

Study on identification of leather industry wastewater constituents and its photocatalytic treatment

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Abstract The present research work was intended to find out the useful information on identification, separation and photocatalytic degradation of organic compounds present in leather industry wastewater. The separation of organic compounds present in leather industry wastewater was carried out by solvent extraction. The separated crude extracted products were purified through column chromatography and characterized by UV–vis spectrophotometer, gas chromatography–mass spectrophotometer, liquid chromatography–mass spectrophotometer, ^1H and ^{13}C Fourier-transform nuclear magnetic resonance spectroscopy. The elemental analysis of wastewater and solid residue was carried out by inductively coupled plasma-optical emission and X-ray fluorescence spectroscopy. The organic compounds such as nonadec-1-ene, 2-phenylethanol, 2,4-di-*tert*-butylphenol and other organic compounds in the leather industry wastewater were identified. Out of these organic compounds, 2-phenylethanol was photocatalytically degraded using standard Degussa P-25 TiO_2 (100 mg) photocatalyst under the irradiation of UV light. Result has been shown that 2-phenylethanol was transformed into 2-*tert*-butyl-4,6-dimethylphenol, 2,6-di-*tert*-butyl-4-methylphenol then the prolonged time (30 h) irradiation leads to 100 % degradation of 2-phenylethanol. Further possible degradation mechanism of 2-phenylethanol was proposed based on the

electrospray ionization mass spectrometry analysis of degraded samples. The degradation of 2-phenylethanol was confirmed by chemical oxygen demand analysis of degraded samples. The physicochemical parameters such as pH, color, chemical oxygen demand, total dissolved solids, electrical conductivity and ionic chromatography analysis of the leather industry wastewater were also measured.

Keywords Degussa P-25 TiO_2 · Nonadec-1-ene · 2-Phenylethanol · Photocatalysis

Introduction

In Asian countries, India is the third biggest leather producer in the world (Selvakumar and Sundar 2007). The leather industry established most important places in the Indian economy on account of its massive potential for employment, growth, and exports. The leather products export from Indian leather industry accounts US\$ 3,400.97 million in 2009–2010 (Selvakumar and Sundar 2007). The main products made up of leather are footwear, leather garments, and leather goods such as hand bags, belts, wallets, gloves, sports goods, harness and saddlers. Among these products, footwear itself consumes about 60 % of the total leather production (Selvakumar and Sundar 2007). Tanning is the main process of converting animal skins and hides to non-putrescible and tough material known as leather. There are about 1,600 tanneries in India where the tanning processes have been carrying out in two ways: (1) beam house process consisting of soaking, liming and deliming and (2) tan-yard process consisting of two main techniques, namely, vegetable tanning and chrome tanning (Manivasakam 1997). During the tanning process, chemicals are being applied as

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synthetic tannins, fungicides and dyes which may inhibit nitrification (Jochimsen and Jekel 1997). According to the reported literature, leather industries are associated with water and land contamination and number of health problem (Battista et al. 1995; Bianchi et al. 1997; Mikoczy et al. 1996). As a result of leather industry pollution, a large number of health effects have been occurring to crops, aquatic, terrestrial biota and humans (Barnhart 1997), toxicity on *Vibrio fischeri* (Jochimsen and Jekel 1997) and *Daphnia magna* (Tisler et al. 2004). To overcome these problems, various literatures have been reported for the assessment of leather industry wastewater (Zhanga and Zhang 2007), evaluation of chromium toxicity (Oral et al. 2007; Scholz and Lucas 2003; Cassano et al. 2001, 2003; Meric et al. 2005; Viero et al. 2002), and removal of endocrine disrupting compounds (Changa et al. 2009) present in the wastewater from leather industry. There are few reports on identification and treatment of organic pollutant present in leather industry wastewater (Carvalho et al. 2009; Castillo et al. 1999; Ganesh and Ramanujam 2009; Farre et al. 2001; Schrank et al. 2009; Diao et al. 2011). The extraction of organic compounds from leather industry wastewater has been carried out by different methods such as liquid–liquid extraction, solid-phase extraction and solid-phase micro-extraction (Santana et al. 2009) and the extracted samples are analyzed by various analytical methods. The leather industry wastewater was also treated with various traditional processes such as adsorption on activated carbon, reverse osmosis, coagulation by chemical agents, ion-exchange on synthetic adsorbent resins, biological method (biodegradation) and electrochemical methods (Kolomaznik et al. 2008; Klinkow et al. 1998; Quinones et al. 2009; Mandal et al. 2010; Kirchner et al. 1981; Panizza and Cerisola 2004; Basha et al. 2009; Sundarapandiyar et al. 2010; Rao et al. 2001) can be used efficiently. However, these techniques are non-destructive, thus creating secondary pollutants. Treatment of secondary pollutants is a highly expensive process (Konstantinou and Albanis 2004). To solve this problem, new technologies have been developed for wastewater treatment as well as to improve the mineralization process of most of the organic pollutants present in the wastewater. The new oxidation technology, known as advanced oxidation processes (AOPs), heterogeneous photocatalysis, appears as an emerging technology for complete mineralization of the organic and inorganic pollutants (Ollis et al. 1991; Hoffman et al. 1995). In heterogeneous photocatalysis, semiconductors such as TiO_2 , ZnO , ZrO_2 , V_2O_5 , WO_3 , SnO_2 , CdO , CdS and ZnS are employed as photocatalysts. Among these semiconductors, TiO_2 is one of the important photocatalysts because of its high chemical stability, inexpensive, high photocatalytic activity and non-toxicity (Hoffman et al. 1995).

The present study was carried out to provide, all the physicochemical parameters of leather industry wastewater. Furthermore, the identification of organic compounds present in leather industry wastewater was carried out by solvent extraction method and confirmed by various spectroscopic analyses. One of the identified organic compounds 2-phenylethanol was further chosen for the photocatalytic degradation in the presence of UV light irradiation. It is reported that 2-phenylethanol was harmful by inhalation, ingestion through skin absorption, irritating to eyes and also affects the central nervous system (http://www.chemblink.com/MSDS/MSDSFiles/60-12-8_Sigma-Aldrich.pdf). The experiments were carried out in March 2010, at Discipline of Inorganic Materials and Catalysis of Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat, India.

