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Contributed Paper

Photocatalysis Using Titanium Dioxide for Treatment of Textile Wastewater Containing Disperse Dyes

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ABSTRACT

Present research work was carried out to investigate the decolorization of synthetic textile wastewater using titanium dioxide as a photo-catalytic agent. Synthetic wastewater was prepared by mixing three disperse dyes. Samples were passed through artificial and solar-assisted photo-catalysis. Photo-catalytic treatment was evaluated with help of different parameters like dose of titanium dioxide (TiO_2), concentration of synthetic dyes wastewater having disperse dyes, pH, concentration of hydrogen peroxide (H_2O_2), and temperature. Artificial photo-catalytic treatment was done using synthetic light lamp, with different light intensities and solar-assisted treatment was carried out at different times of day under optimized conditions. The different parameters were employed for water quality assurance such as total organic carbon (TOC) and chemical oxygen demand (COD). The maximum decolorization and mineralization was obtained with solar-assisted photo-catalysis treatment. The degradation products were studied using FTIR spectral studies.

Keywords: textile effluents, advance oxidation processes, mineralization, titanium dioxide, FTIR

1. INTRODUCTION

A huge amount of water has been used in textile industry for dyeing, printing etc. Around worldwide dye production, 10-20% of dyes are lost during the process of dyeing and discharge into industrial effluents [1]. Industrial dyestuffs contain a large group of organic compounds that result in increasing environmental pollution [2]. Synthetic dyes show resistant towards the light, microbes because of their stable nature, so to protect the aquatic environment there is utmost need of their removal from industrial effluent [3]. The effluent from textile processing unit is sometimes discharged to municipal sewage water plants or directly to waterways [4]. There are several reasons why the colors of dyes cause problems in textile wastewater. The treatment of wastewater from textile dyeing units is a major environmental problem that has received considerable attention [5].

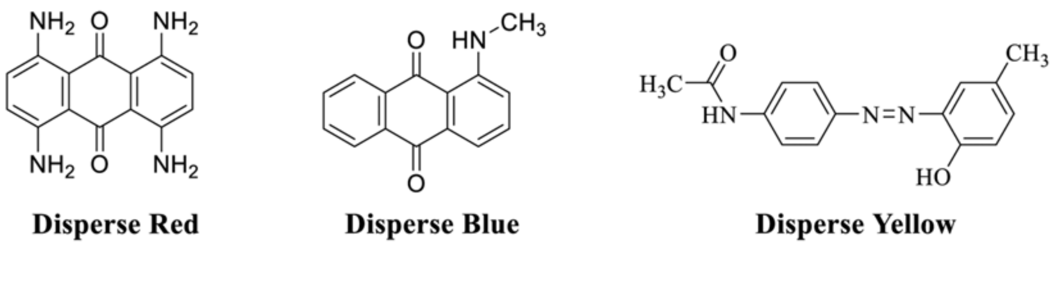
There are numerous physicochemical and biological methods available for treatment of dye contaminated industrial effluent. Physical methods only transfer pollutants from liquid to solid phase or another liquid phase but do not degrade them. On the other hand, biological methods are very easy to apply and show the environmentally friendly relation, but the production of sludge has major drawback [6]. But from last few decades, a newly developed technology known as advanced oxidation process (AOP‘s) has been used for water and wastewater treatment. AOP‘s produce •OH radical that is strong oxidizing species which makes reactions who‘s lead to the destruction of pollutants in aqueous solution whether they are inorganic or organic [7]. In comparison to others, titanium dioxide (TiO_2) is effective photo-catalyst for degradation of contaminants present in water. The choice of TiO_2 is because of its several specific properties such as low cost, chemical stability, highly oxidation strength, non-toxicity and availability in the excess amount [8]. Any photo-catalytic degradation process depends on various parameters such as pH of the solution, the concentration of dye, the concentration of catalyst etc. [9]. The present project is focused on the decolorization of notorious and problematic three disperse dyes using TiO_2 as a photo-catalyst.

2. MATERIALS AND METHODS

2.1 Materials

All the chemicals and reagents were purchased from Merck (Pvt.) Ltd. and further these chemicals were used for experimental analysis without implementation of any analytical technique for purification. But the Disperse Red, Disperse Yellow and Disperse Red were delivered by Sandal dyestuff (Pvt. Ltd) Faisalabad, Punjab, Pakistan for research purpose.

