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Assessment of solar photocatalytic degradation of textile wastewater by ZnO-based reactors

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ABSTRACT

The present study deals with treating the textile wastewater of Jodhpur city in Rajasthan, India employing a photocatalysis technique. Jodhpur has a number of textile industries and efficient treatment of its effluents has been a major problem in the region. An effort has been made to resolve this issue through this study. A wastewater treatment unit was setup which involved coagulation and flocculation, sand filter, photoreactor, and activated carbon filter processes. ZnO-based semiconductor, coated on galvanized iron (GI) plates, served as a photoreactor. The water quality parameters removal efficiency at the end of each process operation was recorded for different detention periods in the photoreactor. Water quality parameters analyzed were biochemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), and pH. The optimal retention time for the photoreactor was found and the BOD of the wastewater reduced to 25 from 740 mg/l (97% reduction), and TSS from 1,430 to 12 mg/l (99% reduction) for the corresponding retention time. TDS reduction efficiency was 25% and pH changed from 9.2 in raw wastewater to 8.4 in treated wastewater. Results show that the pilot treatment plant was efficient for BOD and TSS removal from the textile wastewater.

Key words: BOD, photocatalysis, textile wastewater, ZnO semiconductor

HIGHLIGHTS

- Treatment of wastewater generated from textile industries located in Jodhpur city, Rajasthan.
- Setting up of a pilot wastewater treatment plant involving a sedimentation unit, sand filter unit, photoreactor unit, and activated carbon filter unit.
- Biochemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), and pH were determined after passing through each treatment unit.

INTRODUCTION

Textile industries use large amounts of water and subsequently, a large amount of wastewater is generated. This effluent wastewater comprises dyes, inorganic salts, grease and oils, detergents, suspended solids, mineral oils, heavy metals, surfactants, and fibers (Lopez *et al.* 1999; Lau & Ismail 2009). The textile effluent wastewater is generally characterized in terms of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), color, pH, total dissolved solids (TDS), and total suspended solids (TSS). This wastewater with a high organic load needs to be treated before it can be discharged into the environment. Textile wastewater treatment systems are usually based on the combination of an aerobic biological process and physicochemical processes (Lau & Ismail 2009). Some of the conventional methods involve coagulation–flocculation, activated carbon adsorption, ozonation, and membrane filtration techniques such as ultra-filtration and nano-filtration (Marmagne & Coste 1996) (these techniques used for dye/color removal). Apart from the conventional treatment systems, photocatalysis involving zinc oxide (ZnO) as a photocatalyst has attracted much attention (Danwittayakul *et al.* 2015; Sadi *et al.* 2015; Lee *et al.* 2016; Mahajan & Sonwane 2016; Souza *et al.* 2017; Dihom *et al.* 2022;

Folawewo & Bala 2022). The use of sunlight makes this process, a sustainable method for treating the highly polluted wastewater.

Photocatalysis is a light-induced catalytic process that oxidizes organic molecules to less harmful compounds, through redox reactions. These oxidation and reduction reactions occur simultaneously when photons are absorbed resulting in the generation of electron (e^-)–hole (h^+) pairs over the metal oxide semiconductor surface (Danwittayakul *et al.* 2015). ZnO is a promising candidate as a solar light photocatalytic material as it demonstrates high photocatalytic efficiency for the degradation of organic pollutants in comparison to other metal oxides (Abebe *et al.* 2020). ZnO has a higher effective surface area, which leads to higher organic molecules adsorption and in turn leads to enhanced photocatalytic activities. This leads to the efficient degradation of organic pollutants. Semiconductor-based photocatalytic degradation is mathematically summarized as below (Equations (1a)–(1e)) (Sadi *et al.* 2015).

