

Original Research

Using Combined UV and H₂O₂ Treatments to Reduce Tannery Wastewater Pollution Load

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Abstract

Contaminated wastewater discharged from tanneries in Pakistan creates a lot of pollution problems. This study presents the treatment of wastewater samples collected from inlet and outlet sections of Kasur Tannery Waste Management Agency (KTWMA) in Kasur, Pakistan. The procedure utilizes hydrogen peroxide (H₂O₂) in the presence of ultraviolet (UV) radiation for the successful degradation of pollutants present in tannery water. The treatment of polluted water samples with UV/H₂O₂ for the duration of either 45 minutes or 90 minutes has greatly affected the water quality parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), chlorides, chromium, pH, total dissolved solids (TDS) and total suspended solids (TSS). It was concluded that the contaminants were degraded and changed to a great extent as compared to their original concentrations. This process can be considered to be a clean process as it is an environmentally friendly process and does not produce pollutants and solid wastes like other conventional processes.

Keywords: tanneries, wastewater, UV, H₂O₂, environment

Introduction

The tannery industry belongs to one of the most polluting industrial sectors [1]. A large quantity of wastewater is produced during the leather tanning process [2, 3]. Such water contains higher concentrations of organic matter, sulfates, chlorides, heavy metals,

TDS, TSS, lime and other pollutants [3]. The toxicants arise from the skins of animals and the chemical reagents that are added during the leather tanning process. Heavy metals such as chromium, nickel, etc. do not decompose and start to accumulate in the bodies of living creatures and may affect the functions of the cells. Hexavalent chromium can cause cancer even in small quantities. So these pollutants must be removed from tannery effluents before their discharge into water bodies [4]. Many conventional methods such as chemical process, oxidation process, electrocoagulation

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and biological process are used to treat tannery wastewater, but these methods are inefficient on a large scale due to economic and maintenance problems [4-6]. Although reverse osmosis (RO) and nano-filtration (NF) are readily considered the best available techniques, both require a high operating pressure to get the desired output (permeate flux). Ultrafiltration has also been applied in many industries, however, it requires further filtration by either NF or RO [7].

The treatment of drinking water by advanced oxidation processes (AOPs) was proposed first in the 1980s and later this technique was expanded for the treatment of various wastewaters [8, 9]. AOPs presented a greater performance as compared to the conventional chemical treatment procedures [10], and has been successfully employed for the treatment of industrial wastewater, particularly in the case of non-biodegradable compounds [11]. AOPs cause degradation of the organic molecules and convert them completely into non-toxic components such as CO_2 and/or water. AOPs have also been proven to be extremely effective in killing pathogens (fecal coliform, total coliform, fecal streptococci, *E. coli* and salmonella) due to their strong oxidative characters [12].

The advanced oxidation processes (AOPs) involve the utilization of free radicals, and many of them employ UV photolysis of conventional oxidants such as H_2O_2 , ozone, and S_2O_8 , etc. [13]. The hydroxyl radical ($\cdot\text{OH}$) plays a major role in AOPs due to its extremely reactive and nonselective nature; it can cause oxidation, degradation and destruction of organic chemicals as well as inorganic pollutants [14, 15]. The rate of decomposition of compounds by oxidation depends upon temperature, pH, concentration of ions, concentration of pollutants and number of OH radicals [3]. The catalysts such as TiO_2 , Mn or Fe can be used to increase the efficiency of AOPs [16]. There are reports on the use of Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) to decrease the toxicity level of industrial waste water [17, 18] and degradation of dyes [19], amines [20] and phenolic compounds [21]. It has been reported that iron powder could be used to replace iron salts as a catalyst for Fenton reaction [22].

In the present work, we report the impact of UV radiation along with H_2O_2 for the treatment of wastewater samples collected from Kasur Tannery Waste Management Agency (KWTMA) in Kasur, Pakistan. The samples were treated by UV/ H_2O_2 and were subjected to analysis for quality parameters such as pH TDS, TSS, chlorides, chromium, COD and BOD before and after treatment according to standard methods [23].

