods ($UV/O_3$, $UV/H_2O_2$, $O_3/H_2O_2$ and $UV/H_2O_2/O_3$) in different reaction times and pH on dye removal and COD (chemical oxygen demand) were determined. The results were compared with complex repetition method.

***Results:*** The results of this research showed that dye removal impact and COD based on the type of process and reaction time in $UV/H_2O_2/O_3$ by 30 minute time duration, was the most effective method. $UV/H_2O_2$ in 10 minute time duration was the least effective method. COD and color removal, based on the process in $UV/H_2O_2/O_3$ and pH = 6 was the most effective. The effect of $UV/H_2O_2$ and pH = 4 was the least efficient method on dye material removing. Results showed that the treatment time was effective on color removing (P < 0/001) statistically.

***Conclusion:*** It can be concluded that $UV/H_2O_2/O_3$ was the most efficient on color removing process, compared to the others, due to co-incidence presence of strongly numerous oxidants and their aggravating effect through producing active hydroxyl radicals (OH˚).

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## Introduction

Nowadays, industries are developing so fast and attention to their environmental economic consequences is neglected. The sewage treatment should specially be done using different processes, such as using the chemical material and physical agent [1]. Textile industries produce sewage which contains numerous chemicals material which are poisonous and resistant against biodegradation as well as stable in the environment [2, 3].

The most significant characteristic of textile sewage is its color [4]. In textile industries, the process of dyeing and finishing generate a lot of sewage with a large amount of dyes [5, 6]. Dyes are synthetic compounds which make our world beautiful, and their use is increasing [7]. Moreover, they are organic compounds which are considered as one of the most significant chemicals used in industries such as textile, tanning, manufacturing of paper and so on [8].

Annually more than 10,000 dyes are produced in 7 $\times10^5$ metric tons, which are commercially available worldwide. About 15% of the dyestuffs are missed in the industrial effluents throughout the manufacturing processes. The statistics indicate that 100 L of wastewater is produced per kilogram of textile product that is equivalent to 3.7 million liters worldwide [9].

Discharge of these sewages into the environment causes disturbance of aquatic environment due to preventing the sunlight shining on them and slowing the process of photosynthesis, then threatening the aquatic plants and ecosystem totally [10]. Dye compounds are usually made to resist fading while washing by soap and water or being in sunlight and this make them more stable against biodegradation [11.] So, their elimination is necessary as a pollutant.

Dyes resist degradation, are chemically stable and non-biodegradable. They also have toxic and carcinogenic characteristics. Therefore, we need to design a proper treatment strategy to meet the pollution control requirements. The conventional treatment methods mostly include adsorption, coagulation, filtration and biological treatment. However, these methods are not so efficient because dyes are stable against biological degradation and this leads to sludge formation, membrane fouling and incomplete Advanced Oxidation Processes [12].

Advanced Oxidation Process (AOP) is the most effective way in dye removal and the application of this process in wastewater treatment leads to the degradation of the pollutants rather than transferring them to another phase, making the relevant technologies effective in the omit of organic pollutants in solution [13]. In this context, AOP has been recognized as an effective technology to obtain a full degradation of organic compounds and their intermediates, based on the active reaction of powerful oxidant species, such as hydroxyl radical ($HO^{\bullet}$).

Dye molecules under the action of such radicals can be easily degraded and reach a complete mineralization [14]. AOPs processes use powerful oxidants ($O_3$, UV, UV/$O_3$, UV/$H_2O_2$, $H_2O_2$/$O_3$ and $O_3$ /UV/$H_2O_2$) for destroying organic pollutants in the presence or absence of sunlight [3, 15]. The main advantage of this process is preventing the environmental secondary products formation which can be contaminant, removing the risk of increasing oxidant factors and high speed of processing and utilizing [16]. Various studies showed that ozonation process can approximately remove 58% of dyes from raw sewage of textiles and 98% by using combined processes of UV, UV/$H_2O_2$[3]. Another research done on the removing of textiles sewage indicated that the removal efficiency of dyes and COD are 91% and 82% by using oxidation process respectively [8].