$$ZnO + h\nu = e^- + h^+ \quad (1a)$$

$$e^- + O_2 = O_2^- + h^+ \quad (1b)$$

$$h^+ + \text{Organic pollutant} = CO_2 \quad (1c)$$

$$h^+ + H_2O = H^+ + {}^{\cdot}OH \quad (1d)$$

$${}^{\cdot}OH + \text{Organic pollutant} = CO_2 \quad (1e)$$

The hydroxyl radical formed in the process acts as an oxidizing agent and thus oxidizes the organic pollutant to carbon dioxide. Sadi *et al.* (2015) showed the efficiency of ZnO-based photocatalysis in the treatment of wastewater collected from the effluent of different industries in Oman including textile and municipal sewage. Danwittayakul *et al.* (2015) synthesized zinc oxide/zinc tin oxide nanocomposite for photocatalytic degradation of textile wastewater collected from a textile manufacturer located in Samutprakarn province in Thailand. Mahajan & Sonwane (2016) synthesized ZnO nanocatalyst and studied the ultrasonic, photocatalytic and sonophotocatalytic degradation of organics in the effluent from the textile industry located in Pandesara, Surat. The degradation efficiency was measured in terms of the percentage reduction in TOC of the effluent. Souza *et al.* (2017) investigated the solar photocatalytic degradation of textile industry effluent using TiO_2, ZnO, and Nb_2O_5. The industry was located in the northwestern region of the state of Paraná, Brazil.

Present study

Jodhpur is a city lying in the semi-arid region of North West India. The city has a number of textile industries generating huge amounts of wastewater. Efficient treatment of this waste has been a problem since last many years. The main issue in treatment is the reduction in BOD, as this is because of the presence of complex dyes in wastewater. A common effluent treatment plant (CETP) has been set up in the region for treating industrial effluent which uses conventional treatment techniques. CETP receives effluent wastewater from the textile industries and steel industries situated in the area. The total amount of effluent received by the plant is 15 million liters per day (MLD) out of which 14 MLD is effluent from textile industries and 1 MLD is effluent from steel industries. The present study aims to assess the degradation potential of solar photocatalysis using zinc oxide (ZnO). This study differs from others as we have incorporated a pilot treatment plant having the convention treatment units along with the ZnO reactor. The aim of this study is to assess the individual degradation efficiency of each treatment unit involved in the treatment plant including the ZnO-based reactor. Also, the study aims to find the optimal retention time required to treat the textile wastewater, for a given ZnO-based photoreactor (PR).

MATERIALS AND METHODOLOGY

A small-scale treatment plant was set up to assess the photocatalytic-based degradation of the organic loading of the textile industry effluent. The schematic diagram of the unit operations/processes involved in the study is shown in Figure 1. The capacity of the pilot plant was 150 l.

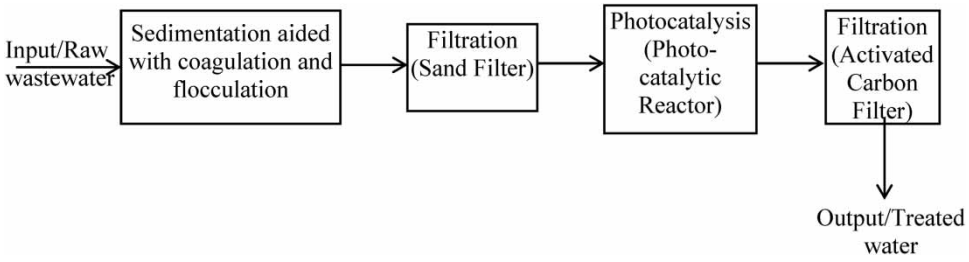

Figure 1 | Schematic representation of the processes involved in the study.

Textile effluent

CETP Jodhpur receives wastewater from several textile and steel industries in the Jodhpur region. The treatment plant receives 15 MLD of wastewater from the textile and steel industries. The wastewater/effluent from these industries is collected in a neutralization tank. As the wastewater from textiles is highly alkaline and the wastewater from the steel industry is highly acidic, both sources of wastewater tend to reduce (neutralize) their extremities. Further, this water is kept in an equalization tank for a uniform wastewater loading rate. This water from the equalization tank served as input/raw wastewater for the proposed study.