Decolorization of synthetic effluent (having a mixture of three dyes) was investigated in the present study.



2.2 Preparation of Synthetic Wastewater

A synthetic textile effluent (wastewater) was made in the laboratory by mixing disperse dyes (Disperse Red, Disperse Yellow & Disperse Blue), hydrolyzed starch (0.003 g/L), Na_2SO_4 (0.027 g/L) and Na_2HPO_4 (0.02 g/L) in de-ionized water. Tymol N-N, dispersing agent was used for homogenization. The reaction vessel was placed on magnetic stirrer bar for 1.5h at 80 °C.

2.3 Experimental Procedure

70 mL of each solution (synthetic effluent, hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2) solution) were taken in a reaction chamber. The reaction vessel was placed on magnetic stirrer bar for 1h at 70°C. After each 10-minute, sample solution was taken to measure absorbance at 410 nm (λ_{max}) [10, 11]. Different experimental parameters like synthetic effluent concentration (1-5%), pH (4-8), H_2O_2 (0.003-0.03M), TiO_2 (0.001-1 g/L) were optimized. Optimization of parameters was done by changing one parameter at one time while keeping others as same.

2.4 Photo-catalytic Treatment

After optimization of parameters, photo-catalysis was studied using TiO_2 in artificial light source and solar light. While using the artificial light source, different levels of light intensity (500-2500 lx) were studied following the same methodology discussed above. With solar light, experimental samples were evaluated in the morning, noon and afternoon [12].

2.5 Chemical Analysis

All experiments were done in triplicate. The absorbance of all samples was evaluated at wavelength 410 nm using UV/Visible spectrophotometer (Model UV-1650PC, Shimadzu Co., Japan). The following formula was used to calculate the decolorization efficiency (%) of the process:

$$\text{Decolorization (\%)} = (I - F)/I \times 100$$

Whereas I showed the absorbance of the untreated sample; F showed the absorbance the of treated sample

2.6 Mineralization Study

Different quality assurance parameters like chemical oxygen demand (COD) and total organic carbon (TOC) were determined to study the mineralization efficiency following the standard protocols [13].

2.7 Spectral Study

The degradation products were characterized by FTIR.

3. RESULTS AND DISCUSSION

3.1 Determination of λ_{max} for Synthetic Dyes Wastewater Under Study

For analysis of synthetic dyes wastewater, the wavelength of maximum absorbance (λ_{max}) is normally used. For determination of wavelength of maximum absorbance (λ_{max}), the absorbance from 400 nm to 650 nm was measured. The λ_{max} of the synthetic dyes was found to be 410 nm.

3.2 Optimization of Experimental Conditions for Decolorization of Synthetic Wastewater

Various experimental parameters like concentration (1-5%) of synthetic dyes wastewater, pH (4.0-8.0), H_2O_2 concentration (0.003-0.03M) and TiO_2 concentration (0.001-1g/L) were optimized by changing one parameter at one time while keeping other factors the same. Increase in the concentration of synthetic effluent from 1 to 2%, increased the decolorization from 51.11 % to 73.10 % in 50 min. Further increase in concentration of synthetic effluent resulted in a decline in decolorization (Figure 1). A literature survey showed that as the dye concentration increases, the amount of dye adsorbed on the catalytic surface also increases [5, 14].

To optimize the evaluated catalyst dose, a series of experiments having concentration of TiO_2 (0.001, 0.005, 0.01, 0.1 & g/L) were carried. It was revealed that as titanium dioxide (TiO_2) concentration increased from 0.001 to 0.1 g/L, the percentage (%) decolorization also increased from 60.65 % to 73.57 %. Above the concentration 0.01 g/L of titanium dioxide (TiO_2) dose, it showed that, there was no significant increase in the degradation of dye (Figure 2). So, the concentration (0.01 g/L) of titanium dioxide (TiO_2) has been observed as an optimized dose of titanium dioxide (TiO_2) for decolorization of synthetic effluent for later experiments. Present experimental observations are in accordance with the literature [15].

pH is an important parameter. Therefore, it is very necessary to understand the character of pH on degradation of dye [7]. The decolorization (%) increased with increase in pH with maximum decolorization (79.95 %) of effluent was observed at pH 6.0 (Figure 3). Further, increase in pH caused decrease in decolorization. Catalyst works efficiently at an optimum pH, beyond which no appreciable decolorization of dyes could be obtained [16, 17].