Another research conducted by Perkowski and Ledakowicz emphasized that advanced oxidation process can remove dyes completely [17].

Since textile sewage dye is considered as the main environmental pollutant, this study has been done to use advanced oxidation process in dye removal from dying sewage. Meanwhile, the low cost, stability and high efficiency of the AOPs process compared to the other methods as well as advancing industries in Iran along with dying sewage were the main motivation for this research.

The main goal of this study was to assess the efficiency of different AOPs: UV/$O_3$, UV/$H_2O_2$, UV/$H_2O_2$/$O_3$ and $O_3$/$H_2O_2$ in the treatment of a real textile wastewater in a pilot scale unit with compound parabolic collectors (CPCs), under natural radiation, and evaluate the influence of the main photocatalytic reaction variables of the most efficient AOP, in a lab-scale prototype in controlled conditions using artificial solar radiation [14].

## Materials and Methods

This experimental study was performed at chemistry laboratory of water and wastewater in

Faculty of Health in Kashan University of Medical Science. It was conducted on the sewage of Kashan textile industry in laboratory scale and closed system. Collected samples having $4^0$C temperature degree were transferred to the laboratory and tested at $20^0$C. The treating reactor made of Pyrex cubic form with 20 × 20 × 30 cm dimensions, containing an inner cubic with dimensions of 10 × 10 × 25 cm. The produced ozone was introduced into the reactor by a tube. In order to sewage irradiation, a UV lamp was set inside the container, which had 3 liters capacity of sewage sample. Magnetic stirrer was used on the floor of the reactor mixing wastewater mixture. A French ozone maker (ARDA) with a capacity of generating of 10.5 grams per hour was used. UV ray was radiated by UV lamp made in German company (NARVA) (NEF model- 125 watt). pH meter (Fanavary Tajhizat Sanjesh model, pH 262) was used to measure hydrogen ion potential of samples. For measuring color, (based on standard method, Book 212OC) [18], spectrophotometer (APEL model, PD-UV 303) was used. The method 522OC of standard book was used for measuring COD [18]. Raw and treated samples color were measured by spectrophotometer at various 30 waves length which measured the density of transmitting light. So the removal efficiency of color at various condition was calculated by light transmitting. The method was followed by stages. At first, the optimized $O_3$ and $H_2O_2$ were achieved for treating in $UV/H_2O_2/O_3$ compound method, i.e. in pH = 10 and time duration of 30 minutes with changing $H_2O_2$, mg/l concentrations per a litter of wastewater between amounts of 5, 10, 15, 20 minutes and dosages of Ozone between amounts of 1, 4, 7, 10 g/h. 48 samples were collected through 3 repeated optimization. Secondly, treating wastewater at optimized conditions by considering Ozone dosage and fixed hydrogen peroxide concentration in 4 advanced oxidation methods including: $H_2O_2/O_3$, $UV/H_2O_2$ and $O_3/UV/H_2O_2$ in 10 g/h and 10 g/l were performed respectively. Also, UV had stable radiation during experiments. The experiments were carried out by repeating 3 times in four pH 4, 6, 8, 10 and during 10, 20 and 30 minutes' time lapse for 4 advanced Oxidation methods that totally 144 samples were tested for each of 4 methods. For doing so, firstly 3 liters of the raw filtered sample were added to the concerned pH, and then purred into the reactor. Hydrogen peroxide was used by adding to the sample and stirring for 10 minutes. In the case of ozone treating, ozone maker started and oxygen tap was opened to produce ozone. In the experiment by UV treatment, UV ray was radiated to the sample above the reactor in a closed area. Then, the sample stayed under the hood until ozone was ventilated. In the last stage of experiment, the color of the treated wastewater color was read by spectrophotometer in 30 nm wave length. Finally, the obtained results were firstly examined by kolmogorov-smirnov according to normality and then their normal effects were analyzed by repeated measurement.

## Results

The results from optimizing $O_3$ and $H_2O_2$ for COD and color removing showed that the best dosage of ozone and concentration of hydrogen peroxide regarding their cost and efficiency for removing color and COD were 10 grams of ozone per litter per hour, and 10 grams of hydrogen peroxide per litter per hour respectively.