Raw wastewater was allowed to pass through different treatment units of the pilot plant (schematic shown in Figure 1) for different retention times (t) in the ZnO reactor. Effluent from each unit was collected for the analysis of the following water quality parameters: pH, TDS, TSS, and biological oxygen demand (BOD). The water quality parameters were analyzed/determined in accordance with standard methods (BIS 1993). Percentage change for each parameter after passing wastewater through each treatment unit was estimated by applying the following formula (Equation (2)).

$$P = \frac{C_I - C_F}{C_I} \times 100 \tag{2}$$

where P indiactes the percentage change in the water quality parameter, C_F and C_I are the final and initial values of the parameter.

Coagulation and flocculation chamber

A sedimentation tank having a capacity of 150 l was built. Ferric chloride was used as a coagulant which was mixed with the input wastewater for 1 min. The optimum coagulant dose for the wastewater determined by thee jar test was 1 g/l. A handheld stirrer was used to maintain a constant rotation. The coagulant was added and the water was allowed to settle for 30 min. After settling, the sample was collected and the supernatant liquid was allowed to pass through the sand filter (SF).

Sand filter

The gravity SF was designed by assuming the hydraulic loading rate (HLR) of the filter to be 12.7 m^3/m^2/day. The capacity of the plant (C) was 0.15 m^3. For retention time (t) = 2 h, flow rate (Q) is estimated to be 1.8 m^3/d by using Equation (3). Accordingly, for $t = 8$ h, $Q = 0.45$ m^3/d.

$$Q = \frac{C \times 24}{\text{Retention time}} \tag{3}$$

$$d = \sqrt{\frac{A \times 4}{\pi}} \quad \text{where} \quad A = \frac{Q}{\text{HLR}} \tag{4}$$

The diameter of the filter for $Q = 1.8$ m^3/d was calculated to be 0.42 m and for $Q = 0.45$ m^3/d it was 0.2 m. Therefore, the diameter of filter (D) was considered to be 0.4 m, which represents the diameter for maximum flow rate and minimum detention time.

The depths of the sand layer, coarse aggregate, and fine aggregate were kept to be 7.6, 11.4, and 11.4 cm, respectively. A sample was collected from the output of this unit, which was further passed to the photocatalytic reactor unit.

Photocatalytic reactor

Transmission of light through the water plays a significant role in sunlight-assisted wastewater treatment. To address the proper transmission of sunlight into the wastewater, the photoreactor unit was made of a transparent acrylic sheet. A rotating flat plate-type batch reactor was fabricated for the ZnO-based photocatalysis of wastewater. ZnO was synthesized using the sol-gel method and the galvanized iron (GI) plates were coated with ZnO which were attached to axles rotating at the speed of 2–3 rpm. The effluent of the SF was then poured into this reactor and was kept for a retention time of 2, 4, 6, and 8 h. The procedure adopted for the ZnO synthesis and subsequently the reactor fabrication is described in detail in the following sections.

ZnO synthesis

Zinc acetate (0.025 M) and sodium hydroxide were added in a mixture of isopropyl alcohol and methanol. The solution was coated on a GI and stainless steel porous plate at a temperature of 200 °C. This formed a layer of ZnO nano seeds on the top of the surface in the following manner (Equations (5) and (6)).

$$Zn(CH_3COO)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2CH_3COONa \quad (5)$$

$$Zn(OH)_2 \xrightarrow{\text{Temperatue } 200^\circ C} ZnO + H_2O \quad (6)$$

Material seeded with ZnO nanoparticles, when immersed in an aqueous solution of hexamethylenetetramine (HMT) or methenamine and zinc nitrate ($Zn(NO_3)_2$) at 90 °C yields an extended array of ZnO on the substrate surface (Ashfold *et al.* 2007). The coated plates generated in the above section (Equations (5) and (6)) were then dipped in the solution of 0.05 M HMT also known as methenamine and 0.01 M zinc nitrate, hydrated in distilled water, this provided zinc ion atmosphere at 90 °C for 4 h. Thermal degradation of HMT leads to the formation of formaldehyde (HCHO) and ammonia (NH_3) (Equation (7)). The ammonia released, helped in the formation of hydroxyl ions (OH^-), which react with Zn^{+2} ions to form ZnO as shown in Equations (8) and (9) (Baruah & Dutta 2009).

