Chapter 11
Solar Photocatalytic Treatment of Tannery Effluents

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Contents

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Abstract Leather industries have a predominant place in the economic growth of various countries and have been a substantial contributor to export and employment potential. However, due to environmental impacts and water consumption, they are categorized as red-category industries, and as a result of the complex nature of their wastewater, currently available water treatment technologies are still inefficient to meet the standard discharge limits set by various pollution control authorities. This situation demands the need to introduce green technologies to decrease the pollutant load, and in recent years enormous research and progress has been observed in solar energy utilization, which has shown a great potential and has been extensively implemented for the removal of organic and inorganic compounds from industrial wastewater.

This chapter contributes the basic knowledge of tannery wastewater, and various treatment approaches along with the description of geometrical concept of photocatalytic reactors. The chapter provides an overview and application of solar photocatalysis in wastewater treatment. Various factors such as solar irradiance, oxygen concentration, potential of hydrogen production, temperature and catalysis load which affects solar photocatalysis have been explained in detail.

Keywords Leather industries · Environmental impact · Green technologies · Pollutant load · Tannery wastewater · Solar photocatalysis · Photocatalytic reactor

11.1 Introduction

In the context of increased energy demand, and the rapid depletion of conventional energy resources, attention has been focused towards the development of long-term permanent energy sources. The development of unique solar-powered technologies is considered as a key solution to fulfil the worldwide energy demand since the use of solar energy has been known to mankind and nature from a long time in terms of food production and heat utilization. Another vision of solar research is related with the diminishing worldwide carbon emission which is a significant social and environmental issue worldwide (Kabir et al. 2018). Approximately 4×10^6 exajoules of solar energy that reaches the earth annually can be easily harvestable. Efficient technologies are readily available to harvest and properly utilize this energy, solar energy has a potential to fulfil the worldwide energy demand (Blaschke et al. 2013).

Research over the past few decades made possible to harvest solar energy to generate mechanical and electrical power, but the utilization of solar energy in the field of wastewater treatment is limited and gaining the interest of researchers from the last two decades to develop clean, efficient and economic approaches.

11.2 Advantages and Limitations of Solar Energy

Solar energy is an ultimate source which can deliver secure self-governed energy. Such an ability is tremendously imperative for people as well as for the social and economic growth of the nation. However, solar energy is considered as a generous and consistent segment for electricity production in many developed and developing countries besides the various constraints and benefits related to solar energy utilization.

11.2.1 Advantages

Solar energy is a sustainable non-polluting, virtuous and consistent energy source, which is never going to deplete. The utilization of solar energy will not discharge volatile organic compounds and toxic gases into the atmosphere. Approximately 25% of anthropogenic greenhouse gases emissions is due to the power plants (Jerez et al. 2015). Thus, the replacement of fossil fuel-based power sources with solar-based energy will inevitably be advantageous to accomplish sustainable development. In addition, there is massive water consumption due to fossil fuel-driven power plants, which is a critical issue for droughts and heat affected areas. At the same time, the power generation from solar power plants doesn't require any water source to operate (Kabir et al. 2018).

Furthermore, to enhance the energy generation capacity, additional modules can also be added in the course of time. Over the years an increase in the efficiency of solar-powered technologies has been observed along with reduced capital and operating cost. All these points highlight the adaptability of solar-powered technologies over existing conventional technologies (Kabir et al. 2018).

11.2.2 Limitations

The high initial capital investment is a major disadvantage for solar-based technology, and the extended payback time with a limited revenue decreases the estimation of credits for such frameworks. On the other hand, less efficiency (10–20%) of domestic solar panels is another deficiency for the development of solar technology. However, there is an availability of more efficient solar pales (>20%) but at more expensive rates (Kabir et al. 2018).

The large space required by solar-based accessories such as batteries and inverters is another concern. Furthermore, a short lifespan of the batteries and their disposal are the other side effects regarding this system. Other variables related to such systems is the scarcity of skilled workforce to meet the demands for the establishment, support and assessment of solar powered systems. Another inadequacy is the day-to-day and area-to-area variation of solar light intensity (Kabir et al. 2018). Therefore this is not authentic for an area with unsustainable climate or atmospheric conditions.

11.3 Solar Energy Application in Wastewater Treatment

From the last few decades, the mechanism of solar energy utilization along with the combination of heterogeneous catalysis to treat wastewater has gained considerable attraction for many researchers; such process is known as photocatalysis which is a kind of advanced oxidation processes.

Numerous reports have been published conferring the various application and mechanism of photocatalysis with a favourable laboratory and pilot-plant-based studies, and most of these studies have discussed the detailed, complex reaction mechanisms of photodegradation of many organic and inorganic pollutant present in wastewater (Ollis and Turchi 1990; Kisch and Twardzik 1991; Künneth et al. 1993; Vidal et al. 1994; Herrmann 1995; Serpone 1995; Serpone et al. 1996; Peral et al. 1997; Kemeny et al. 2000; Botta et al. 2002; Ustinovich et al. 2005; Doll and Frimmel 2005; Gonçalves et al. 2005; Augugliaro et al. 2006; Sirtori et al. 2006; Guo and Hu 2007; Bayarri et al. 2007; Palmisano et al. 2007; Robert 2007; Sadik et al. 2007; Fujishima et al. 2007; Kiliç and Çinar 2008; Lair et al. 2008; Rodrigues et al. 2008; Chen et al. 2008; Du et al. 2008; Augugliaro and Palmisano 2010; Kisch 2010; Shan et al. 2010; Bickley 2010; Khataee et al. 2011; Valencia et al. 2011; Wang et al. 2011b; Xiong et al. 2011). Hence, these studies support the possibility of complete degradation of pollutant through solar photocatalysis.

11.4 Nature of Tannery Effluent

Extensive volume of water and pollutants, which has an adverse effect on the environment, is released during the tanning operations. Table 11.1 (Dixit et al. 2015) illustrates the details of the wastewater and characteristics of pollutants generated throughout the various tanning process.