The obtained results from textiles sewage by using 4 AOPs are summarized in tables 1 and 2, including: using four methods of advanced oxidation according to the type of method and time consumed. The efficiency of dye removal and COD based on the type of method and time lapse is shown in table 1 and based on the type of method and pH in table 2. In all methods, the amount of removal increased in proportion to increasing the treatment time from 10, 20, and 30 minutes. The relative amount of dye and COD, treating by $O_3/UV/H_2O_2$ method was 89.2% and 76.7% respectively. The process of $UV/O_3$ was the next which could remove 73.7% of color and 66.5% of COD from the sewage during the highest time duration. The third method, $H_2O_2/O_3$, with the little degree of the previous method could remove 11.2% color and 66.5% COD. But the last method,

$UV/H_2O_2$, had the least amount of removal efficiency, which is, 58.3% and 48.1% for color and COD respectively. As shown in table, 2, the most amount of removal was related to $O_3/UV/H_2O_2$ in pH = 8 that has been able to remove 84.7% color and 76.5% COD while in $UV/O_3$ that stands after the compound process, in pH = 8 had the most amount of removal equal to 72.5% for color and 69.4% for COD. $H_2O_2/O_3$ had also a high amount of removal in pH = 10 by 71% for color and 64.2% for COD, where $UV/H_2O_2$ stood in the last place with pH = 4 that was able to decrease level of 59.4% and 49.5% for dye and COD in sewage, respectively.

**Table 1:** Mean and standard deviation of dye and COD removal efficiency based on the type of process and time.

| Method | Parameter | Time (min.) 10 | 20 | 30 |
|---|---|---|---|---|
| $UV + O_3$ | Color | 62.7 ± 2.9 | 67.5 ± 3.3 | 73.7 ± 6.9 |
| | COD | 61.6 ± 8.4 | 61.4 ± 6.9 | 67.6 ± 3.9 |
| $UV + H_2O_2$ | Color | 40.7 ± 8.3 | 52.1 ± 11.1 | 58.3 ± 9.1 |
| | COD | 35.2 ± 7.6 | 44.5 ± 6 | 48.1 ± 6.5 |
| $O_3 + H_2O_2$ | Color | 58.6 ± 8.9 | 66.3 ± 6.6 | 71.2 ± 7.4 |
| | COD | 55.3 ± 3.2 | 60.6 ± 5.4 | 66.5 ± 3.2 |
| $UV + H_2O_2 + O_3$ | Color | 69.7 ± 6.9 | 81 ± 6.4 | 89.2 ± 4.3 |
| | COD | 69.7 ± 3.3 | 73.2 ± 3.4 | 76.7 ± 3.9 |

**Table 2:** Mean and standard deviation of dye and COD removal efficiency based on the type of process and pH.

| Method | Parameter | pH 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|
| $UV + O_3$ | Color | 66.1 ± 5.1 | 64.3 ± 3.1 | 72.5 ± 7.6 | 68.9 ± 6.8 |
| | COD | 59.4 ± 7.4 | 60.2 ± 6.7 | 69.4 ± 3.5 | 65 ± 5.8 |
| $UV + H_2O_2$ | Color | 59.4 ± 10.6 | 49.1 ± 7.6 | 50.3 ± 13.1 | 42.7 ± 11.2 |
| | COD | 49.5 ± 5.2 | 47.2 ± 6.6 | 38.9 ± 4.2 | 34.8 ± 8.1 |
| $O_3 + H_2O_2$ | Color | 59.6 ± 9.6 | 62.1 ± 8.2 | 68.8 ± 7.5 | 71 ± 7.9 |
| | COD | 57.1 ± 6.4 | 59.2 ± 5.6 | 62.7 ± 5.3 | 64.2 ± 5.3 |
| $UV + H_2O_2 + O_3$ | Color | 79.8 ±10.1 | 84.7 ± 9 | 76.3 ± 10.4 | 79.2 ± 10.3 |
| | COD | 73.8± 3.6 | 76.5 ± 5.4 | 71.7 ± 3.5 | 70.9 ± 3.2 |