$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad (7)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (8)$$

$$2OH^- + Zn^{+2} \rightarrow ZnO + H_2O \quad (9)$$

Reactor fabrication

GI sheets were used as a substrate or base for the ZnO fabrication. ZnO nanocrystals were fabricated by a sol-gel method in the following manner.

A coating solution was prepared by adding 400 ml of isopropyl alcohol, 250 ml methanol and 1.43 g zinc acetate (0.019 M) together and then stirred for 30 min. Simultaneously, a saline solution was prepared by adding 0.4 g Sodium hydroxide in 350 ml deionized water and was stirred for 30 min. The coating solution was then kept on a hot plate at 65 °C, constantly stirred and the saline solution was added dropwise. The whole solution took 3 h to get mixed. This solution was then mixed thoroughly in a sonicator (at 45 °C, 17s-3 s pulse, for 20 min). The GI sheet was placed on a hot plate at 200 °C and the prepared solution was then coated on it. Simultaneous a nano growth solution was prepared in which 3 g zinc nitrate (0.015 M solution) and 7 g hexamine/methenamine (0.05 M solution) were added in 1 l of water and stirred for 20 min. The coated plates were placed in a container. The container was then filled with the growth solution to such a level that the plate was completely submerged into it. This container was then kept inside an oven and heated at a temperature of 90 °C and was allowed to stand that way for almost 2 h. The plates were then taken out and dried. These plates were then attached to two rotating units hence making them into the two reactor units, as shown in Figure 2.

The capacity of a single photocatalytic batch reactor unit was 150 l. HLR for the reactor was assumed same as that of the SF unit. The depth of the reactor unit was 0.75 m, a diameter of the unit was 0.6 m. The volume of the wastewater (SF outlet) in each reactor unit was 135 l. GI sheets were custom-made for the reactor with 2-1 equidistant holes over the sheet each of a diameter of 2 mm (details provided in Figure 2). These holes increased the surface area and thus the interaction of the wastewater with the ZnO coating. The specific area of the ZnO deposited over the GI sheets in the solution was 40 m^2/g. The photocatalytic efficiency of the reactor units was