Mostly the tannery wastewater is of dark brown in colour, possessing a strong odour with a large chemical oxygen demand, biochemical oxygen demand, total dissolved solids, chrome and a phenolic compound which has an adverse effect on the environment (Kusturica et al. 2015). Even after conventional treatment processes, there is a difficulty to remove them, and approximately 90% of total tannery pollution results from traditional tanning and pre-tanning processes. These processes cause an increment of chemical oxygen demand, sulphates, chlorides and total dissolved solids with a variation in potential of hydrogen (Dixit et al. 2015). The usage of lime with sodium sulphite in the liming process contributes to 92%

Table 11.1 Volume of wastewater generated during various tanning processes (Dixit et al. 2015)

	Pollutant load kg/ton of hide								
Process	Waste water generated (kilolitres)	Chemical oxygen demand	Biochemical oxygen demand	Chromium	Ammonical nitrogen	Total Kjeldahl nitrogen	Suspended solids	Sulphates	Chlorides
Soaking	9.0–12.0	22–33	7–11	–	0.1–0.2	1–2	11–17	1–2	85–113
Liming	4.0–6.0	79–122	28–45	–	0.4–0.5	6–8	53–97	1–2	5–15
Deliming	1.5–2.0	13–20	5–9	–	2.6–3.9	3–5	8–12	10–26	2–4
Chrome tanning	1.0–2.0	7–11	2–4	2–5	0.6–0.9	0.6–0.9	5–10	30–55	40–60
Post tanning	1.0–1.5	24–40	8–15	1–2	0.3–0.5	1–2	6–11	10–25	5–10
Finishing	1.0–2.0	0–5	0–2	–	–	–	0–2	–	–

suspended solids, 75% chemical oxygen demand and 84% biochemical oxygen demand to tannery wastewater (Dixit et al. 2015).

Furthermore, in the course of tanning operation, a number of chemicals such as tanning agents (organic and inorganic), dyes, acids, salts, and sulphonated oils were applied to mutate animal skins into a persistent product. This makes leather withstand against thermal, chemical and microbial degradation, and due to the non-biodegradability of tanned leather, management of sludge produced from tanneries is a challenging task (Lofrano et al. 2008). In addition to that, the implementation of such chemicals and their low biodegradability makes the effluent a severe environmental and technological threat (Schrank et al. 2004).

The pre-tanning operations such as liming deliming are marked as alkaline in nature as they impart high organic and sulphide contents, while the existence of a high concentration of chromium, ammonium, sulphate and chloride salts in tanning operations makes the effluent highly acidic with a high chemical oxygen demand value (Saxena et al. 2016).

The existence of various toxic chemicals, for example, formaldehyde, resins, chlorophenols, oils, chrome, phthalates and detergents categorized the tannery wastewater as a substantial contributor of pollutants (Lofrano et al. 2013). The poisoning potential of chemicals utilized during numerous tanning operations is summarized in Table 11.2 (Saxena et al. 2016).

The partially treated tannery wastewater is of dark brown colour and is a prime cause of harmful effects in water and soil; in addition to that, tannery wastewater restricts sunlight insertion to water bodies resulting in a reduced photosynthetic activity and thus causing a deleterious effect to aquatic system (Saxena et al. 2016). Furthermore, the exhaustion of dissolved oxygen in water promotes anaerobic conditions causing a rotten smell through water (Rai et al. 2005; Verma et al. 2008). Tannery wastewater restraint the nitrification process with the formation of foam on the water surface, and the high organic and inorganic pollutant content leads to the growth of an extensive range of pathogenic bacteria in water bodies (Saxena et al. 2016).

Chandra et al. studied tannery wastewater collected from common effluent treatment plant, with respect to seedling growth and seed germination on mung bean, and they found that there was a presence of bacterial communities along with various organic pollutants (Chandra et al. 2011).

The practice to discharge tannery wastewater (directly or indirectly) to rivers and canals and their use in irrigation leads to a severe toxic effect on the plant, animals and human (Saxena et al. 2016). Despite that, hexavalent chromium modulates the structure of microbes present in soil and diminishes their growth to inhibit bioremediation process, and its input in food chain prompts ulceration, nasal irritation, lung carcinoma and skin irritation in human being (Saxena et al. 2016).

Improper discharge of high salt content of tannery wastewater results in relevant soil pollution; the presence of high sulphide in tannery wastewater creates inadequacy of micronutrients present in soil (Raj et al. 2014). The removal of azo dyes present in tannery wastewater is one of the difficult tasks as they are complex and xenobiotic in nature, and their discharge to water bodies gives rise to eye and skin

Table 11.2 Poisoning potential of chemicals used in the tanning process (Saxena et al. 2016)

Chemical	Use	Lethal dose in rats, oral (milligrams/kg)	Intent organs
Lead chromate	Fastening agent and material surfacing	1000	Liver, lung, issues and reproductive system
Anthracene	Additive in tanning	16,000	Liver and kidney
Arsenic	Used in the finishing process	763	Liver, lung, kidney, skin and lymphatic system
Pentachlorophenol	Preservative	2000	Liver, kidney, skin, eyes, nose, blood, respiratory tract, immune and reproductive system
Methyl isothiazolinone	Biocide	1800	Skin and eyes
Short chain chlorinated paraffin	Oiling agent used for smoothness	3090	Liver, kidney and thyroid
Cobalt dichloride	Used in dyeing and finishing	80	Lung, liver, kidney, skin and heart
Benzyl butyl phthalate	Used in micro-porous artificial coating	2330	Eyes, lung, liver and reproductive system
Formaldehyde	Used in finishing	100	Eyes and lungs
Nonylphenol	Used in finishing	1475	Eyes, lungs, skin, kidney, blood and central nervous system
Di-butyl phthalate	Used in artificial leather production	7499	Gastrointestinal tract, lungs and eyes
2-Ethylhexyl phthalate	Used in artificial leather production	30,000	Liver
Chromium	Tanning agent	3250	Kidney, central nervous system and hematopoietic system
Azo dyes	Used for dyeing	3418	Liver and blood
Hexachlorobenzene	Applied as a preservative for raw hide and skin	10,000	Reproductive system

irritation, aesthetic, dermatitis and respiratory problems (Saratale et al. 2010; Gang et al. 2011). Hence there is a need for appropriate treatment of tannery wastewater before discharge to the environment.

11.5 Treatment Methodology for Tannery Wastewater

11.5.1 Primary Treatment

Primary treatment includes coagulation, flocculation and sedimentation process and is focused on the separation of colloidal particles (Fig. 11.1).