Materials and methods

Study site

Leather industry wastewater samples were collected from leather processing laboratory, Central Leather Research Institute, Ahmedabad, Gujarat, India, in the month of March 2010, preserved and physicochemical parameters of samples were measured.

Chemicals and reagents

The organic solvents namely diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$, 99 %), chloroform (CHCl_3 , 99.5 %), carbon tetrachloride (CCl_4 , 99 %) were procured from S.D. Fine Chemicals Ltd., Mumbai, India and used for the extraction of leather industry wastewater. 2-Phenylethanol ($\text{C}_8\text{H}_{10}\text{O}$, 95 %) was purchased from Aldrich, Mumbai, India.

Titanium dioxide (Degussa P-25) was purchased from Degussa Corporation (Degussa AG, Frankfurt, Germany). It has an average particle size of 30 nm and BET specific surface area of $55 \text{ m}^2/\text{g}$. The anatase and rutile percentages were 70 and 30 %, respectively. Standard chemical reagents for chemical oxygen demand (COD) measurements were purchased from E. Merck India Ltd., Mumbai, India. The double-distilled water was used to prepare photocatalytic experimental solutions.

Preliminary analysis

The leather industry wastewater was filtered through filter paper to separate the solid particles present in the wastewater. After filtration, the physicochemical parameters such as pH, color, COD, total dissolved solids (TDS), and electrical conductivity were measured and the filtrate was



also analyzed by ionic chromatography. The results were given in the Table 1. The filtrate was analyzed by Cary 500 UV–vis spectrophotometer (Varian, Palo Alto, CA) and subjected to solvent extraction to separate organic compounds present in the filtrate.

X-ray fluorescence (XRF) and inductively coupled plasma (ICP) analysis

The leather industry wastewater was filtered using filter paper and the obtained solid residue was analyzed by WD-X-ray fluorescence spectrophotometer (Bruker AXS GmbH, S4 PIONEER, Germany) to detect the presence of metals in the solid residue. After solvent extraction, wastewater was analyzed by ICP analysis (Perkin Elmer optical emission spectrometer, Optima 2000 DV, USA) for the detection of elements present in wastewater.

Extraction and identification of extracted compounds

Solvent extraction

About 500 mL of filtered wastewater was extracted with diethyl ether ($C_4H_{10}O$), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) for five times separately. The solvent was evaporated using Buchi Rotavapor and dried under vacuum. The solvent extracts were analyzed by UV–visible spectrophotometer (Fig. 1).

Gas chromatography and mass spectroscopy analysis (GC–MS)

The extracted sample which was dissolved in diethyl ether was analyzed by gas chromatography (Shimadzu Chromatograph GC-2010) using conditions such as column oven temperature of 50 °C, helium as a carrier gas, inlet pressure 243 kPa, and the column flow of 1.20 mL/min. On the basis of GC–MS results, the obtained compound

name, their molecular formula and molecular weight are given in Table 3.

Thin layer and column chromatography analysis

After GC–MS analysis of extracted sample, it was observed that the extracted sample consists of different organic compounds. For separation and identification, each compound present in extracted mixture was analyzed by thin layer chromatography (TLC) under UV light, using hexane and ethyl acetate as eluent. The result shows the presence of mixture of some active compounds in extracted sample. The mixture of compounds was further purified through column chromatography (CC) using hexane and ethyl acetate (95:5) as eluent. The solvent was evaporated using rotavapor and dried under vacuum. The column purified compounds were analyzed by 1H and ^{13}C Fourier-transform nuclear magnetic resonance (1H and ^{13}C FT-NMR), liquid chromatography–mass spectroscopy (LC–MS), GC–MS, and fluorescence spectroscopy.

Characterization of organic compounds

1H and ^{13}C FT-NMR measurements were done using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal reference on Bruker Avance DPX 200 MHz FT-NMR (Bruker, Switzerland). The UV–visible spectra of extracted samples were analyzed by Cary 500 UV–vis spectrophotometer (Varian, Palo Alto, CA). The LC–MS

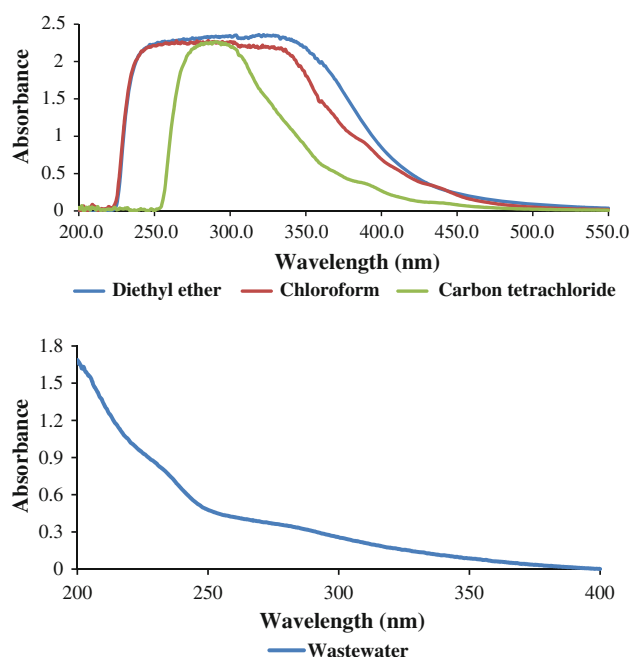


Fig. 1 UV–visible spectrum of leather industry wastewater (before and after extraction with different solvent)

Table 1 Physicochemical parameters of leather industry wastewater

S. no.	Parameters	Values
1.	Color	Brown
2.	pH	8.20
3.	COD (mg/L)	47.15
4.	Total dissolved solid (ppm)	1770
5.	Electrical conductivity (mS/cm)	3.55
6.	Chloride (mg/L) ^a	696.8
7.	Sulfate (mg/L) ^a	157.7
8.	Fluoride (mg/L) ^a	1.6
9.	Nitrate (mg/L) ^a	7.0

^a Analyzed by ionic chromatography



analysis of extracted and purified samples was done by Water Q-TOF micro Y A-260 (Micromass) tandem quadruple orthogonal TOF instrument fitted with a lock spray source. After column separation, the compounds were analyzed by fluorescence spectroscopy with 290 nm as excitation wavelength and compared with standard compounds. The fluorescence spectrum of the compound was analyzed by Fluorolog Horiba JOBNYVON fluorescence spectrophotometer.