The role of hydrogen peroxide (H_2O_2) is also very important because it was used as the oxidizing agent in present treatment [18]. It was shown that the addition of concentration of hydrogen peroxide (H_2O_2) from 3×10^{-3} to 9×10^{-3} (M), increased the decolorization from 45.47% to 72.04% and a further increase in concentration resulted in a decline in decolorization (49.65 %) (Figure 4). Hydrogen peroxide has an important role in degradation of dyes wastewater but it has a drawback that at the same time H_2O_2 is unstable in basic medium and rapidly decomposed to oxygen and water at neutral to higher pH values as a result lost its oxidation ability [19].

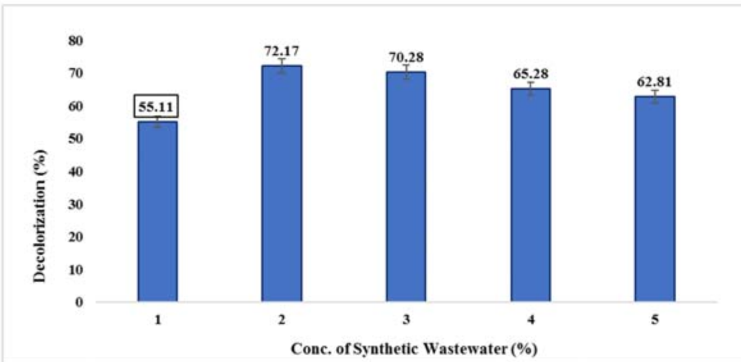


Figure 1. Effect of concentration of synthetic dyes wastewater on its decolorization (%) using TiO_2.

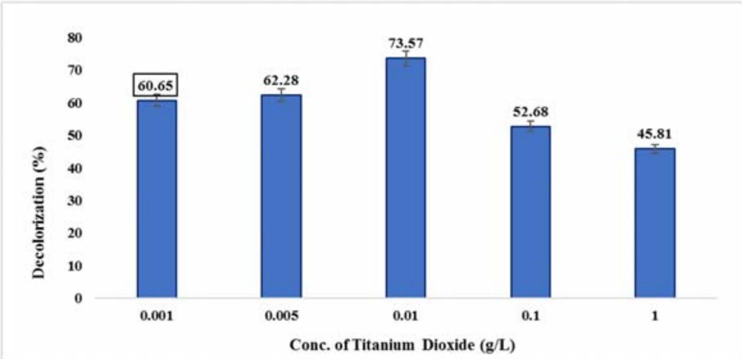


Figure 2. Effect of conc. of TiO_2 on decolorization (%) of synthetic dyes wastewater.

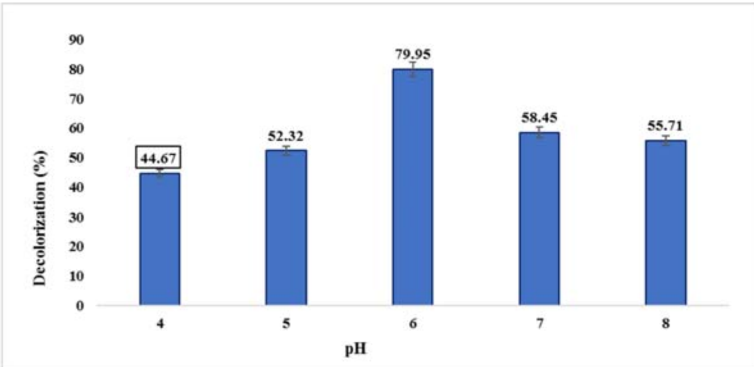


Figure 3. Effect of pH on decolorization (%) of synthetic dyes wastewater using TiO_2.