In the coagulation process, a coagulant (like iron chloride, iron sulphate, aluminium and sulphate) is applied with rapid mixing to neutralize the negative charges contained in the wastewater within a short contact time. However, the concentration and effectiveness depend on potential of hydrogen and nature of wastewater (Song et al. 2004). During flocculation, the applied flocculent increases the size and density of flocs and allows them to stick together to accumulate. While in sedimentation, the flocs are removed by solid-liquid separation (Song et al. 2004).

The next stage of treatment is adsorption (Fig. 11.2), which is generally used to separate metals, usually chromium (Fabbricino et al. 2013). This is a solid-fluid operation where the sedimented water is allowed to contact with adsorbent, and the certain pollutant present in the water gets adsorbed on the surface of adsorbent, and the treated water is discharged to next stage (Faust and Aly 2013).

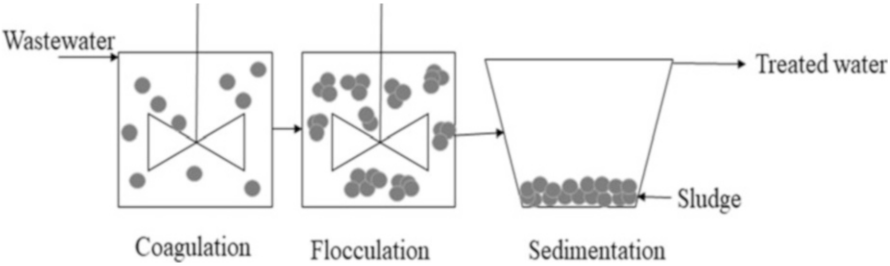
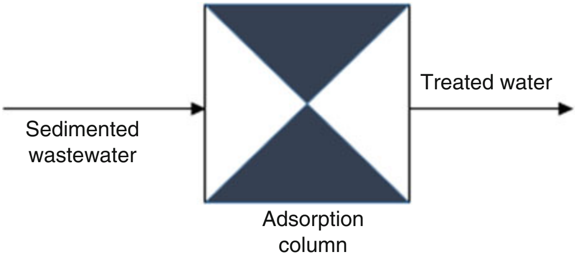


Fig. 11.1 Separation of colloidal particles through coagulation, flocculation and sedimentation process. (Modified after Song et al. 2004)

Fig. 11.2 Separation of toxic metals present in wastewater through solid-fluid operation in a packed adsorption column. (Modified after Faust and Aly 2013)



11.5.2 Treatment Ponds/Constructed Wetlands

The utilization of these systems has been expanded and effectively implemented to expel various contaminates from wastewaters. They are a man-made environmentally friendly system intended for the dismissal of pollutants from industrial and municipal wastewater (Mant et al. 2006). Their functioning depends on various parameters such as type of soil, nature of wastewater, microorganisms and plants. Hence, there is a need to develop a categorized microbial populations to treat wastewater (Calheiros et al. 2007).

The findings of Calheiros et al. indicates the development of *P. australis* and *T. latifolia* in constructed wetlands under 0.3 and 0.6 m/day hydraulic load leads to a chemical oxygen demand reduction 41–73%, and 41–58% biochemical oxygen demand in tannery wastewater (Calheiros et al. 2007). In a study conducted by Mant et al. for chrome removal, P. *purpureum* and removes 97–99.6% chrome, while *B. decumbens* removes 78.1% and 68.5% within 24 h (Mant et al. 2006). The establishment of two plant species, i.e., *Arundo donax* and *Sarcocornia fruticosa*, in constructed wetland to treat tannery wastewater results in 51 and 80% chemical oxygen demand and 53 and 90% biochemical oxygen demand reduction (Calheiros et al. 2012).

The integrated treatment pond system can be employed to treat tannery wastewater on pilot scale and a combination of maturation pond, and the secondary facultative pond was also an efficient approach for tannery wastewater treatment (Tadesse et al. 2004).

11.5.3 Biological Treatment

Biological treatment includes the decomposition of waste by aerobic or anaerobic processes to form innocuous solids. Usually activated sludge process, as shown in Fig. 11.3, is used for aerobic treatment, which has a fast decomposition rate in

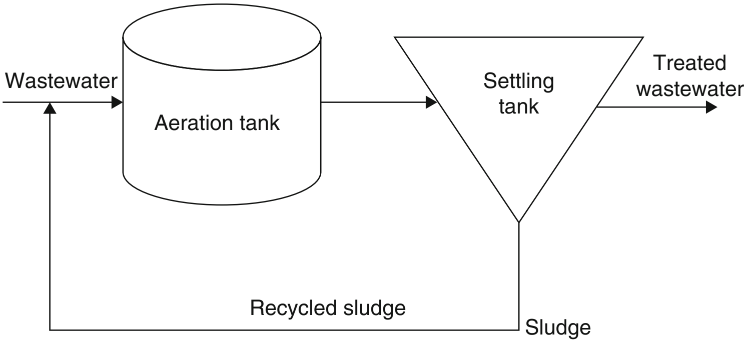


Fig. 11.3 Layout of an activated sludge process including aeration tank where air is injected in mixed liquor and settling tank to allow the biological flocs to settle. (Modified after Ram et al. 1999)

Table 11.3 Various microorganisms used in activated sludge process for tannery wastewater treatment

Microorganisms	Chrome reduction (%)	Chemical oxygen demand reduction (%)	Biochemical oxygen demand reduction (%)	References
Bacterial strain	87	–	–	Shakoori et al. (2000)
Hirsutella sp.	70	–	–	Srivastava and Thakur (2006)
A. thiooxidans	99.7	–	–	Yuan-Shan et al. (2007)
Acinetobacter sp.	90	–	–	Srivastava et al. (2007)
S. condensate and *R. hieroglyphicum*	>75	–	–	Onyancha et al. (2008)
Trichoderma sp.	97.93	–	–	Vankar and Bajpai (2008)
E. coli	68.3	90	90	Noorjahan (2014)
Brachymonas denitrificans	88.5	98.3	–	Kim et al. (2014)

conjunction with the generation of enormous amount of sludge. Table 11.3 indicates the various microorganisms used in this technique to treat tannery wastewater.

Due to the saline nature of tannery wastewater, there is a limited adaption of conventional cultures, and the variation in ionic strength results in cell disruption, which sometimes leads to a failure in the biological treatment process. Likewise, the existence of inadequately degraded tannins, chromium and toxic materials restrains the biological treatment by inhibiting the growth of heterotrophs and bacteria (Schrank et al. 2004). Hence, to conquer this issue, many researchers suggested the use of sequencing batch reactor to treat tannery wastewater (Ram et al. 1999; Cooman et al. 2003; Rameshraja and Suresh 2011; Lofrano et al. 2013).