## Discussion

The Results of this research indicated that the $O_3/UV/H_2O_2$ method is effective and preferable on dye removing and COD comparing other processes. The preference is observable in removing dye and COD based on the type of reaction and pH as well as the reaction time. In treating textiles sewage, the significant factor which must be effectively removed is dye material and COD. The obtained results indicated that $O_3/UV/H_2O_2$ compared to other processes is the most effective in removing dye due to some potent coincident oxidant and their aggregative effect through the more production of active hydroxyl radicals ($OH^0$). When UV is radiated to the sewage including $H_2O_2$, hydroxyl radicals are produced. They are strong oxidants, which easily oxides organic compounds [19]. The high efficiency of $UV/H_2O_2$ process in pH = 4 of dye removing is refering to increasing hydroxyl radicals production in the low pH, hydroxyl radicals interact with organic compounds [20]. In the methods, $H_2O_2/O_3$, in higher pH such as 10, $O_3$ converts to $HO_2^0$ in presence of $H_2O_2$ which would be the starting point of more effectiveness. In acidic pH, $H_2O_2$ gradually reacts with $O_3$ [21]. Ozonation and $UV/H_2O_2$ on sewage containing two dye materials - Blue 199 and Black 22–during 10, 20, and 30 minutes suggested that treating by ozone is more effective than $UV/H_2O_2$. So, low function of it in the reactor is due to short-term penetration of UV blocked by AZO color [22]. Galindo and Kalt reported that the $UV/H_2O_2$ was the most effective on acidic environment (pH = 3-4) in removing color, which is similar to the present results [23].

In a research by using of $H_2O_2/O_3$ on sewage of dying industries, it was suggested that treating sewage by this process depends on pH of sewage. The researchers reported that 74% and 11% of ozone can be absorbed in pH = 11.5 and pH = 2.5 respectively [24]. Attribution of the phenomenon to this fact is that the higher the level of pH, the more conversion of $H_2O_2$ to $HO_2$ ions. Therefore, the amount of ozone analysis increases in proportion to the increase of pH which corresponds to this study.

In a study conducted by Thanh and coworkers on removing non-biodegradable organic campers from bioreactor with membrane infiltration by $H_2O_2/O_3$, indicated that the trend of oxidation with peroxide ($H_2O_2/O_3$) removes 53% and 54% of dye in pH = 8.5 during 25 minutes and $UV/O_3$ oxidation respectively [25].

A research done by Yonar et al. on textile sewage, the best result for color removal was 99% and 96% for $O_3/UV/H_2O_2$ and $UV/H_2O_2$ during 60 minutes respectively. The optimal pH for the process $UV/H_2O_2$ was threefold. Treating by $UV/O_3$ in optimal pH = 9 during 60 minutes was 98% degree in color removing [26].

The study of Azbar and coworker on sewage decoloration of polyester and acetate fibers by using $AOP_S$ suggested that the maximum removal efficiency of color was 50% degree, in the case of $O_3/UV/H_2O_2$, the best result for removal was 96% which corresponds to the findings of this study [27].

Obtained results from the study of Perkowski and Ledakowicz on color removal in water solution during oxidation processes suggested that the highest efficiency can be obtained for color removal in $O_3/UV/H_2O_2$ and the minimum efficiency is referred to ozone and hydrogen peroxide treatment. Perkowski research showed that the required time for obtaining 80% of decoloration was 55 and 42 minutes for $UV/O_3$ simultaneously. In the case of $UV/H_2O_2$ treating during 30 to 40 minutes 50% of removing was observed. These results correspond to this study [17].

## Conclusion

It can be concluded that $O_3/UV/H_2O_2$ process used in this study is preferable compared to other processes in removing colors from textile industries sewage. The optimized pH for the process was 6 and the best reaction time was 30 minutes. Having low costs, not requiring expensive instruments and laboratory equipment simplicity of the process are the advantage of this method. Its application in different areas for preventing environmental pollution is recommended.

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## Conflict of interest

There is not conflict of interest



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