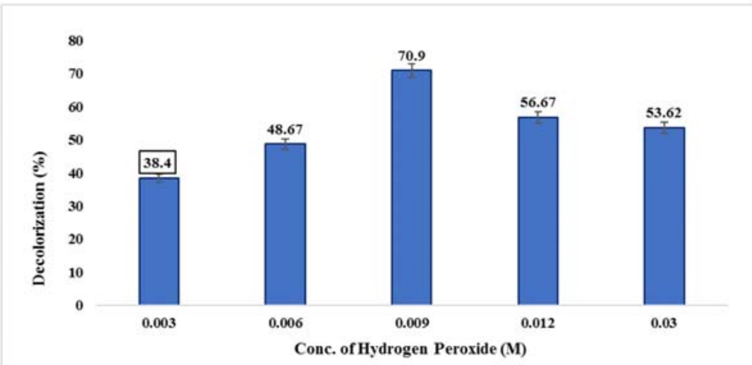


Figure 4. Effect of conc. of H_2O_2 on decolorization (%) of synthetic dyes wastewater using TiO_2.

3.3 Photo-catalysis using the Artificial Light Source

The artificial light is found to be an important source of photons crucial for the transfer of electrons from valence band (VB) to the conduction band (CB) of a catalyst like TiO_2. The energy of a photon is directly connected with wavelength and the overall energy in the process is dependent on light intensity [20]. A series of experiments were made using artificial light (500, 1000, 1500, 2000 & 2500 lx). It was observed that as the light intensity was increased from 500 to of 2000 lx, the percentage decolorization was increased from 55.57% to 74.29% as shown in Figure 5.

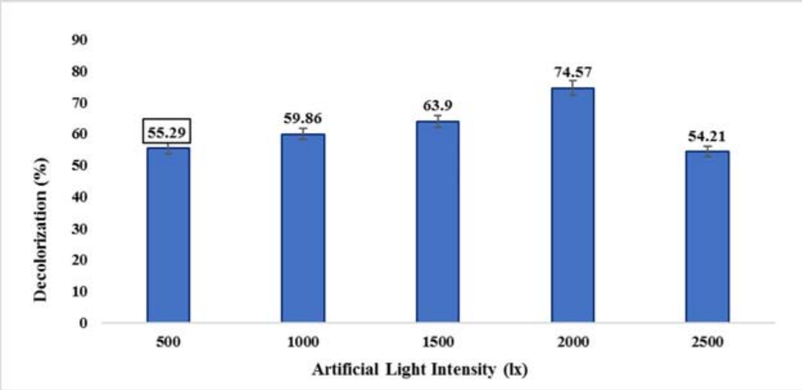


Figure 5. Photocatalysis of synthetic dyes wastewater using artificial light intensity (lx) and TiO_2.

3.4 Photo-catalysis Using Solar Light

The consequence of UV/Solar light energy source on the decolorization by the photo-catalytic process has been investigated under optimized conditions. For this reaction proceeded in the different light intensity of sunlight like in the morning, noon and afternoon. It is evident from the result that at noon there was maximum decolorization (80.17%) shown in Figure 6. Titanium dioxide (TiO_2) assisted photo-catalytic using solar light energy source has been successfully used and is an economically very inexpensive process that can replace artificial light energy sources which are very costly and harmful [21]. Normally, due to economically very cheap source, solar light photo-catalysis degradation was used [22].

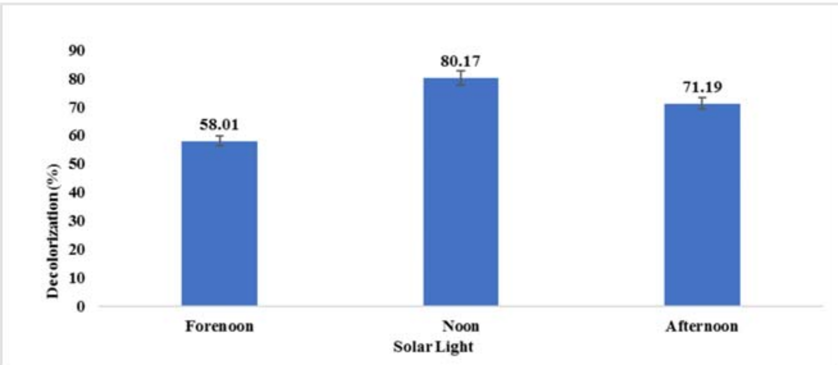


Figure 6. Solar-assisted photocatalysis of synthetic dyes wastewater using TiO_2.