Another problem in aerobic biological treatment of tannery wastewater is the temperature variation which affects the efficiency of process in terms of organic carbon and nitrogen removal, as there was 60% nitrogen removal efficiency reported in 21 °C to 35 °C temperature range (Görgün et al. 2007; Insel et al. 2008).

Owing to low energy consumption in comparison to aerobic treatment, anaerobic processes are one of the good options to treat tannery wastewater, but the absence of electron acceptor during sulphate reduction leads to form sulphide, and the high content of protein in effluent slows down the hydrolysis kinetics. Further, to reduce high chemical oxygen demand, there is a need of aerobic treatment (Mannucci et al. 2010, 2014).

11.6 Modern Technologies for Tannery Wastewater Treatment

As discussed in the previous sections after the conventional treatment process, the complete pollutant removal is still a major task. Hence, there is a need for the implementation of new modern techniques; some of them are discussed below.

11.6.1 Membrane-Based Technologies

Membrane technology has several advantages over conventional processes, which includes the high quality of treated water, effective removal of organic micropollutants, reduced sludge production and better process consistency. These techniques employ permeable membranes for separation and purification of industrial wastewater. Due to their continuous cost reduction and extended applications, their utilization to treat tannery wastewater is getting importance (Ranganathan and Kabadgi 2011). For the treatment of tannery wastewater, this technique provides many cost-effective benefits such as the recovery of chrome (Ranganathan and Kabadgi 2011), reduction of load in degreasing (Wang et al. 2011a), removal of salt during biological treatment and the reuse of water in many other processes (Scholz and Lucas 2003).

De Gisi et al. suggested that the reverse osmosis can be used as a post-treatment process after the biological treatment with an objective to reuse tannery wastewater and hence to reduce the freshwater consumption. In their study, the treatment was carried out through a plane reverse osmosis membrane which has reduced chemical oxygen demand along with the generation of high-grade permeate and enabled the reuse of water in the production cycle (De Gisi et al. 2009).

Scholz and Lucas used membrane technology to retrieve chemicals from tanning and deliming process and to reuse saline stream. The implementation of membrane filter results in the recovery of 90% treated liquors, and the obtained permeate out of the various process was confined with a high concentration of chemicals which were reused in the tanning processes (Scholz and Lucas 2003).

11.6.2 Membrane Bioreactors

This is a combined technology comprising membrane and bioreactor and has been developed as an alternative to the conventional activated sludge process. The advantages of this system include less space requirement, no need for secondary clarifiers, shorter hydraulic retention times, less sludge production and high removal of pollutants (Iorhemen et al. 2016).

Keerthi et al. have reported 90 and 93% of reduction in chemical oxygen demand and colour in tannery wastewater through hybrid membrane bioreactor (Keerthi et al. 2013). However, the severe fouling due to the plugging of several pollutants is the main disadvantage of this process, but extensive research is in process to overcome this issue, such as the integration of membrane bioreactors with another treatment process will reduce the fouling and mineralize majority of the pollutants (Fazal et al. 2015).

11.6.3 Anaerobic Ammonium Oxidation

This process is also known as anammox technology, used to separate nitrogen from wastewater, and compared to conventional nitrification and denitrification processes anammox process consumes low energy, with high efficiency (Ali and Okabe 2015). In the presence of nitrogen dioxide as an electron acceptor, this process transforms ammonium cation to dinitrogen and produces 90% less sludge in comparison to conventional nitrification and denitrification. This is a two-step process: in the first step, oxidation of ammonium cation to nitrogen dioxide happens, and in the second stage, ammonium cation oxidizes with nitrogen dioxide to form dinitrogen; afterwards, the process was introduced to single-stage reactor (Ali and Okabe 2015).

The anammox methodology was implemented by Anjali and Sabumon to remove ammonia from tannery wastewater, which saved 90% of operational cost in sludge discharge, and ingests 100% less organic carbon and 50% less oxygen (Anjali and Sabumon 2014). Hence, for the industries having effluent of high ammonia concentration, anammox oxidation could be a good economic approach (Ali and Okabe 2015).

11.6.4 Advanced Oxidation Processes

The drawbacks of conventional treatment technologies encouraged the scientific community to develop novel approaches towards efficient removal of contaminants from wastewater generated through various industries. To this context, advanced oxidation processes can fill the gap between the treatability limit of conventional process and rigorously increasing limit of environmental regulations (Dewil et al. 2017).

Usually, advanced oxidation processes are applied after secondary treatment of wastewater, and hence they are considered as tertiary treatment techniques (Audenaert et al. 2011). Advanced oxidation processes are the inclusion of heterogeneous and homogeneous photocatalysis, ozonation, ultrasonication, electrochemical processes, Fenton process and wet oxidation processes (Dewil et al. 2017). The main benefit of these processes is the effective degradation of pollutant without generation of secondary waste, and maximum pollutants get transformed to water, carbon dioxide and salts during mineralization (Saxena et al. 2016).

The general objective of advanced oxidation processes to treat tannery wastewater is to lessen the contamination load to such a degree that they might be restored to the water reservoirs or reused during the other operations. Table 11.4 highlights the various advanced oxidation processes applied over tannery wastewater.

As shown in above table, there are few studies which implements solar energy as photocatalysis to treat tannery wastewater, and in the context to current environmental scenario, the use of solar energy in terms of photocatalysis could play a key role to treat groundwater, drinking water and industrial wastewater. However, solar photocatalysis technique has been used for water splitting to produce hydrogen and degradation of toxic elements, dyes and chemicals (Shimura and Yoshida 2011). Hence, the treatment of tannery wastewater through solar photocatalysis could be an economic and cost-effective approach.