Materials and Methods

Sample Collection

Wastewater samples were collected from inlet and outlet sections of KWTMA. The collected samples were

stored and labeled in airtight polyethylenetetraphaete (PET) bottles in order to proceed for analyses and treatment with UV/ H_2O_2 .

Experimental Procedures

The samples were subjected to UV/ H_2O_2 treatment for 45- and 90-minute durations. UV source was composed of UV lamps emitting radiation of 354 nm and the radiation intensity of ultraviolet light was 140 watt. Standard procedures [23] were adopted to evaluate the water quality parameters such as TDS, TSS, chlorides, pH, chromium, COD and BOD before and after the treatment of water samples with UV/ H_2O_2 .

Total Dissolved Solids (TDS)

The samples were shaken using a magnetic stirrer in a flask. The investigated sample (100 mL) was transferred on a glass fiber with the help of a pipette and it was then filtered by applying a vacuum; 10 mL of distilled water was used for complete drainage. After three minutes of complete filtration, the suction was continued. Subsequently, the filtrate and the washings were transferred to a pre-weighted petri dish that was then heated in an oven to evaporate its contents to complete dryness. The dried residual sample was placed in a desiccator for cooling. After cooling, the weight of the petri dish was measured again. TDS was calculated as follows [23]:

$$\begin{aligned} & \text{mg total dissolved solids/L} \\ & = (A - B) \times 1000 / \text{Volume of sample in mL} \end{aligned}$$

...where A is the weight of dried residue + dish and B is the weight of the dish.

Total Suspended Solids (TSS)

The samples were shaken by magnetic stirrer to shear large particles in order to get a homogeneous particle size sample. After shaking, from the center of the container, 100 mL volume of each sample was taken with the help of a pipette. Each sample was washed with distilled water for complete drainage. In this way, all the dissolved particles with distilled water were obtained in the Petri dish as filtrate. More washing was performed for a sample containing a large amount of dissolved solids. For this type of filtration, a very small pore size of nearly 0.25-micron Whatman filter paper was used. Before filtration the weight of the filter paper was measured. After complete filtration the filter paper-containing residue was heated to dryness. Then it was placed in a desiccator to bring it to room temperature. Then the weight of the filter paper was again measured. TSS was calculated as follows [23]:

$$\begin{aligned} & \text{mg of total suspended solids/L} \\ & = (A - B) \times 1000 / \text{Volume of sample in mL} \end{aligned}$$

...where A is the weight of the filter paper + dried residue and B is the weight of the filter paper.

Chromium

a. Formation of calibration curve

The solutions of chromium of different concentrations ranging from 0.2 mg/L to 1.2 mg/L were prepared and their absorbance was noted at 540 nm one by one by taking their volume in a 1 cm absorption cell using reagent water as a reference. Then a graph was plotted between concentration and absorbance [23].

b. Preparation of blank

To prepare a blank, 50 mL of distilled water was taken in a 100 ml flask. Then 8 drops of phosphoric acid and 2 ml of diphenyl carbazide solution were added and the volume was made up to the mark. The absorbance of the blank was noted at 540 nm by transferring an appropriate amount of sample to a 1 cm absorption cell [23].

c. Oxidation of Cr (III) TO Cr (VI)

10 ml of waste water sample was taken in a 100 ml volumetric flask. Then 10 ml of H₂SO₄ was added to the flask and it was placed for 30 minutes. Then distilled water was added in order to make the volume up to 100 ml and it was cooled to bring to room temperature.

From the above solution, a 20 ml test sample was taken in a beaker. Then KMnO₄ was added dropwise till its color was changed and heated to a brown color. Then sodium azide was added dropwise until the full color was developed; the solution was then heated until the brown color was developed. Then it was cooled in a water bath tub to bring it to room temperature. The mixture was then transferred to a flask of 100 ml capacity and approximately eight drops of phosphoric acid (H₃PO₄) were added. Phosphoric acid made the colour shine. Subsequently, 2 ml of diphenyl carbazide solution was added and the volume was made up to the mark. Then it was placed for some time until the color developed.