Photocatalytic activity

The photocatalytic degradation of leather industry wastewater and one of the organic compounds, 2-phenylethanol, was carried out using a reactor, which was designed and fabricated locally. The reactor consists of two parts (Fig. 2): the first part is the double-walled quartz vessel having an empty chamber at the center. The irradiation source lamp was immersed in the chamber and it was facilitated with inlet and outlet for the water circulation to maintain the temperature of reaction mixture. The 125 W mercury vapor lamp (Crompton, high pressure mercury vapor lamp, with the glass bulb removed, radiation wavelength of 280–450 nm, photon flux = 0.51 mW/cm^2) was used as a UV irradiation source for reactions. The spectral distribution of the high pressure mercury vapor lamp was reported earlier (Tayade et al. 2006). The second outer part consists of a borosilicate glass container possessing volume of 250 mL after the insertion of inner part and the solution to be degraded was placed inside the borosilicate glass container.

In this reaction, a suspension containing 100 mg of Degussa P-25 TiO_2 catalyst and 250 mL of an aqueous

solution of 2-phenylethanol ($4.09 \times 10^{-4} \text{ M}$) was taken; it was ultrasonicated for 5 min, then continuously stirred for 30 min in the dark prior to irradiation of UV light for determining the adsorption on the catalyst; a 5-mL sample was withdrawn by syringe for the analysis. The reaction mixture was stirred for continuous dispersion of catalysts. The concentration of the bulk solution prior to irradiation was used as the initial value for the measurements of 2-phenylethanol degradation. 5 mL of sample was withdrawn by syringe from the irradiated suspension at the time intervals of every 1 h upto 4 h and then after every 4 h upto 30 h. The catalyst was separated by centrifugation from the aqueous solution prior to analysis. The reaction solution was kept homogeneous throughout the reaction by stirring continuously throughout the reaction. All experiments were carried out without the addition of any sacrificial agent and the irradiation source was cooled by circulating water to 20°C during the experiment. The concentration of 2-phenylethanol was determined from the absorbance at $\lambda_{\text{max}} = 257 \text{ nm}$ using a Cary 500 UV–vis spectrophotometer.

Chemical oxygen demand analysis

The oxygen equivalent of the organic matter of a sample, i.e., COD, was measured using a SPECTROQUANT NOVA 60 photometer. The reagents for COD analysis and 3 mL of sample taken at different time intervals were mixed together in glass cells and digested in a Spectroquant TR 320 thermodigester for 2 h at 150°C . After digestion, the mixture was cooled to room temperature and COD was measured using the photometer for the original solution and samples taken out at different time intervals during photocatalytic experiments.

Results and discussion

XRF and ICP analysis

X-ray fluorescence analysis of solid residue is shown in Table 2. It is evident from the analysis that the elements such as calcium (62.46 %), chromium (6.77 %), iron (8.8 %), magnesium (3.73 %), silicon (9.77 %), aluminium (2.80 %) and sulfur (2.11 %) were present in higher percentage in the solid residue. The ICP analysis of leather industry wastewater demonstrated that the maximum amount of sulfur (168.7 mg/L), calcium (42.43 mg/L), magnesium (36.34 mg/L), potassium (23.37 mg/L), silicon (2.955 mg/L), chromium (0.120 mg/L) were present. From the XRF and ICP analysis, it is clear that elements present in wastewater and solid residue material were comparable (Table 2). Similar results were also reported for the

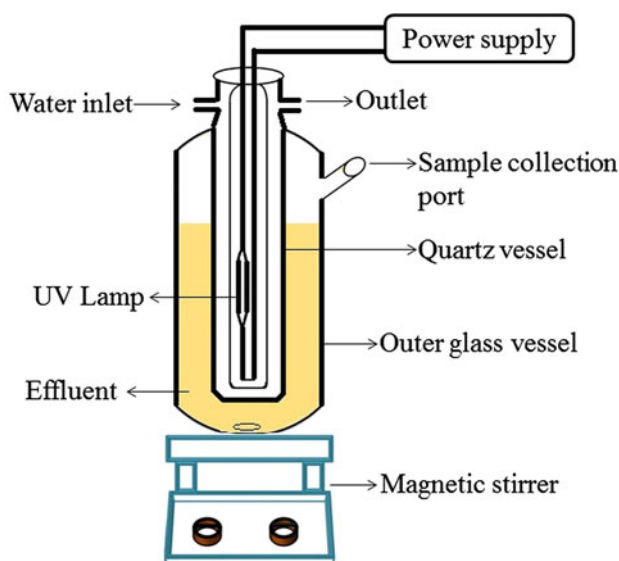


Fig. 2 Photocatalytic reactor setup for photocatalytic reaction

Table 2 Elemental analysis of solid residue and wastewater

S. no.	Name of element	Percentage ^a	Amount present (mg/L) ^b
1.	Mg	3.730	36.34
2.	Ca	62.46	42.43
3.	Al	2.800	0.074
4.	Cr	6.770	0.120
5.	Si	9.770	2.955
6.	Fe	8.851	0.601
7.	S	2.110	168.7
8.	K	0.455	23.37
9.	Ti	0.808	0.003
10.	Sr	0.161	0.742
11.	Cu	0.083	0.155
12.	P	0.444	0.051

^a Elements present in the solid residue measured by XRF analysis^b Elements present in the wastewater measured by ICP analysis

presence of elements in leather industry wastewater (Labunska et al. 2000; Babu 2011).