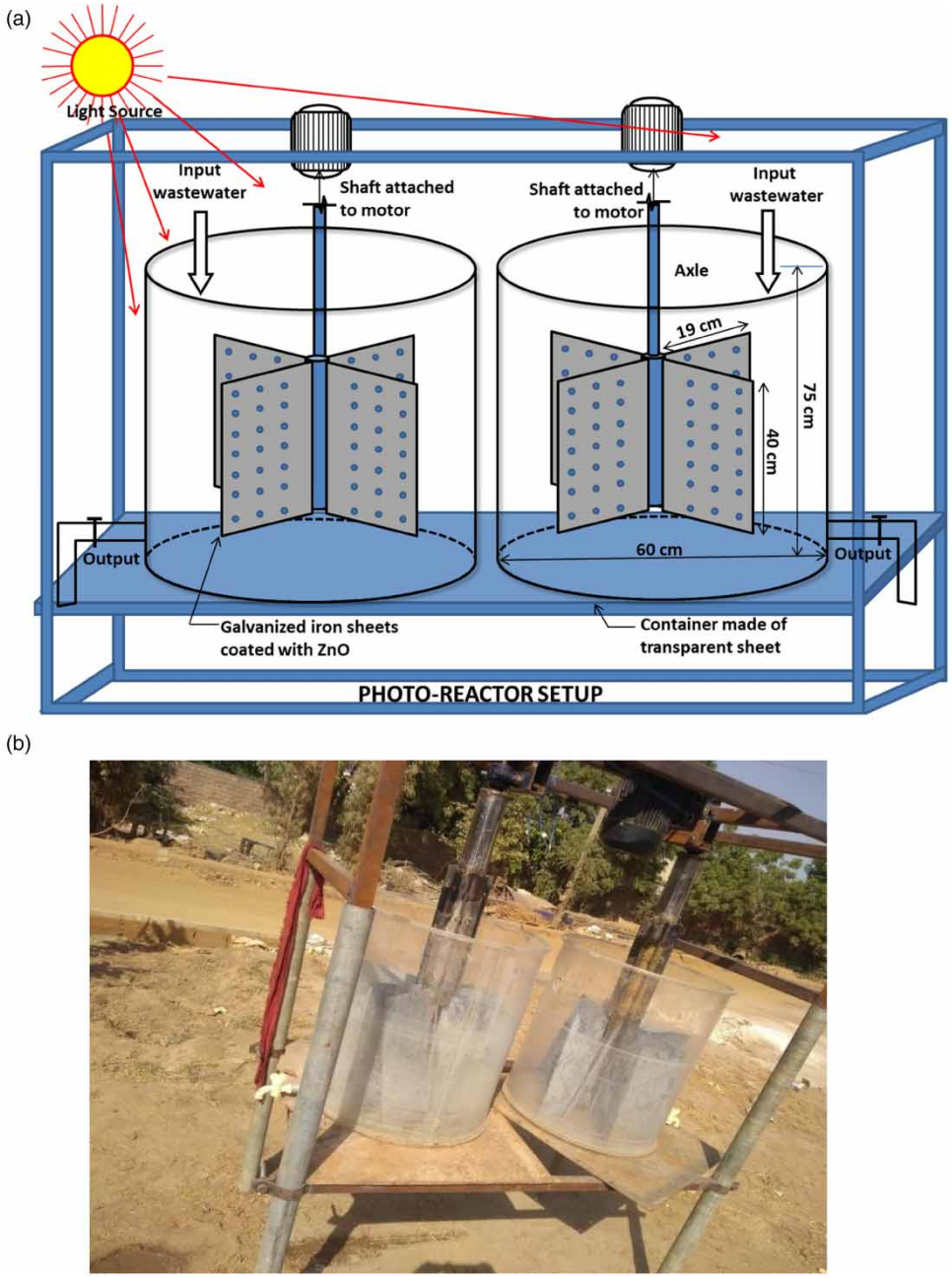

Figure 2 | ZnO-based fabricated photocatalytic reactor: (a) schematic diagram and (b) field setup.

analyzed by measuring the ultraviolet–visible absorbance spectra of the effluent for different contact periods/retention times. The sample was collected from this reactor outlet and was then fed to the activated carbon filter (ACF) unit.

Activated carbon filter

The depth of the carbon filter was 15 cm, and the depth of the fine aggregate layer and the depth of the coarse aggregate layer were kept at 7.6 cm. The diameter of the filter was 0.4 m and the HLR was 12.73 m^3/m^2/day. The empty bed contact time was calculated as 40.5 min. The effluent from the ACF unit was considered as final treated water.

RESULTS AND DISCUSSION

The ultraviolet–visible absorbance spectra of the pilot treatment plant effluent obtained for different retention times are shown in Figure 3. As the retention time is increased the absorbance decreases, this shows the

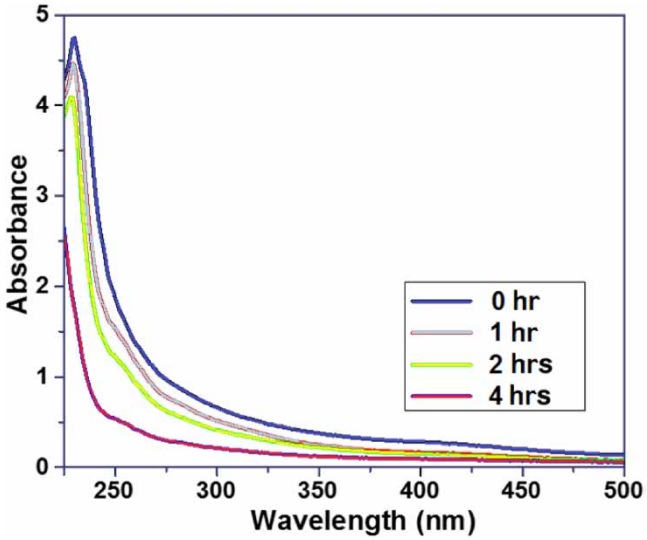

Figure 3 | Ultraviolet–visible absorbance spectra for the effluent of the pilot wastewater treatment plant.

degradation of organic pollutants with increasing retention time. The color of wastewater represents the impurities present in it. Raw/inlet wastewater had a brownish-grey color and it changed to nearly transparent for the final treated water.