3.5 Effluent Characteristics Before and After Treatment

After different treatments (without light, artificial light-assisted, solar-assisted) of synthetic dyes wastewater under optimized conditions, characterization of reduction in TDS was done. All treatments showed a positive reduction in TDS value. However, reduction in TDS (86.66%) under solar-assisted photo-catalysis was comparatively higher (Table 1).

Table 1. Characteristics of synthetic dyes wastewater after different treatments.

Treatment Type	TDS (ppm)	% Reduction
None	414	-
Without light source	185	55.32
Artificial light assisted	110	73.43
Solar assisted	55.25	86.66

3.6 Mineralization Study

Analyses of water assurance quality parameters like chemical oxygen demand (COD) and total organic carbon (TOC) of all treated samples were carried out to find their mineralization efficiency. Treated wastewaters by all advanced oxidation processes (AOP's) increased in removal percentage of all quality assurance parameters as the reaction time was increased depicted the mineralization progress [5]. In photo-catalytic treatment, the percentage reduction in COD, and TOC were observed to be 80.20 and 79.43 for synthetic effluent (Figure 7). Our results are in accordance with the literature [23].

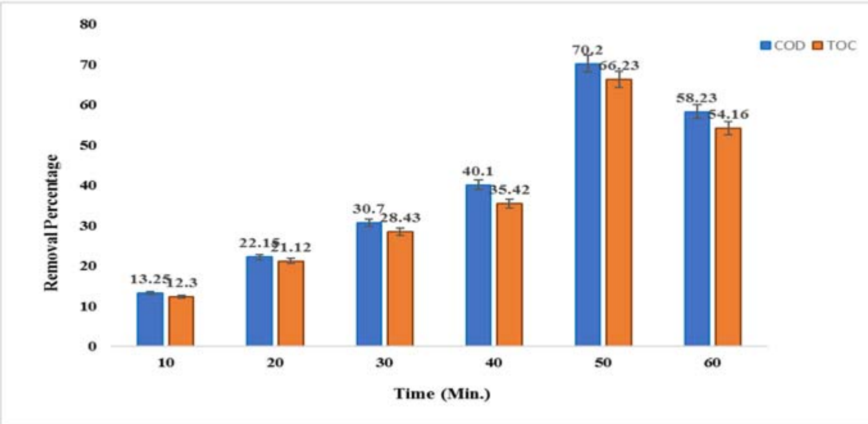


Figure 7. Effect of photocatalytic treatment contact time on water quality parameters.

3.7 Spectral Analysis

FTIR spectrum of untreated dyes wastewater displayed peaks at 3344.59, 2352.21, 1646.3, 619.15 and 613.956 cm^{-1} for -OH stretch of phenol, N=N stretch and C=C stretching of mono-substituted benzene ring (Figure 8) while the FTIR spectrum of the degradation products showed appearance of peaks at 2364.64 cm^{-1} for =C-H stretch, 1562.06 cm^{-1} for aromatic ring skeleton and 610-690 cm^{-1} for mono-substituted benzene ring (Figure 9 and 10). The absence of peaks between 3650 to 3590 cm^{-1} indicated no formation of phenolic compounds and absence of peaks between 3400 to 3380 cm^{-1} for -NH stretches indicated that no aliphatic and aromatic amines were formed by degradation of synthetic dyes wastewater by both photo-catalytic treatments. FTIR spectral analysis indicated the degradation of dyes wastewater into intermediate products. The peak characteristic of the azo bond at 1646.3 cm^{-1} was absent in the decolorized medium, indicating degradation of dyes wastewater due to aromatic amines as intermediate products which were subjected to oxidation giving rise to simpler compounds. Our results were supported by the literature [24].

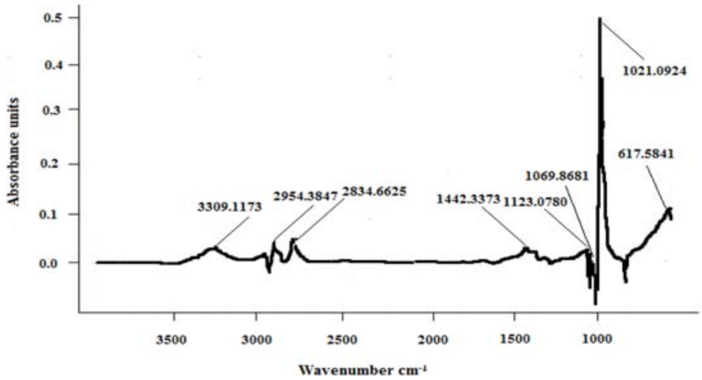


Figure 8. FTIR spectrum of synthetic dyes wastewater before photocatalytic treatment.