GC–MS analysis

From the UV spectroscopy analysis, it is understood that some of the dissolved organic compounds are also present in the wastewater. The solvent extracted samples were analyzed by GC–MS analysis as shown in Table 3. The results demonstrated that 2-phenylethanol, nonadec-1-ene, ocatdec-1-ene, 2,4-di-*tert*-butylphenol, (3*R*,6*S*)-3-methyl-6-(*prop*-1-en-2-yl)-cyclohex-1-enol and 2,3-epoxypinane were present in major amount, whereas tetradec-1-ene, dodecan-1-ol, icosan-1-ol, pentadecane, 4-nonylphenol, and benzoic anhydride were present in small amount in leather industry wastewater and compared with commercial reference compounds. Many researchers also reported the presence of phenolic and long chain aliphatic compounds in wastewater (Diao et al. 2011; He et al. 2007). Among these identified organic compounds, 2-phenylethanol has a pleasant floral odor, occurs widely in nature, and found in a variety of essential oils, including rose, carnation, hyacinth, Aleppo pine, orange blossom, and geranium. It is therefore a common ingredient in flavors and perfumery, particularly when the smell of rose is desired. 2,3-Epoxypinane also has been used in fragrance industry. Alpha olefins and their derivatives are used as co-monomers in polymer such as low density polyethylenes for the properties of lighter, thinner, better flexibility and more tearing resistance. They have been used in the production of linear plasticizers, oxo-alcohols, motor fuels, lubricants, automotive additives, biodegradable surfactants, paper

size, and in a wide range of specialty applications in the production of mercaptans, flavors and fragrances, alkyl metals, halides, alkyl silanes. But the presence of these organic compounds in wastewater leads to life threatening to aquatic animals and human beings. To degrade these mixture compounds, first this mixture of organic compounds were analyzed by thin layer chromatography and further purified through column chromatography. The column purified compounds were characterized by NMR and LC–MS spectroscopy analysis and compared with authentic samples. After characterization of organic compounds, the same commercial standard solution of organic compound was prepared and photocatalytically degraded using Degussa P-25 catalyst under the irradiation of UV light.

¹H, ¹³C FT-NMR and LC–MS spectral analysis

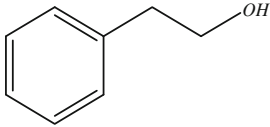
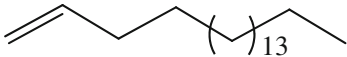
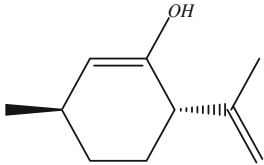
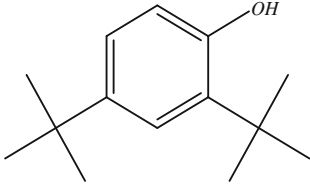
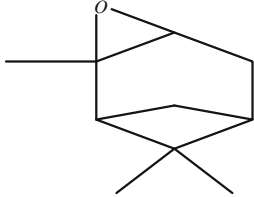
The column purified compounds were characterized by ¹H and ¹³C NMR analysis. After column purification, nonadec-1-ene was separated in pure form and 2-phenylethanol was found to contain some other mixture of compounds. 2-Phenylethanol was analyzed by GC–MS analysis and compared with standard 2-phenylethanol. The ¹H and ¹³C NMR data of purified compounds were given below, nonadec-1-ene, ¹H NMR: δ 0.81(3H), 1.968(10H), 1.113 (18H), 1.27(2H), 2.24(2H), 4.88(1H), 5.29(1H), 5.76(1H); ¹³C NMR: 139.297 (ethylene–CH–), 114.07 (ethylene–CH₂–), 33.6 (–CH₂–), 31.950 (–CH₂–), 29.721 (–(CH₂)₁₀–), 29.71 (–(CH₂)₂–), 29.384 (–CH₂–), 22.71 (–CH₂–), 14.127 (–CH₃–) (supporting information, Fig. S1, S2), LC–MS, MS ES+ = 266.81. ¹H, ¹³C NMR data were compared with standard compounds and it was exactly matching with standard compounds. From the ¹H, ¹³C NMR and LC–MS analysis, the presence of nonadec-1-ene in the leather industry wastewater was confirmed.

Fluorescence spectroscopy analysis

The extracted purified compounds were analyzed by fluorescence spectroscopy to check for the fluorescence activity and compared with commercial standard compounds. Results demonstrated that 2-phenylethanol showed good fluorescence activity, whereas no fluorescence activity was observed in nonadec-1-ene. The fluorescence spectrum was exactly matching with 2-phenylethanol (Fig. 3). From the fluorescence spectroscopy results, it was confirmed that 2-phenylethanol is one of the active fluorescence compounds present in the leather industry wastewater. Additional confirmation of 2-phenylethanol was also done by GC–MS analysis.



Table 3 Organic compounds present in wastewater identified using GC–MS analysis

S. no.	Name of the compound	Molecular structure, molecular formula and molecular weight
1.	2-Phenylethanol	 $C_8H_{10}O$, 122.16
2.	Nonadec-1-ene	 $C_{19}H_{38}$, 266.51
3.	(3 <i>R</i> ,6 <i>S</i>)-3-Methyl-6(-prop-1-en-2-yl)-cyclohex-1-enol	 $C_{10}H_{16}O$, 152.23
4.	2,4-Di- <i>tert</i> -butylphenol	 $C_{14}H_{22}O$, 206.32
5.	2,3-Epoxy-pinane	 $C_{10}H_{16}O$, 152.23

Photocatalytic activity

The photocatalytic degradation of leather industry wastewater results revealed that it could not completely degrade due to the presence of different kinds of organic compounds. This result indicated that separate degradation studies have to be carried out for every organic compounds present in the wastewater. In view of this, 2-phenylethanol organic compound was chosen for photocatalytic

degradation study which was present in leather industry wastewater. The photocatalytic degradation of 2-phenylethanol was investigated using Degussa P-25 TiO_2 as a photocatalyst under irradiation of UV light. The photocatalytic degradation reaction has been carried out in two conditions: (1) degradation reaction in the presence of Degussa P-25 TiO_2 and UV light and (2) degradation reaction in the presence of UV light only. The results are shown in Fig. 4. The results demonstrated that 100 % of