11.7 Solar Photocatalysis Process

The solar photocatalysis process involves the use of solar energy to excite a semiconductor catalyst also known as a photocatalyst, and the electronic structure of a photocatalyst (consists of a valence band and conduction band) can act as a sensitizer for the light-driven redox reaction. If a surface reaction has more positive oxidation potential in comparison to valence band potential, then there will be no oxidation; similarly if a surface reaction has more negative reduction potential compared to conduction band, then reduction will not take place, which denotes the absence of hydroxyl and superoxide radicals (Simonsen 2014). Hence, the position of conduction and valence band potential plays an important role in solar photocatalysis. If a photocatalyst is exposed through light having a wavelength equal or larger than its band gap energy, an electron will be excited to the conduction band leaving a positive hole in the valence band, and these electron and hole initiate reduction and oxidation process. Furthermore, the electron and hole tend to recombine very rapidly; if an appropriate surface defect or scavenger restricts this recombination rate, then there will be an efficient photocatalytic effect to mineralize organic impurities present in wastewater. In addition, the oxygen present in the atmosphere leads to produce superoxide ions which are a dominant oxidant (Spasiano et al. 2015).

The fundamentals of this technique are well established, and the characteristics of solar photocatalysis which make the applicability to treat industrial effluent are followed (Malato et al. 2009):

1. The process takes place at ambient condition.
2. Complete oxidation of polluting substance into carbon dioxide and other inorganic species.

Table 11.4 Various advanced oxidation processes employed for tannery wastewater treatment

Type of tannery wastewater	Advanced oxidation process applied	Pollutant reduction	References
Raw tannery wastewater	Fenton reagent	70% reduction in chemical oxygen demand	Lins et al. (2003)
Coagulated/ flocculated tannery wastewater	Photocatalysis (ultraviolet rays/ titanium dioxide)	6% reduction in chemical oxygen demand, 15% reduction in biochemical oxygen demand removal and 11% total organic carbon	Schrank et al. (2004)
Biological treated tannery wastewater	Ozone	30% reduction in chemical oxygen demand	Serdar Dogruel M.D., Esra Ates Genceli (2004)
Coagulated tannery wastewater	Fenton reagent	80% reduction in chemical oxygen demand	Schrank et al. (2005)
Coagulated tannery wastewater	Ultraviolet rays/hydrogen peroxide	60% reduction in chemical oxygen demand	Sauer et al. (2006)
Raw tannery wastewater	Electrochemical process	70% reduction in chemical oxygen demand	Kurt et al. (2007)
Equalized tannery wastewater	Electrochemical process	83.9% phenol degradation 40.5% total organic carbon reduction	Costa et al. (2008)
Chromium-containing tannery wastewater	Electrocoagulation	95% of chromium removal	Kongjao et al. (2008)
Equalized tannery wastewater	Electrochemical process	51–56% reduction in chemical oxygen demand 30–700% total suspended solids reduction	Espinoza-Quiñones et al. (2009)
Raw tannery wastewater	Ozone	60% reduction in chemical oxygen demand	Preethi et al. (2009)
Pre-treated tannery wastewater	Ozone	85% reduction in chemical oxygen demand	Schrank et al. (2009)
Synthetic tannery wastewater	Electrochemical	89% reduction in chemical oxygen demand	Sundarapandiyan et al. (2010)

(continued)

Table 11.4 (continued)

Type of tannery wastewater	Advanced oxidation process applied	Pollutant reduction	References
Biological treated tannery wastewater	Ozone	97% reduction in chemical oxygen demand	Di Iaconi et al. (2010)
		91% total Kjeldahl nitrogen reduction	
		96% total suspended solids reduction	
		98% surfactant reduction 96% colour reduction	
Pre-alkalized tannery wastewater	Ozone	30–70% reduction in chemical oxygen demand	Houshyar et al. (2012)
Equalized tannery wastewater	Photo-Fenton	90% reduction in chemical oxygen demand	Módenes et al. (2012)
		50% total suspended solids reduction	
Coagulated tannery wastewater	Coagulation + hydrogen peroxide/ultraviolet rays + electro-oxidation	97.5% reduction in chemical oxygen demand	Naumczyk and Kucharska (2017)
Common effluent treatment plant of tannery	Coagulation + aeration + ozone	80–90% reduction in chemical oxygen demand	Sivagami et al. (2018)
Pre-treated tannery wastewater	Ultraviolet rays/titanium dioxide	93.06% phenol reduction	Tripathi and Narayanan (2018)
		85.62% reduction in chemical oxygen demand	
		80.23% colour reduction	
Pre-treated tannery wastewater	Solar photocatalysis	84.22% phenol reduction	Tripathi and Narayanan (2019a)
Pre-treated tannery wastewater	Solar photocatalysis	89.06% phenol reduction	Tripathi and Narayanan (2019b)

3. The essential oxygen for the reaction can be directly obtained from the atmosphere.
4. The catalyst can be attached to different types of inert matrices.
5. The energy for the photo-excitation of the catalyst can be obtained from the sun.

The capability of this process to completely mineralize organic pollutants to carbon dioxide, water and inorganic ions, applicability at ambient conditions, and the absence of fouling differentiate solar photocatalysis with other conventional techniques of wastewater treatment (Mamba and Mishra 2016).

11.7.1 Key Steps of Pollutant Degradation During Solar Photocatalysis

The solar photocatalysis, as shown Fig. 11.4, is very complex and may involve a lot of possible reaction mechanism for pollutant degradation. Still there is a general concurrence to summarize solar photocatalysis in five key steps:

1. The dissemination of organic pollutants from bulk solution to the surface of the photocatalyst.
2. Photoexcitation of catalyst along with the adsorption of the organic pollutant.
3. Degradation of pollutant through oxidizing species.
4. Detachment of degraded products from photocatalyst surface.
5. The degradation products diffuse from the photocatalyst interface into the bulk solution.

11.7.2 Transformation of Contaminants

Mineralizing and eliminating organic compound present in wastewater is the primary objective of solar photocatalysis; so far for s-triazine herbicides, complete mineralization has been observed with a final product named as cyanuric acid which is non-toxic in nature. Today there is a need to pay attention towards the solar photocatalytic degradation of contaminants emerging from various industrial sources which have adverse effect on health and on the environment; many of them are still unknown and are in the focus of research (Petrović et al. 2003).