The effluent from each unit (viz. coagulation and flocculation (C&F), SF, PR, and ACF) was analyzed for BOD, pH, TSS and TDS. The values obtained are shown in Figures 4 and 5.

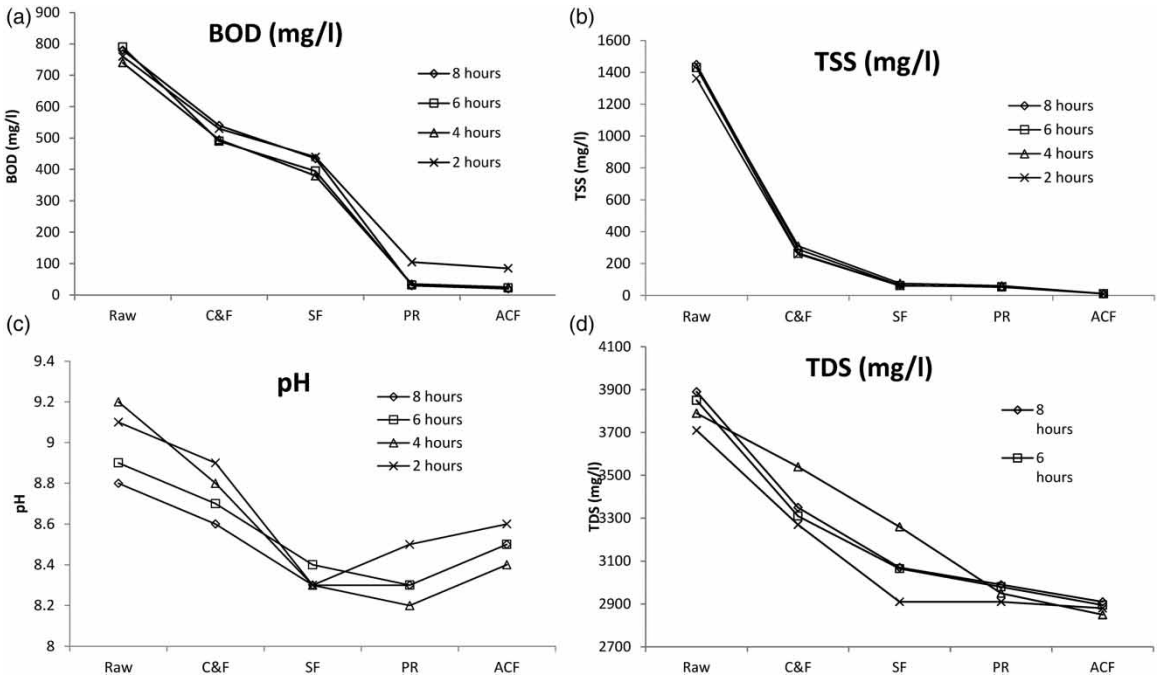

Figure 4 | Results obtained at the end of each treatment unit for different retention times: (a) BOD, (b) TSS, (c) pH, and (d) TDS.

It can be seen from Figure 4(a), that there was a considerable decrease in BOD as the wastewater was passed from the SF to the PR and as moved further from the PR to the ACF the reduction was not significant. Also, the reduction in BOD seemed significant for 4 h of detention time as compared to 2 h of detention time. Further