Then the absorbance of the sample was noted at 540 nm. For accurate absorbance measurements, the absorbance of the blank was subtracted from the absorbance of the sample. The amount of chromium present in the sample was measured by the reference of the calibration curve [23].

Chlorides

100 ml of each sample was measured into a porcelain dish and its pH value was noted. The pH of all these samples was maintained in a range of 5.0 to 9.5. For the samples having pH more than 9.5 there was an addition of 0.1 molar HNO₃ drop wise to fix the pH around 8. Then the solution was stirred. For the samples having pH less than 5.0, CaCO₃ was added in a small quantity and the solution was then stirred. After adjusting the pH and stirring, 1-2 drops of potassium chromate were added as an indicator. The color of solution became

reddish. The solution was titrated with 0.0141 N silver nitrate solution until the pinkish yellow color was obtained, which was the endpoint. Then the solution of 0.0141 N silver nitrate solution was standardized by using a reagent blank by the titration method given above. Concentration of chlorides was calculated by applying the following formula [23]:

$$\text{Cl}^- \text{ in mg/L} = \frac{(\text{A}-\text{B}) \times \text{N} \times 35450}{\text{Volume of sample}}$$

Where

A = Volume of AgNO₃ required by sample

B = Volume of AgNO₃ required by blank

N = Normality of AgNO₃

Biological Oxygen Demand (BOD)

Incubation bottles of 300 mL capacity were taken and 1 mL of each wastewater sample was taken in a separate bottle. Seedling water (distilled water aerated through a mechanical source for 15 minutes per liter), MgSO₄ solution, CaCl₂ solution and phosphate buffer for 1 mL/liter were added to each sample. An incubation bottle for zero-day titration and incubation bottle for 5 days titration were used. 1 mL of MgSO₄ solution and 1 mL of alkaline iodized azide were added in an incubation bottle. Excess solution was drained and shaken very well until precipitates were formed at the bottom. 1 mL H₂SO₄ was added and mixed very well. 20 mL of this solution was added in a titration flask and 2-5 drops of starch solution were added as an indicator. The solution was then titrated with 0.025N Na₂S₂O₄ solution until a colorless endpoint was obtained. The same procedure was performed for after 5 days sample [23].

Calculations

$$\text{BOD (g/L)} = \frac{(\text{A}-\text{B}) \times (\text{C}-\text{D}) \times 300}{\text{Volume of sample}}$$

Where

A = Volume of Na₂SO₄ used for sample in zero days

B = Volume of Na₂SO₄ used for sample in five days

C = Volume of Na₂SO₄ used for blank in zero days

D = Volume of Na₂SO₄ used for blank in five days

Chemical Oxygen Demand (COD)

The samples were shaken very well and 50 mL of each sample was taken in a 500 mL refluxing flask. Then 1 gram of mercuric sulphate was added. Subsequently there was an addition of 5 ml sulphuric acid reagent added very slowly to avoid the loss of volatile compounds. Then a 25 ml solution of 0.04167M K₂Cr₂O₇ was added and mixed. The flask was attached to a condenser and cold water was turned on.

Then 70 mL of H_2SO_4 reagent was added from the open end of the condenser and covered with a small beaker so that foreign material could not enter the reflux mixture and it was refluxed for two hours. The condenser was cooled and washed with distilled water. The reflux condenser was disconnected and the mixture was diluted by adding 300 mL of water. It was cooled at room temperature. Approximately 2 to 3 drops of 0.025M ferroine indicator were added and the solution was titrated against 0.25 N ferrous ammonium sulphate (FAS) solution until a reddish brown color was obtained. The blank solution was prepared by adding 2.5 ml of 0.025 N $K_2Cr_2O_7$ solution and 30 ml of concentrated H_2SO_4 solution in 75 ml of distilled water. Then it was cooled at room temperature and titrated against 0.025 M ferrous ammonium sulphate [23].