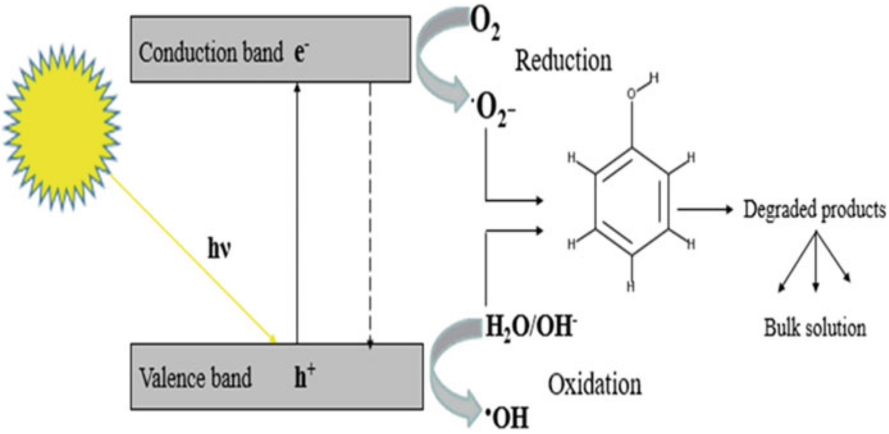


Fig. 11.4 Photocatalyst is exposed to light having a wavelength equal or larger than its band gap energy, leading to excitation of an electron and leaving a hole in valance band; these electrons and holes initiate reduction and oxidation process. (Modified after Spasiano et al. 2015)

The mineralization of nitrogen-containing compounds leads to form ammonium cation and nitrate, these ammonium cation are relatively consistent, and their proportionality is influenced by irradiation time and oxidation phase of organic nitrogen. For the amine compounds, the primary product exists in the form of ammonium cation, and the invasions of hydrogen-containing species on the amino group govern the formation of ammonium cation. Hence at the end of experiments, the amount of nitrogen-containing ions existing in the solution are much lesser than expected from stoichiometry, implying the adsorption of nitrogen-containing species on the surface of photocatalyst (Calza et al. 2005).

The generation of nitrogen in azo compounds can be represented by similar procedures which are accountable for ammonium cation formation and comprises of an exemplary case of decontamination reaction involving total innoxious nitrogen as a concluding product (Konstantinou and Albanis 2004). In the case of photo-Fenton treatment of phosphates, more iron is necessary, and at potential of hydrogen below 4, the phosphate ions stay adsorbed on the surface of photocatalyst (Malato et al. 2009).

The photo-induced hydroxide radicals attack on sulphur-containing atom present in wastewater to mineralize as sulphate ion; in most of the cases during the final stage of photoreaction, stoichiometric formation was observed when organic intermediates remained present in effluent solution (Malato et al. 2009). The strong adsorption of sulphate ion on photocatalyst surface could inhibit the reaction rate and forms non-stoichiometric sulphate ions. The presence of sulphate ion, chloride ion and phosphate ion in concentration > 1 milli-molar can reduce the reaction rate because of adsorption on the photo-activated reaction sites (Malato et al. 2009).

Industrial wastewater treatment is one of the major advantageous applications of solar photocatalysis, and there is always a need to assess the probable pollutant for optimized operations (Malato et al. 2007a). Generally, the compounds which have been degraded by solar photocatalysis comprise of dyes, aliphatic alcohols, alkanes, carboxylic acids, polymers, aromatics, alkenes, pesticides, surfactants, alkanes and herbicides. Equation 11.1 represents a general mechanism of organic pollutant degradation (Malato et al. 2009):

$$C_xH_yO_z + \left(\frac{y-2z}{4} + x\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \tag{11.1}$$

From an analytical point of view, determination of degraded products and the intermediate compounds is a most challenging task due to not selective nature of hydroxyl radicals. There are following types of degradation products (Malato et al. 2009):

1. Hydroxylated and de-halogenated products
2. Derived products of alkali chain oxidation
3. Products from aromatic contaminants
4. Isomerization and cyclization products
5. Decarboxylation products

The determination of these complex reaction mechanism is very difficult, and their estimation is restricted to identifying the dissipation of primary pollutant, in combination with a reduced total organic carbon. Therefore, the oxidation rate and kinetic of the process are usually evaluated (Malato et al. 2009).

11.8 Factors Affecting Solar Photocatalysis

11.8.1 Solar Irradiance

In case of solar photocatalysis, the reaction rate increases with increase in solar irradiance, and beyond a certain point, the rate of reaction depends as the square of the solar irradiance which is due to higher recombination rate of electron-hole pair. Furthermore, at high solar irradiance, the effect is negligible, and the rate remains constant. Such condition appears due to the deficiency of electron scavengers or excess of products conquering the catalyst surface which implies the lesser contact of catalyst with the effluent (Silva et al. 2007; Spasiano et al. 2015).

11.8.2 Oxygen Concentration

The degradation of organic pollutant present in wastewater can be summarized by Eq. 11.2 which concludes that in the absence of oxygen, there is no photodegradation.

$$\text{Organic pollutant} + \text{Oxygen} \rightarrow \text{mineral acids} + \text{carbon dioxide} + \text{water} \quad (11.2)$$

The availability of oxygen in water not only serves as an electron acceptor but also leads to the formation of oxidative species (Malato et al. 2009).

11.8.3 Potential of Hydrogen

Usually, solar photocatalysis indicates a strong potential of hydrogen dependency, and with the variation in potential of hydrogen, the valence and conduction band edges of a photocatalyst move by 0.059 per unit potential of hydrogen, which makes electrons of valence band more effective, and holes of conduction band less effective (Hoffmann et al. 1995). Another notable characteristic of solar photocatalysis generally not taken into consideration during water decontamination is the formation of intermediate compounds which may respond divergently depending on potential of hydrogen.

Furthermore, potential of hydrogen also affects the surface charge of a photocatalyst which could affect the efficiency of photocatalysis process (Spasiano et al. 2015). Hence, potential of hydrogen is one of the most important parameters which must be considered during the study of any photocatalytic process.

11.8.4 Temperature

Due to the photonic activation, the photocatalysis systems do not require heating and can be operated at ambient conditions. Many studies concludes that at temperature below 0 °C, the rate-limiting step is controlled by the final product desorption, and at this point the apparent activation energy increases (Malato et al. 2009; Nan et al. 2010). While at temperature above 80 °C the exothermic adsorption of reactants becomes rate-limiting step, the apparent activation energy becomes negative. Furthermore, at higher temperature, recombination of electron-hole pairs increases and demonizes the adsorption of organic compounds onto the photocatalyst surface (Malato et al. 2009; Nan et al. 2010).