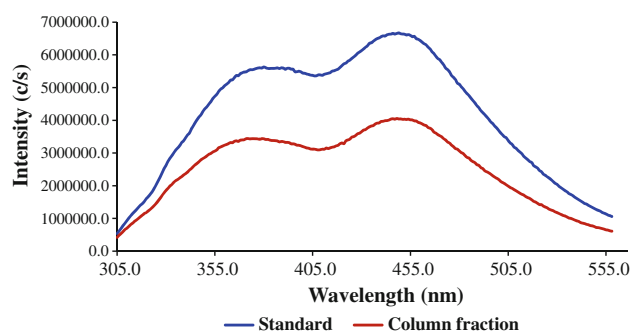
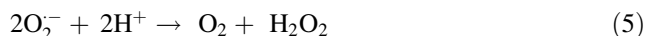
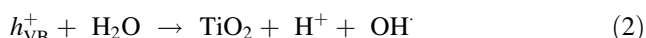
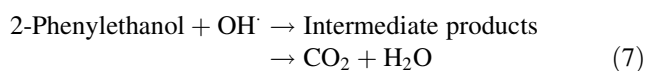


Fig. 3 Fluorescence spectrum of 2-phenylethanol

2-phenylethanol was degraded after 30 h of photocatalytic reaction, but it was 70 % in the presence of UV light only (Table 4). The photocatalytic degradation of 2-phenylethanol is supposed to take place by the following mechanism. When photocatalyst absorb a photon with energy equal or higher than the band gap energy (E_g), electrons (e^-) are promoted from valence band (VB) to conduction band (CB), leaving an electron vacancy or hole (h^+) in the valence band. The hydroxyl radicals are generated either through the combination of water molecule and valence band holes or that of adsorbed oxygen and conduction band electrons. In aqueous solutions, the holes are scavenged by surface hydroxyl groups to generate the strong oxidizing hydroxyl radical (OH^\cdot), which can promote the oxidation of organic compounds as follows:



The formed OH^\cdot reacts with the adsorbed 2-phenylethanol and further degraded into CO_2 and H_2O .



To find out the degradation mechanism of 2-phenylethanol, the reaction samples were analyzed by LC–MS analysis. Based on the LC–MS results (supporting information, Fig. S4), a possible mechanism for 2-phenylethanol degradation has been proposed (Scheme 1). At the same time, to find out the intermediates, photocatalytic irradiation reaction was stopped after 4 h and the catalyst particles were separated by centrifugation and finally filtered through 0.2 μm Millipore membrane filter. Then, the reaction samples were extracted with diethyl ether solvent

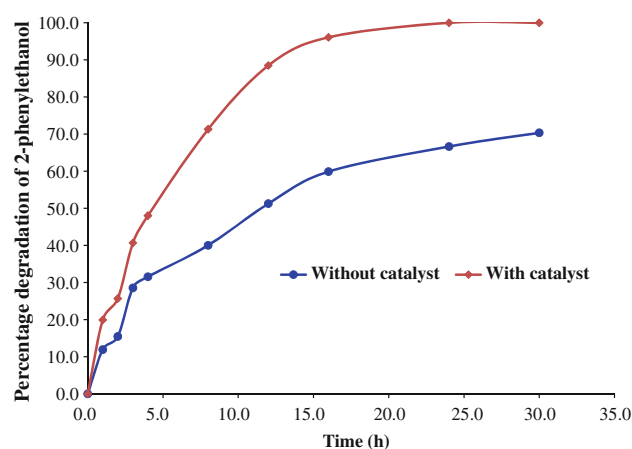


Fig. 4 Photocatalytic degradation of 2-phenylethanol (4.09×10^{-4} M) with and without catalyst in the presence of UV light irradiation

and analyzed by GC–MS analysis. The results were shown in Fig. 5a. The results revealed that during the photocatalytic experiment, 2-phenylethanol was transformed into 2-*tert*-butyl-4,6-dimethylphenol, 2,6-di-*tert*-butyl-4-methylphenol and some other hydroxylated products. The retention time at 11.07 min confirms the formation of 2,6-di-*tert*-butyl-4-methylphenol and compared with the authentic samples. When the concentrations of 2-phenylethanol was increased from 4.09×10^{-4} to 8.19×10^{-4} M, the conversion of 2-phenylethanol was decreased (Fig. 5b). The crude product mixture was purified through column chromatography using hexane and ethyl acetate (95:5) as eluent. The solvent was evaporated using rotavapor and dried under vacuum. The column purified products were further confirmed by 1H NMR spectroscopy analysis (supporting information, Fig. S3). LC–MS results reveal that further irradiation leads to cleavage of formed hydroxylated products and oxidized by the formed hydroxyl radical into hexa-2,4-dienedioic acid ($m/z = 142$), benzoic acid ($m/z = 122$), succinic acid ($m/z = 118$), fumaric acid ($m/z = 115$), benzaldehyde ($m/z = 106$), benzyldineoxonium ($m/z = 105$), benzene ($m/z = 78$) and other low molecular weight intermediates. Finally, the oxidized products were further mineralized into CO_2 and H_2O as shown in Eq. (7) (Scheme 1). This implies that 2-phenylethanol was completely degraded after 30 h of photocatalytic reaction. The photocatalytic degradation of 2-phenylethanol was further confirmed by COD analysis. The COD values were given in Table 4. The results confirmed that about 100 % of COD values were reduced after 30 h irradiation reaction in the presence of Degussa P-25 TiO_2 photocatalyst, whereas in the case of without catalyst 85 % of COD values were reduced. The reductions in COD values were in agreement with the percentage degradation calculated using UV–visible spectrophotometer.



Table 4 COD value of photocatalytic degradation of 2-phenylethanol (4.09×10^{-4} M)

Time (h)	Percentage degradation (%) ^a		COD value (mg/L)	
	Without catalyst	With Degussa P-25 TiO ₂ catalyst	Without catalyst	With Degussa P-25 TiO ₂ catalyst
0	0	0	126.67	126.67
1	11.92	19.94	107.08	113.57
2	15.46	25.66	98.97	107.98
3	28.57	40.66	93.04	98.81
4	31.56	48.02	87.89	96.70
8	40.02	71.31	81.71	76.21
12	51.25	88.48	62.04	68.63
16	59.89	96.08	54.37	24.87
24	66.65	100	31.81	4.47
30	70.34	100	17.06	0.00