Calculations

$$\text{COD as mg O}_2/\text{L} = \frac{(A-B) \times M \times 8000}{\text{Volume of sample (ml)}}$$

Where

A = mL of FAS used for blank

B = mL of FAS used for sample

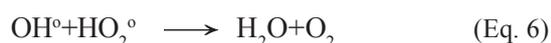
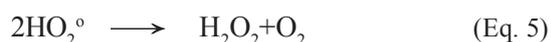
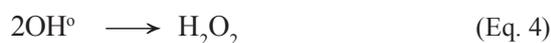
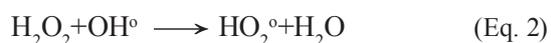
M = molarity of FAS, and

8000 = milliequivalent weight of oxygen \times 1000mL/L

Results and Discussion

Mechanism

In the method, O-O bond in H_2O_2 is cleaved to generate hydroxyl radicals (OH^\bullet) by using UV radiation. The reactions of the UV/ H_2O_2 process are:



Eq. 1 is the rate-determining step because the rates of other reactions are much higher than equation 1. In this way, in the UV/ H_2O_2 process a higher concentration of OH radicals is produced, which can decompose the target pollutants, but an optimum concentration of H_2O_2 is required for this process because an extra concentration of H_2O_2 can re-combine with OH^\bullet to reproduce H_2O_2 (Eq. 2-6) [24].

Effect of UV/ H_2O_2 on pH

There was an increase in the value of pH of wastewater with the increase in concentration of H_2O_2 along with UV radiation. This increase in the value of pH is due to the generation of OH radicals. The G-value of the OH radicals (G-OH) is more than other radicals. Therefore, a high concentration of OH free radicals remains in water, which increases the value of pH. There was more increase of the pH value after 90 minutes duration as compared to that observed after 45 minutes. The increase in percentage of pH value of inlet and outlet wastewater treated by UV/ H_2O_2 for 45 minutes observed was 6.7% and 4.6%, respectively; the increase in percentage of pH value of inlet and outlet wastewater treated by UV/ H_2O_2 for 90 minutes observed was 8.2% and 9.5%, respectively. These results are in agreement with Schrank et al. 2005 [15].

Effect of UV/ H_2O_2 on Total Suspended Solids (TSS)

UV treatment along with H_2O_2 resulted in the decrease of TSS. The decrease in TSS is due to the reason that there was decomposition of organic matter and suspended particles in the wastewater. The decrease in TSS is more for those samples which were treated for higher duration with UV radiation. The decrease in percentage of TSS for inlet and outlet wastewater treated by UV/ H_2O_2 for 45 minutes observed was 21.3% and 21.8%, respectively, and the decrease in percentage of TSS for inlet and outlet wastewater treated by UV/ H_2O_2 for 90 minutes observed was 29% and 27%, respectively, as shown in Fig. 1.

Effect of UV/ H_2O_2 on Total Dissolved Solids (TDS)

Total dissolved solids were decreased by treating samples with UV radiation along with H_2O_2 . The reason for the decrease of TDS is that the dissolved organic materials are converted into dimers or trimers. Another reason for the reduction of TDS may be the degradation of the organic substances into simple molecular compounds. The decrease in percentage of TDS for inlet and outlet wastewater treated by UV/ H_2O_2 for 45 minutes observed was 47% and 48%, respectively, and the decrease in percentage of TDS for inlet and outlet wastewater treated by UV/ H_2O_2 for 90 minutes observed was 45% and 49%, respectively.

Effect of UV/ H_2O_2 on Chlorides

When samples of tannery wastewater were treated with UV radiation there was a decrease in chloride concentration with an increase in H_2O_2 concentration. The decrease in the concentration of chlorides might be due the conversion of chlorides into insoluble precipitates. The decrease in the percentage of chlorides