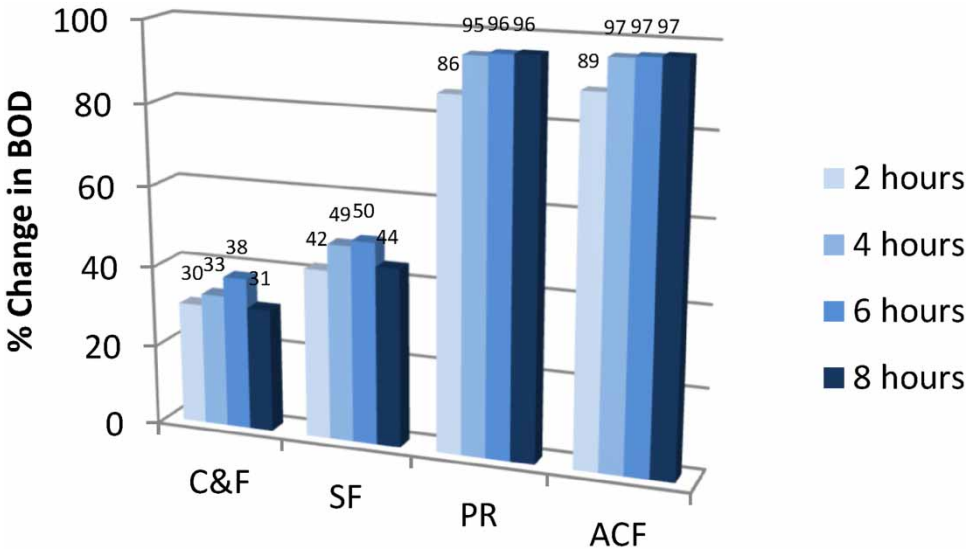

Figure 5 | Efficiency of each treatment unit in terms of wastewater BOD reduction for 2 h of the retention period.

reduction in BOD with increasing retention time was there but the difference in the reduction values could be considered comparatively insignificant, and hence 4-h detention time was considered to be optimal. The same was the case for TSS as shown in Figure 4(b). pH had a very little decrease as shown in Figure 4(c). The proposed treatment methodology is based on the oxidation of the organic pollutants by the hydroxyl radicals. It does not include any addition/removal of ionized chemicals. Thus the pH values in the process did not change significantly. Further, the experiment revealed that the TDS of the wastewater was not removed significantly with the proposed treatment method (Figure 4(d)). The TDS comprise organic and inorganic impurities. Since the proposed treatment methodology degrades the organic pollutant, the remaining inorganic pollutants (which were not degraded during the processes) could be the reason for lower TDS removal.

For 4 h of detention time, the BOD, TSS, and TDS of wastewater reduced from 740, 9.2, 1,430, and 3,790 mg/l to 25, 8.4, 12, and 2,850 mg/l, respectively.

The efficiency of each treatment unit in terms of percentage change in BOD, pH, TSS, and TDS was estimated as per Equation (2) and the results obtained are shown in Figures 5–7, respectively.

It can be seen from the Figure 5 that, for 4 h of retention time, the percentage reduction in BOD was 48% after it was passed from the SF and the reduction increased to 95% in the PR (for 4 h of retention time). The percentage reduction in TSS was 95% after the SF, which was increased to 96% after the PR (Figure 6). This is because most

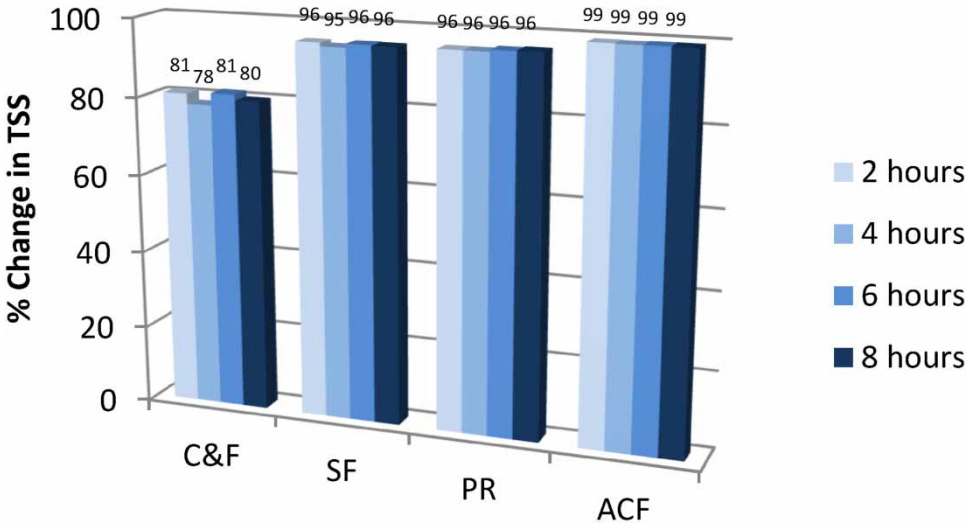

Figure 6 | Efficiency of each treatment unit in terms of wastewater TSS reduction for different retention periods.