^a Percentage degradation was calculated using UV–Vis spectrophotometer analysis

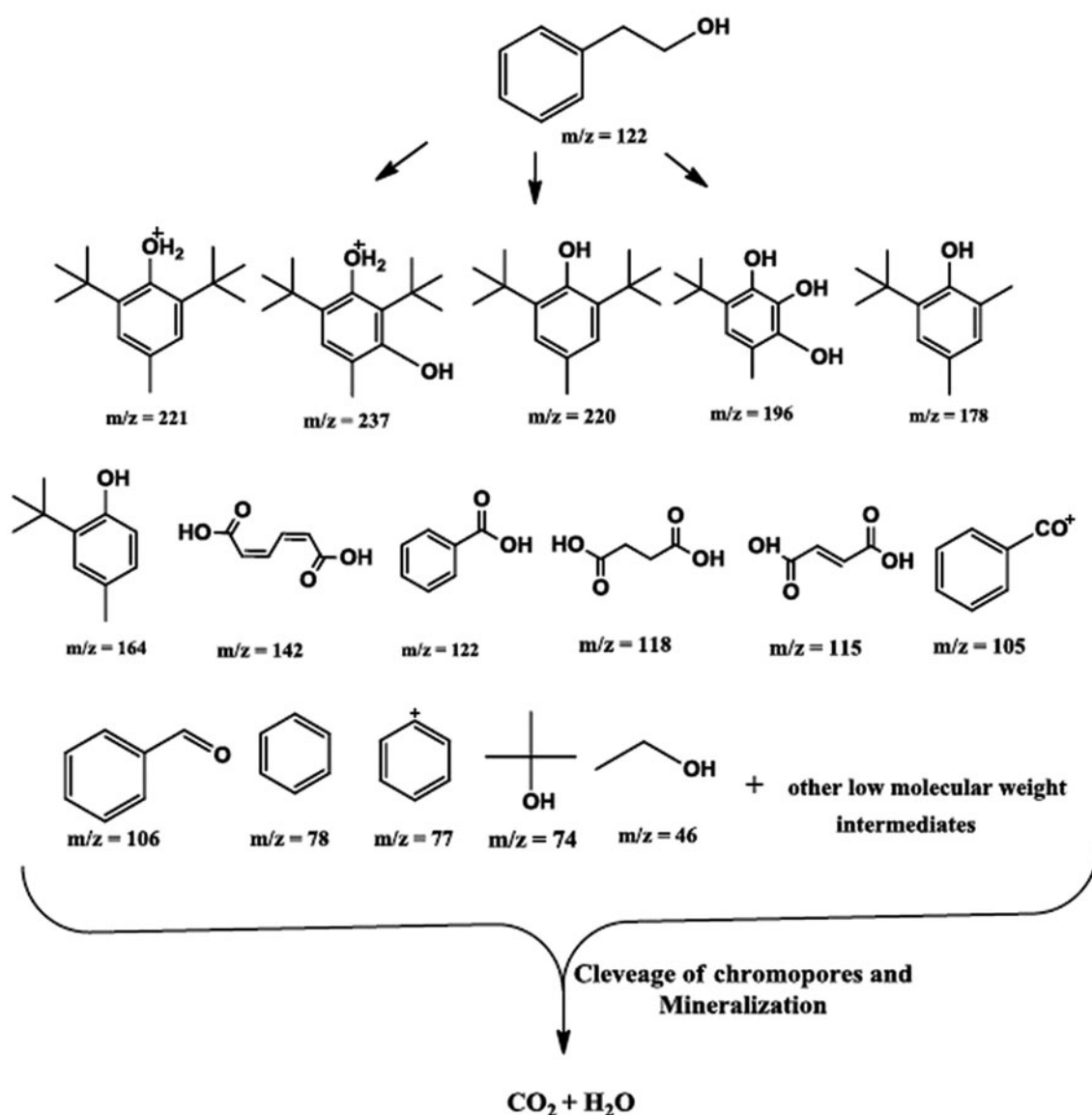
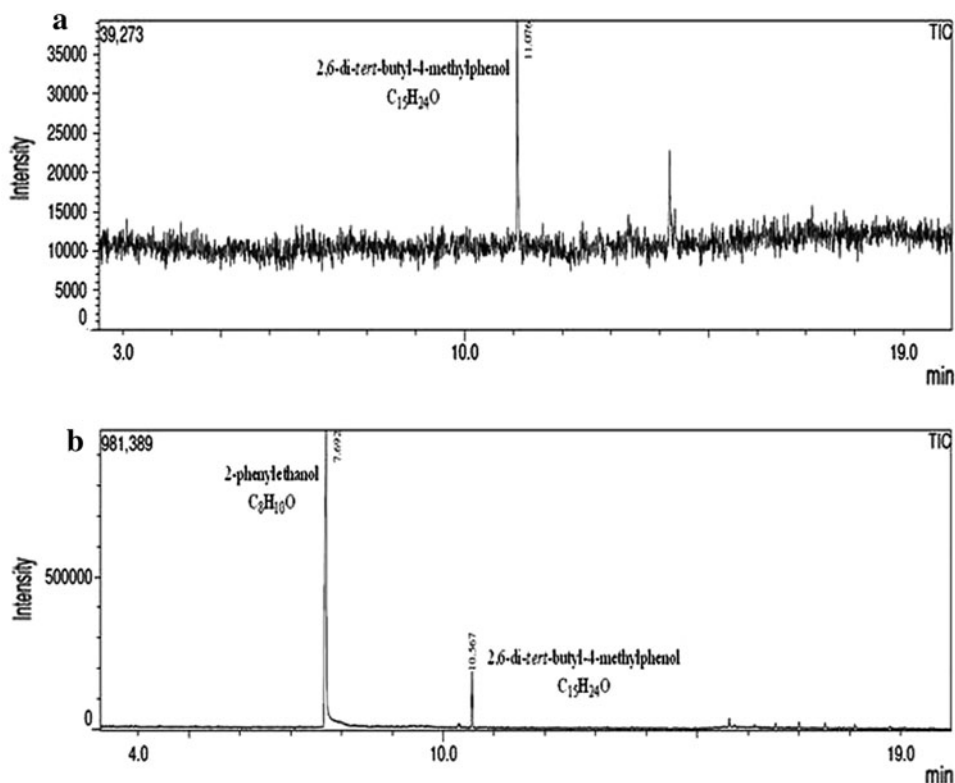
**Scheme 1** Possible degradation pathway of 2-phenylethanol degradation