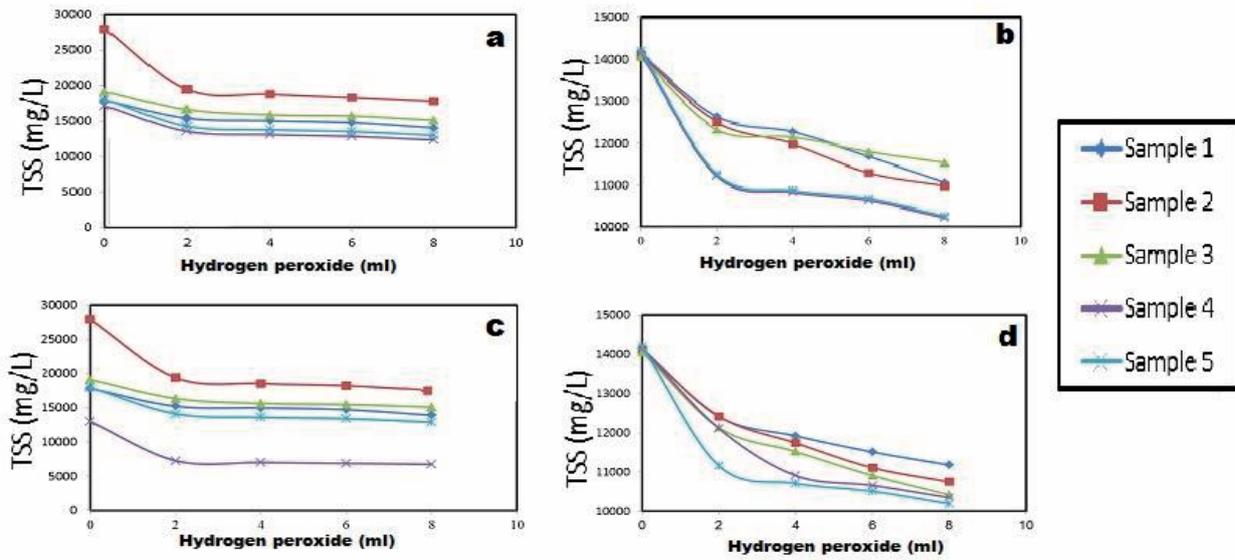


Fig. 1. Effect of UV/H₂O₂ on TSS on inlet a) and outlet b) wastewater after 45 minutes; effect of UV/H₂O₂ on TSS on inlet c) and outlet d) wastewater after 90 minutes.

for inlet and outlet wastewater treated by UV/H₂O₂ for 45 minutes observed was 32% and 21.8%, respectively, while it was decreased to 38% and 43% in inlet and outlet sections, respectively, when time duration was increased to 90 minutes.

Effect of UV/H₂O₂ on COD and BOD_s

The values of COD and BOD_s were decreased with the increase in the concentration of H₂O₂ along with

UV radiation. The decrease in COD and BOD_s occurred because micro-organisms are destroyed, which consume oxygen. Micro-organisms are very sensitive to UV radiation. Radiation also has a tendency to degrade the organic matter present in the biological system. The COD value of inlet and outlet wastewater samples treated by UV/H₂O₂ for 45 minutes was decreased to 14% and 21.8%, respectively. There was also a decrease in the percentage of COD to 16% and 30.2% for inlet and outlet wastewater samples, respectively, treated with