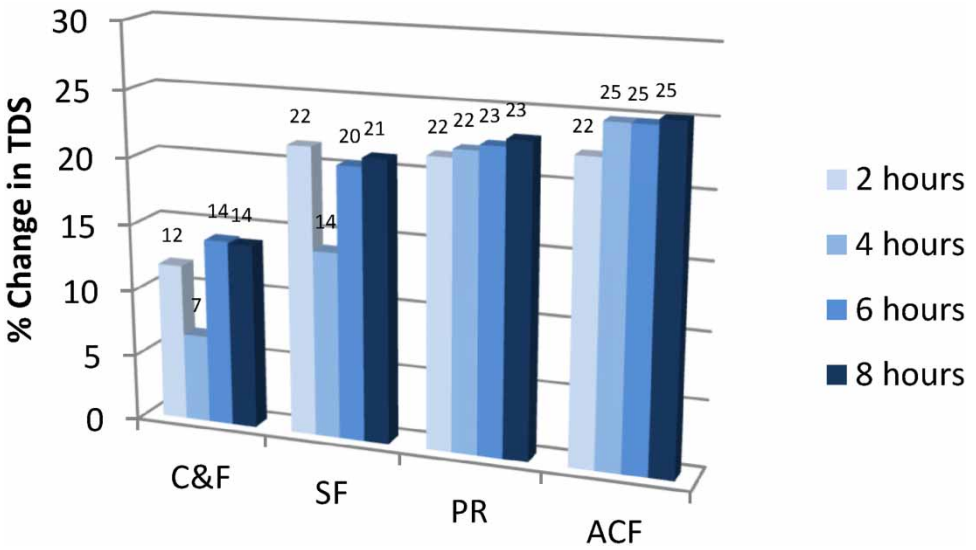

Figure 7 | Efficiency of each treatment unit in terms of wastewater TDS reduction for different retention periods.

of the suspended solids were removed during the filtration process. The SF was deliberately provided to reduce the suspended solids load in the PR which in turn might have hindered the solar radiation entering the reactor. TDS reduction efficiency was 22% after passing through a PR (Figure 7). TDS comprise organic and inorganic impurities. Since the proposed treatment methodology degrades the organic pollutant, the remaining inorganic pollutants (which were not degraded during the processes) could be the reason for lower TDS reduction efficiency.

The results show that the proposed PR-assisted treatment of the wastewater was highly efficient for the BOD and TSS removal. This shows that the proposed wastewater treatment methodology was efficient for the removal of organic pollutants (thereby a significant decrease in the BOD of the wastewater). The efficiency of the treatment plant was not very promising in terms of TDS removal. 25% TDS reduction was there after the wastewater was passed from PR.

CONCLUSION

Photocatalysis-based treatment of textile wastewater is a sustainable technique as it involves the usage of sunlight in the due process. The present study involved the treatment of wastewater generated by the nearby industries in the study area by fabricating a pilot treatment plant having a ZnO catalyst-based PR as one of its treatment units. The catalyst was fabricated on GI plates. Since the positive effects of photocatalysis on textile effluents have already been studied in various forms, in this study a rotating reactor was developed. The GI plates were attached to this reactor and wastewater was retained in them for a retention time of 2, 4, 6, and 8 h in different cycles. The quality of treatment was judged by the percentage change in the values of BOD, TSS, and TDS. The optimal retention time for the PR was found for which any further increase in retention time did not lead to a significant increase in the parameters removal efficiency. Accordingly, 4 h was considered as the retention time for the proposed ZnO-based reactor unit. At this optimal retention time, the BOD was reduced to 25 from 740 mg/l (97% reduction) and TSS was reduced from 1,430 to 12 mg/l (99% reduction). The results show that the pilot treatment plant is efficient for BOD (organic pollutants) and TSS removal of wastewater.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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