Fig. 5 GC–MS spectra of 2,6-di-*tert*-butyl-4-methylphenol sample analyzed during photocatalytic degradation of different concentration of 2-phenylethanol



Conclusion

A Study on physicochemical properties of leather industry wastewater was carried out. The elemental analysis results showed that different elements such as calcium (62.46 %), chromium (6.77 %), iron (8.8 %), magnesium (3.73 %), silicon (9.77 %), aluminium (2.80 %) and sulfur (2.11 %) were present mainly in the wastewater and solid residue. Result demonstrated that organic compounds such as nonadec-1-ene and 2-phenylethanol were present and further confirmed by various spectroscopy techniques. The photocatalytic degradation of 2-phenylethanol was carried out in the presence of Degussa P-25 TiO₂ photocatalyst and irradiation of ultraviolet light. It was found that the complete degradation of 2-phenylethanol was obtained in 30 h and further confirmed by LC–MS and COD analysis. The separation and purification of the other organic compounds present in the wastewater is still under progress.

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References

- Babu SS (2011) Treatability studies of tannery effluent by bacteria. Ind Stream Res J I, ISSN No, pp 2230–7850
- Barnhart J (1997) Chromium chemistry and implications for environmental fate and toxicity. J Soil Contam 6:561–568. doi: [10.1080/15320389709383589](https://doi.org/10.1080/15320389709383589)
- Basha CA, Solomon PA, Velan M, Balasubramanian N, Kareem LR (2009) Participation of electrochemical steps in treating tannery wastewater. Ind Eng Chem Res 48:9786–9796. doi: [10.1021/ie900464s](https://doi.org/10.1021/ie900464s)
- Battista G, Comba P, Orsi D, Norpoth K, Maier A (1995) Nasal cancer in leather workers: an occupational disease. J Cancer Res Clin Oncol 121:1–6. doi: [10.1007/BF01202722](https://doi.org/10.1007/BF01202722)
- Bianchi F, Cianciulli D, Pierini A, Costantini AS (1997) Congenital malformations and maternal occupation: a registry based case-control study. Occup Environ Med 54:223–228. doi: [10.1136/oem.54.4.223](https://doi.org/10.1136/oem.54.4.223)
- Carvalho MF, Duque AF, Moura SC, Amorim CL, Ferreira Jorge RM, Castro PML (2009) Biological treatment of a contaminated gaseous emission from a leather industry in a suspended-growth bioreactor. Chemosphere 74:232–238. doi: [10.1016/j.chemosphere.2008.09.047](https://doi.org/10.1016/j.chemosphere.2008.09.047)
- Cassano A, Molinari R, Romano M, Orioli E (2001) Treatment of aqueous effluents of the leather industry by membrane processes: a review. J Membrane Sci 181:111–126. doi: [10.1016/S0376-7388\(00\)00399-9](https://doi.org/10.1016/S0376-7388(00)00399-9)
- Cassano A, Adzet J, Molirani R, Buonomenna MG, Roig J, Drioli E (2003) Membrane treatment by nanofiltration of exhausted vegetable tanning liquors from the leather industry. Water Res 37:2426–2434. doi: [10.1016/S0043-1354\(03\)00016-2](https://doi.org/10.1016/S0043-1354(03)00016-2)
- Castillo M, Alonso MC, Riu J, Barcelo D (1999) Identification of polar, ionic, and highly water soluble organic pollutants in untreated industrial wastewaters. Environ Sci Technol 33:1300–1306. doi: [10.1021/es981012b](https://doi.org/10.1021/es981012b)