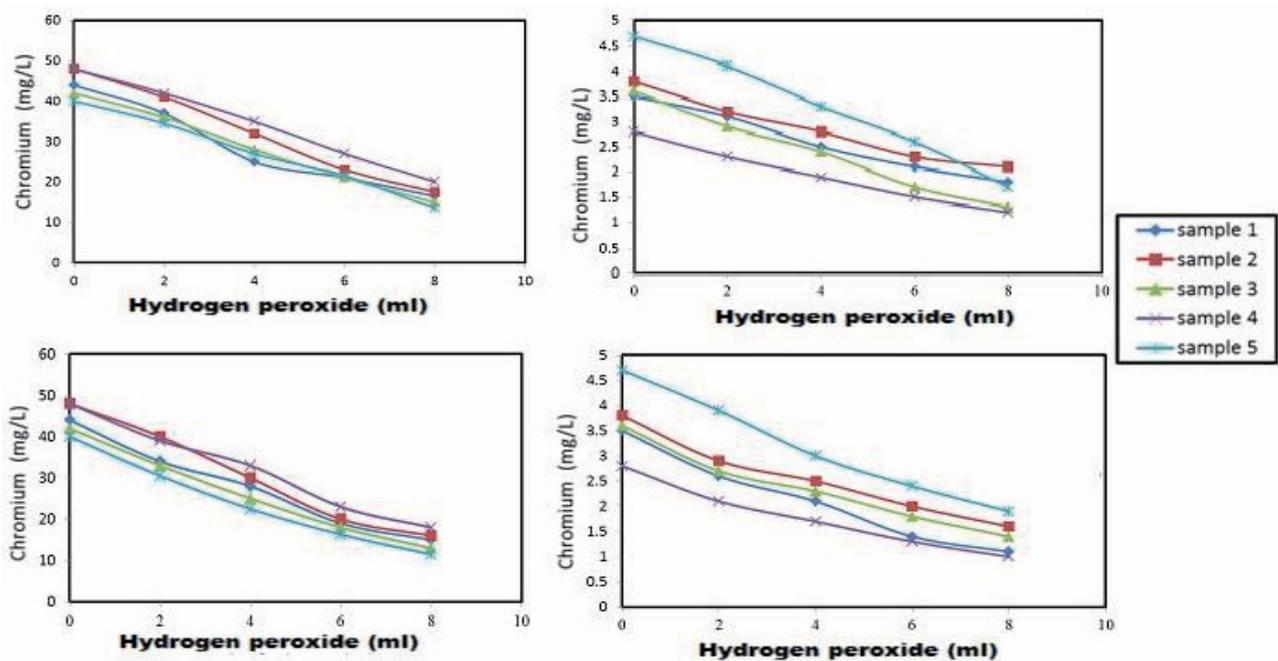


Fig. 2. Effect of UV/H₂O₂ on chromium on inlet a) and outlet b) wastewater after 45 minutes; effect of UV/H₂O₂ on chromium on inlet c) and outlet d) wastewater after 90 minutes.

UV/H₂O₂ for 90 minutes. The decrease in percentage of BOD for inlet and outlet wastewater treated by UV/H₂O₂ for 45 minutes observed was 18.9% and 33%, respectively, and the decrease in percentage of BOD for inlet and outlet wastewater treated by UV/H₂O₂ for 90 minutes observed was 19% and 41.6%, respectively. These results are in agreement with Schrank et al. 2005 and Maruthi et al. 2011 [15, 25].

Effect of UV/H₂O₂ on Chromium

The mobility of hexa-chromium Cr(VI) is higher as compared to trivalent chromium. In this way Cr(VI) is more toxic than Cr(III). The treatment of hexa-chromium requires a reduction process. The reduction of hexa-chromium Cr(VI) in wastewater can be carried out in the presence of H₂O₂, which has a tendency to generate a small amount of sludge. H₂O₂ is beneficial because it has no adverse effects on the environment. When wastewater samples were treated with UV radiation along with H₂O₂, then the reduction in hexavalent chromium increases with the increase in concentration of H₂O₂. So the removal efficiency of chromium from wastewater can be increased by increasing concentrations of H₂O₂ as shown in the graph (Fig. 2). The decrease in percentage of chromium for inlet and outlet wastewater treated by UV/H₂O₂ for 45 minutes observed was 62% and 48.6%, respectively, and the decrease in percentage of chromium for inlet and outlet wastewater treated by UV/H₂O₂ for 90 minutes observed was 65% and 65.7%, respectively, as shown in Fig. 2. These results are in good agreement with those already reported in literature [26, 27].

Conclusion

The treatment of tannery wastewater samples with UV radiation along with different concentrations of H₂O₂ has a strong effect on the degradation of pollutants. There is a greater degradation of pollutants for those samples that were irradiated for greater time duration. This process can be called a clean process because it only uses H₂O₂ that was consumed in the reaction, it is not polluting, and it does not produce solid wastes like the other conventional processes.

Conflict of Interest

The authors declare no conflict of interest.

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