In addition, the solubility of oxygen decreases with increased temperature and affects the photocatalytic kinetics. Hence for the photocatalysis system, 20 and 80 °C temperature range is considered as optimum (Malato et al. 2009; Nan et al. 2010).

11.8.5 Catalysis Load

Catalysis load and solar photocatalytic reactor diameter are interconnected reactor design parameters. In the case of slurry reactors, the rate of reaction is proportional to the load of catalyst, but after a specific dose due to particle agglomeration and poor penetration of sunlight, the photocatalytic activity decreases (Assano and Alfano 1998; Silva et al. 2007). Hence optimization of the photocatalyst dose for a better efficiency is required; various reports conclude that 25–50 mm must be the ideal diameter of a solar photocatalytic slurry reactor. Lesser than this range may result in operating pressure loss (Dillert et al. 1999; Guillard et al. 1999).

In immobilized photocatalytic reactor system, the film thickness plays an important role which depends on photocatalyst deposition technique, optical and physical properties of the material used and the nature of light wavelength. When the film thickness is very low (<1 μm), the photons will absorb on the photocatalyst surface, whereas the thick film gives rise to an unreactive "dark zone" (Chen et al. 2000; Camera-Roda and Santarelli 2007).

11.9 Photocatalytic Reactors

For the detoxification of pollutant, the sun provides UV flux 20–30 Wm^{-2} in the range of 300–400 nm with 0.2–0.3 mol photons $m^2\ h^{-1}$, which suggests the use of sun as an economical source of sensible light, and a photocatalytic reactor is a device which brings photons and pollutant in contact with the photocatalyst (Bahnemann 2004). These reactors are different from chemical reactors in terms of geometry and operating parameters; the primary objective of these reactors is to transmit sufficient light to initiate the reaction mechanism. Figure 11.5 highlights the design concept of these photocatalytic reactor systems. In these systems, temperature doesn't play an important role; hence no insulation is required. The solar photocatalytic reactors can be classified as:

1. Non-concentrating collectors
2. Parabolic trough collectors
3. Compound parabolic collectors

11.9.1 Non-concentrating Collectors

They are also known as an inclined plane collector, over which the fluid flows and interacts with the photocatalyst immobilized on the surface (Fig. 11.6). This reactor is capable of utilizing both direct and diffuse radiations from the sun. Due to simplicity and low capital cost, non-concentrating collectors have been proved an impressive choice for small-scale functions, especially in the areas having an infeasible wastewater treatment plants. Though these reactors demand large area in comparison to other reactors, but they have been successfully implemented for agro-industrial, organic pollutants and bio-refractory wastewater treatment (Spasiano et al. 2015).

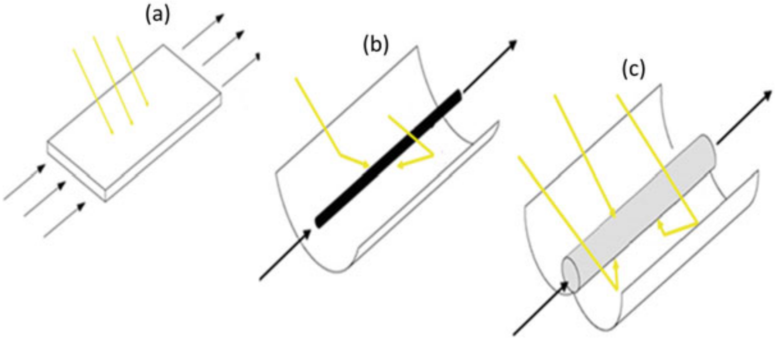


Fig. 11.5 Geometrical concept in terms of incident solar radiations for (**a**) non-concentrating collectors, (**b**) parabolic trough collectors and (**c**) compound parabolic collectors. (Modified after Malato et al. 2009)

Fig. 11.6 Interaction of fluid over photocatalyst immobilized surface of non-concentrating collector reactor operated in continuous recycle mode. (Modified after Bahnemann 2004)

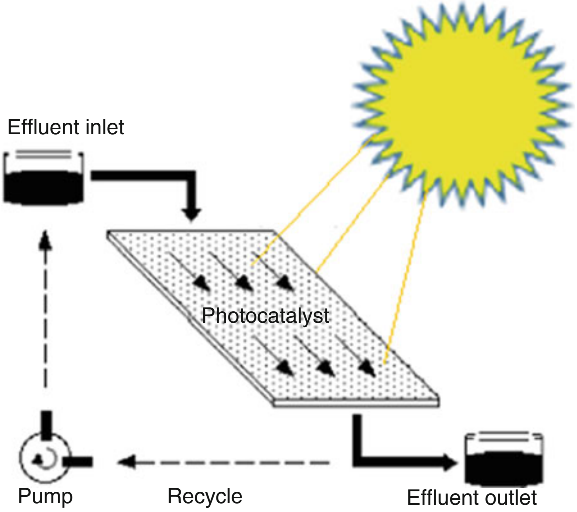
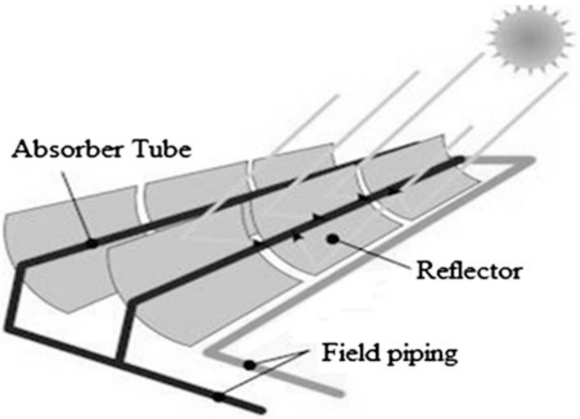


Fig. 11.7 Parabolic trough collectors composed of a parabolic trough-shaped concentrator that reflects direct solar radiation onto a receiver or absorber tube located in the focal line of the parabola. (Modified after Spasiano et al. 2015)



This reactor immobilized with titanium dioxide, and having a 50 m^2 of exposed area with a combination of two bioreactors, was installed in Tunisian textile mill to decolorize water (Spasiano et al. 2015) and has also been used for transformation of 1,1-dicarbonitrile through dicyano tetramethyl benzene as the electron acceptor (Will et al. 2004).

11.9.2 Parabolic Trough Collectors

The design of parabolic trough collectors (Fig. 11.7) is inspired from thermal energy application derived from the sun. Parabolic trough collector contains a reflective parabolic surface used to concentrate the transparent tube through solar radiations by which the fluid flows.