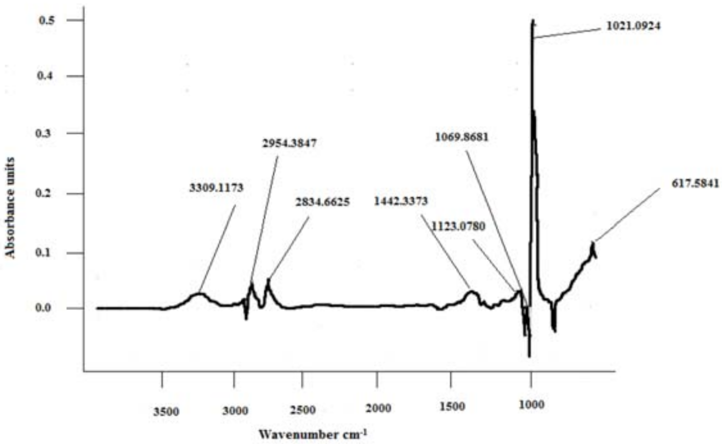


Figure 9. FTIR spectrum of synthetic dyes wastewater after photocatalytic treatment using artificial light source.

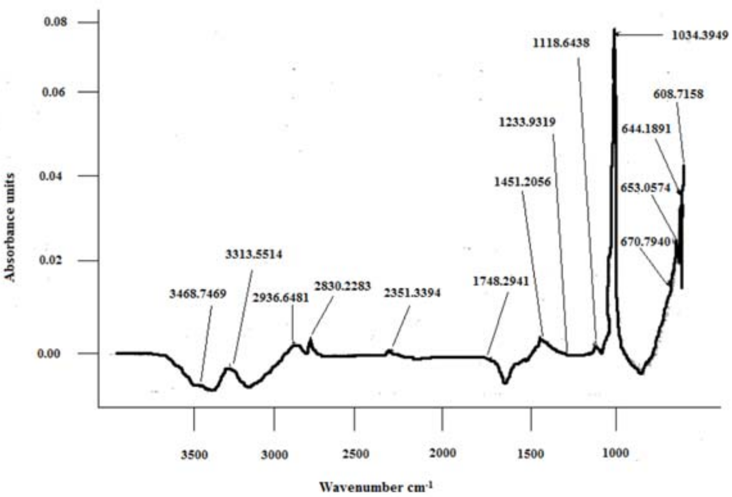


Figure 10. FTIR spectrum of synthetic dyes wastewater after photocatalytic treatment using solar light.

4. Conclusion

The advanced oxidation processes (AOP's) like artificial photo-catalysis, solar-assisted photo-catalysis were used for decolorization and mineralization of textile effluents having dispersed azo dyes in this research work. Various experimental parameters like synthetic wastewater concentration, hydrogen peroxide (H_2O_2), temperature, pH, titanium dioxide (TiO_2) and light intensity were optimized. The different quality assurance parameters like (COD and TOC) were evaluated by standard protocols for treated and untreated dyes wastewater. Mineralization study was confirmed after FTIR spectral analysis. During this work, it was shown that solar-assisted process was more significant, in decolorization and mineralization of effluents, with respect to artificial method, based on the production of many hydroxyl radical (•OH) by the UV radiation and allowed the total decolorization, mineralization of synthetic dyes wastewater.

5. Future Recommendations

The advanced oxidation processes (AOP's) like artificial photo-catalysis, solar assisted photo-catalysis for decolorization, mineralization and degradation of azo dyes are verified to be best to be applicable for industrial effluents having dyes to reduce the water pollution being a big part of environmental pollution. Among chemical treatments, solar-assisted photo-catalysis is the first option and artificial photo-catalysis treatment is the second one. However, to get complete mineralization of notorious dyes, use of sequential strategy will gain more popularity in coming times.

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