- Changa HS, Chooa KH, Leeb B, Choi SJ (2009) The methods of identification, analysis, and removal of endocrine disrupting compounds (EDCs) in water. *J Hazard Mater* 172:1–12. doi: [10.1016/j.jhazmat.2009.06.135](https://doi.org/10.1016/j.jhazmat.2009.06.135)
- Diao M, Ouedraogo N, Moussa LB, Savadogo PW, Guessan AGN, Bassole IHN, Dicko MH (2011) Biodepollution of wastewater containing phenolic compounds from leather industry by plant peroxidases. *Biodegradation* 22:389–396. doi: [10.1007/s10532-010-9410-8](https://doi.org/10.1007/s10532-010-9410-8)
- Farre ML, Garcia MJ, Castillo M, Riu J, Barcelo D (2001) Identification of surfactant degradation products as toxic organic compounds present in sewage sludge. *J Environ Monit* 3:232–237. doi: [10.1039/b100945l](https://doi.org/10.1039/b100945l)
- Ganesh R, Ramanujam RA (2009) Biological waste management of leather tannery effluents in India: current options and future research needs. *Int J Environ Eng* 1:165–186. doi: [10.1504/IJEE.2009.027313](https://doi.org/10.1504/IJEE.2009.027313)
- He Q, Yao K, Sun D, Shi B (2007) Biodegradability of tannin-containing wastewater from leather industry. *Biodegradation* 18:465–472. doi: [10.1007/s10532-006-9079-1](https://doi.org/10.1007/s10532-006-9079-1)
- Hoffman MR, Martin ST, Choi W, Bahnemann DW (1995) Environmental application of semiconductor photocatalysis. *Chem Rev* 95:69–96. doi: [10.1021/cr00033a004](https://doi.org/10.1021/cr00033a004)
- Jochimsen JC, Jekel MR (1997) Partial oxidation effects during the combined oxidative and biological treatment of separated streams of tannery wastewater. *Water Sci Tech* 35:337–345. doi: [10.1016/S0273-1223\(97\)00043-7](https://doi.org/10.1016/S0273-1223(97)00043-7)
- Kirchner K, Krämer P, Rehm HJ (1981) Biodegradation of organic waste gas pollutants with bacterial suspensions. *Biotech Lett* 3:567–570. doi: [10.1007/BF00133435](https://doi.org/10.1007/BF00133435)
- Klinkow N, Frenzel JO, Jekel M (1998) Toxicity-directed fractionation of organic compounds in tannery wastewater with regard to their molecular weight and polarity. *Water Res* 32:2583–2592. doi: [10.1016/S0043-1354\(98\)00017-7](https://doi.org/10.1016/S0043-1354(98)00017-7)
- Kolomaznik K, Adamek M, Andel I, Uhlířova M (2008) Leather waste—potential threat to human health, and a new technology of its treatment. *J Hazard Mater* 160:514–520. doi: [10.1016/j.jhazmat.2008.03.070](https://doi.org/10.1016/j.jhazmat.2008.03.070)
- Konstantinou IK, Albanis TA (2004) TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations a review. *Appl Catal B Environ* 49:1–14. doi: [10.1016/j.apcatb.2003.11.010](https://doi.org/10.1016/j.apcatb.2003.11.010)
- Labunska I, Brigden K, Stringer R, Johnston P, Santillo D, Ashton J (2000) Identification and environmental significance of the organic pollutants and heavy metals in samples associated with Arlei and Meiner tanneries. Las Toscas, Santa Fe Province, Argentina, Technical Note, pp 1–24
- Mandal T, Dasgupta D, Mandal S, Datta S (2010) Treatment of leather industry wastewater by aerobic biological and Fenton oxidation process. *J Hazard Mater* 180:204–211. doi: [10.1016/j.jhazmat.2010.04.014](https://doi.org/10.1016/j.jhazmat.2010.04.014)
- Manivasakam N (1997) Industrial Effluents origin, characteristics, effects analysis and treatment. Sakthi Book Services, Coimbatore
- Meriç S, De Nicola E, Iaccarino M, Gallo M, Di Gennaro A, Morrone G, Warnau M, Belgiorio V, Pagano G (2005) Toxicity of leather tanning wastewater effluents in seaurchin early development and in marine microalgae. *Chemosphere* 61:208–217. doi: [10.1016/j.chemosphere.2005.02.037](https://doi.org/10.1016/j.chemosphere.2005.02.037)
- Mikoczy Z, Schutz A, Stromberg U, Hagmar L (1996) Cancer incidence and specific occupational exposures in the Swedish leather tanning industry: a cohort based case control study. *Occup Environ Med* 53:463–467. doi: [10.1136/oem.53.7.463](https://doi.org/10.1136/oem.53.7.463)
- Ollis D, Pelizzetti E, Serpone N (1991) Photocatalyzed destruction of water contaminants. *Environ Sci Technol* 25:1522–1529. doi: [10.1021/es00021a001](https://doi.org/10.1021/es00021a001)
- Oral R, Meriç S, De Nicola E, Petruzzelli D, Rocca CD, Paganoc G (2007) Multi-species toxicity evaluation of a chromium-based leather tannery wastewater. *Desalination* 211:48–57. doi: [10.1016/j.desal.2006.02.084](https://doi.org/10.1016/j.desal.2006.02.084)
- Panizza M, Cerisola G (2004) Electrochemical oxidation as a final treatment of synthetic tannery wastewater. *Environ Sci Technol* 38:5470–5475. doi: [10.1021/es049730n](https://doi.org/10.1021/es049730n)
- Quinones FRE, Fornari MMT, Modenes AN, Palacio SM, Da Silva Jr FG, Szymanski N, Kroumov AD, Trigueros DEG (2009) Pollutant removal from tannery effluent by electrocoagulation. *Chem Eng J* 151:59–65. doi: [10.1016/j.cej.2009.01.043](https://doi.org/10.1016/j.cej.2009.01.043)
- Rao NN, Somakeshwar KM, Kaul SN, Szpyrkowicz L (2001) Electrochemical oxidation of tannery wastewater. *J Chem Technol Biotechnol* 76:1124–1131. doi: [10.1002/jctb.493](https://doi.org/10.1002/jctb.493)
- Santana CM, Ferrera ZS, Padrón MET, Rodríguez JJS (2009) Methodologies for the extraction of phenolic compounds from environmental samples: new approaches. *Molecules* 14:298–320. doi: [10.3390/molecules14010298](https://doi.org/10.3390/molecules14010298)
- Scholz W, Lucas M (2003) Techno-economic evaluation of membrane filtration for the recovery and reuse of tanning chemicals. *Water Res* 37:1859–1867. doi: [10.1016/S0043-1354\(02\)00560-2](https://doi.org/10.1016/S0043-1354(02)00560-2)
- Schrank SG, Bieling U, Jose HJ, Moreira RFPM, Schroder HF (2009) Generation of endocrine disruptor compounds during ozone treatment of tannery wastewater confirmed by biological effect analysis and substance specific analysis. *Water Sci and Tech* 59:31–38. doi: [10.2166/wst.2009.762](https://doi.org/10.2166/wst.2009.762)
- Selvakumar M, Sundar R (2007) Leather industry. *Scienc Tech Entrepreneur* 8:1–10
- Sundarapandiyan S, Chandrasekar R, Ramanaiah B, Krishnan S, Saravanan P (2010) Electrochemical oxidation and reuse of tannery saline wastewater. *J Hazard Mater* 180:197–203. doi: [10.1016/j.jhazmat.2010.04.013](https://doi.org/10.1016/j.jhazmat.2010.04.013)
- Tayade RJ, Kulkarni RG, Jasra RV (2006) Transition metal ion impregnated mesoporous TiO₂ for photocatalytic degradation of organic contaminants in water. *Ind Eng Chem Res* 45:5231–5238. doi: [10.1021/ie051362o](https://doi.org/10.1021/ie051362o)
- Tisler T, Zagorc-Koncan J, Cotman M, Drolc A (2004) Toxicity potential of disinfection agent in tannery wastewater. *Water Res* 38:3503–3510. doi: [10.1016/j.watres.2004.05.011](https://doi.org/10.1016/j.watres.2004.05.011)
- Viero AF, Mazzarollo ACR, Wada W, Tessaro IC (2002) Removal of hardness and COD from retanning treated effluent by membrane process. *Desalination* 149:145–149. doi: [10.1016/S0011-9164\(02\)00746-4](https://doi.org/10.1016/S0011-9164(02)00746-4)
- Zhang M, Zhang M (2007) Assessing the impact of leather industries on the quality of water discharged into the east China sea from Wenzhou watersheds. *J Environ Manag* 85:393–403. doi: [10.1016/j.jenvman.2006.10.016](https://doi.org/10.1016/j.jenvman.2006.10.016)