For maximum efficiency, the platform of the collector is controlled by two motors in an azimuth and elevation tracking system to keep the aperture of parabolic trough collector in perpendicular to the solar radiation (Fernández-García et al. 2010). With regard to photocatalytic applications, the concentration factor of parabolic trough collectors reactor lies from 5 to 35 suns; the concentration factor is the ratio of collector's aperture area and absorber area (Alfano et al. 2000). This system sustains turbulent flow with well-organized uniforming, and the closed system of the tube prevents the vapourization of volatile compounds during experiments.

In this reactor system, photocatalyst is usually suspended in a fluid, and the main disadvantage of this system is the dependency on the direct radiation beams which makes them impractical during cloudy days; in addition, their tracking system contributes extra capital and operating cost (Fernández-García et al. 2010). The parabolic trough collectors were used to treat wastewater containing heavy metals and chlorinated solvents (Spasiano et al. 2015), for the production of 5-hydroxy-1,4-naphthoquinone (Oelgemöller et al. 2006), for heterocyclization of ethyne (Jung et al. 2005), acylation reaction of naphthoquinones and quinones (Schiel et al. 2001).

11.9.3 Compound Parabolic Collectors

They are immobile collectors having parabolic reflective surface around to a cylindrical reactor tube as shown in Fig. 11.8; compound parabolic collector is an intercross of parabolic trough collector and non-concentrating collector reactors (Islam et al. 2015). Their geometry is capable of capturing both direct and diffuse radiations

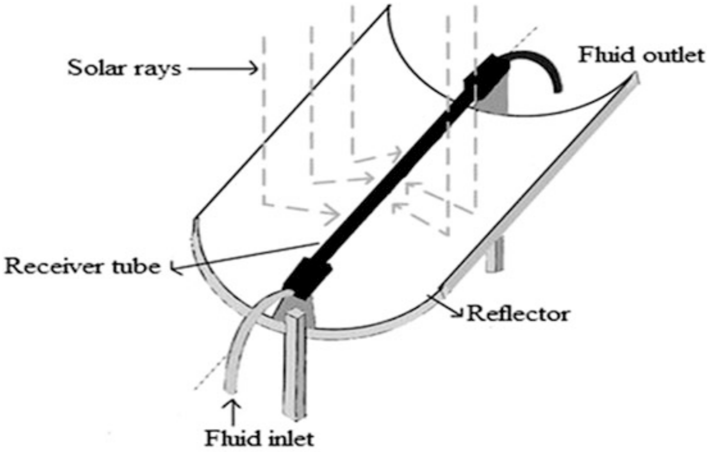


Fig. 11.8 Heating of working fluid in receiver tube using solar radiation falling on reflector of a compound parabolic collectors. (Modified after Islam et al. 2015)

Table 11.5 Advantages and disadvantages of photocatalytic reactors (Spasiano et al. 2015)

Non-concentrating collectors		Parabolic trough collectors		Compound parabolic collectors	
Advantages	disadvantages	Advantages	disadvantages	Advantages	disadvantages
High optical efficiency	Large reactor area required	Small reactor volume	Required tracking	Small reactor volume	Reasonable capital cost
Simple design	Pressure limitations	High flow rate	Utilize direct beams	High flow rate	Reasonable heat generation
Utilization of direct and diffuse beams	Poor mass transfer	Improved mass transfer	Optical losses	Good mass transfer	Complex to scale up
Low cost	Laminar flow	Low catalyst load	Overheating	Turbulent flow	
No heating	Reactant evaporation	Small area required	Low efficiency	Low catalyst load	

from the sun, and the extent of sunlight absorbed by a compound parabolic collectors is far better than parabolic trough collectors. Hence they can be used on overcast days without the use of solar tracking systems which substantially reduces system complexity with cost (Malato et al. 1997).

The pilot-scale compound parabolic collectors, have demonstrated photocatalytic removal of biorecalcitrant compounds (Sarria et al. 2003; Malato et al. 2007b), chlorophenols (Gernjak et al. 2003), bacteria (Fernández et al. 2005), pesticides (Oller et al. 2006), chlorinated solvents (Blanco-Galvez et al. 2007), dyes (Malato et al. 1997) and pathogenic organisms (Sarria et al. 2003; Malato et al. 2007b). They have also been used for urban and olive mill wastewater treatment (Gernjak et al. 2004; Kositzi et al. 2004) and the treatment of sanitary landfill leachate (Silva et al. 2013).

The advantages and disadvantages of these reactors are described in Table 11.5.

11.10 Conclusion

Among all the industrial wastewater, tannery wastewater is very complex in nature and a significant source of environmental pollution; the conventional wastewater treatment methods are not efficient to meet the standards. Hence to achieve cost-effective high-efficiency treatment, advanced oxidation processes in various combinations have been used as a pre- or post-treatment method. In recent years, solar photocatalysis, a kind of an advanced oxidation process, has gained the attention of researchers worldwide; the utilization of natural sunlight as the leading factor is a unique approach compared to other advanced oxidation processes. However, as the number of pollutants and their concentration increases, this process becomes more complicated and results in low photo-efficiency and slow kinetics along with an unpredicted mechanism (Nan et al. 2010). Furthermore, the reliability on the natural light source is another factor which needs to be resolved through the integration of various solar collecting technologies for an efficient outcome (Malato et al. 2009).

Hence to promote solar photocatalytic wastewater treatment technology in the near future, few technical barriers still need to be overcome:

- Development of high photo-efficient catalyst for extensive solar spectrum utilization.
- For cost-effective pollutant separations, catalyst immobilization approach needs to develop.
- Coupling of solar photocatalysis with other treatment techniques.
- Inadequate experimental data and prolonged dependability on solar energy.
- Lack of techno-economic study.
- The effective and efficient design of the photocatalytic reactor.

The photocatalytic reactor design is a major challenge for the scale-up of the solar photocatalytic process. In addition, based on process requirement, optimization of photoreactor must consider into account, as the continuous light exposure to the reactor leads to a rapid and efficient pollutant degradation.

Another issue with the solar photocatalysis process, which is needed to be addressed, is the environmental impact assessment and life cycle analysis studies. Finally, for wide industrial application, solar photocatalysis has to be developed as a sustainable, robust and cost-effective approach.

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