Journal of Water Process Engineering 56 (2023) 104302

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Techno-economic assessment of integrated photochemical AOPs for sustainable treatment of textile and dyeing wastewater

Nipun Bhargava [a,b], Nupur Bahadur [a,b,*], Arun Kansal [a]

[a] Coca- Cola Department Regional Water Studies, TERI School of Advanced Studies, 10 Institutional Area, Vasant Kunj, New Delhi 110 070, India
[b] NMCG - TERI Centre of Excellence(NTCoE), Environment and waste management division, The Energy and Resources Institute, Core 6C, India Habitat Centre, Lodhi Road, New Delhi 110 003, India

ARTICLE INFO

Keywords:
Advanced oxidation processes (AOPs)
Industrial wastewater
Pre-biological treatment
TADOX®
Zero liquid discharge

ABSTRACT

Textile and dyeing industries generate large quantities of wastewater rich in colourants, dyes, chemicals, surfactants, etc. Notably, textile effluents are highly coloured, toxic, odorous, and with high chemical oxygen demand (COD) and low biochemical oxygen demand (BOD). These colour-causing complex organic compounds in wastewater streams are not completely degraded or removed using conventional physicochemical and biological treatment processes. Although as per regulatory norms, COD, colour, and BOD need to be eliminated if the treated water is to be reused. A batch-scale study of photochemical Advanced Oxidation Processes (AOP) to treat textile wastewater from a common effluent treatment plant is aimed to improve biodegradability and downstream performance. The assessment compared the techno-economic feasibility of integrating four photochemical AOPs with existing biological treatment plant in terms of their efficiency, energy requirement, and overall cost of treatment. Photochemical AOPs considered in this study were UV photolysis, UV/H_2O_2, UV photo Fenton, and UV/TiO_2 photocatalysis. Although every treatment improved the quality of treated water, UV/TiO_2 photocatalysis was the most promising for removing COD and BOD and required the least electrical energy per order (10.79 kWh/m^3/order-COD removal and 5.16 kWh/m^3/order-colour removal) whereas UV/TiO_2 was the most economic (0.77 US dollar or INR 59.75/m^3).

1. Introduction

The textile industry, being particularly water intensive, now faces increasingly serious environmental challenges owing to scarcity of freshwater, stringent norms governing wastewater management, and industrial processes that release effluents rich in toxic chemicals including heavy metals. Non-compliance with regulations governing effluent treatment has adverse impacts on terrestrial and aquatic ecosystems and on human health [1]. Therefore, the industry needs to focus its attention on proper treatment of effluents. Conventional methods of treating wastewater, especially as practised in the micro-, small-, and medium-scale enterprises (MSMEs), involve excessive amounts of ferrous salts, lime, and alum as coagulants and flocculants followed by the traditional aerobic biological treatments. The mainstream treatment technologies – coagulation and flocculation, flotation, adsorption, and biological treatment [2–5] – along with a few advanced systems based on membranes or evaporation [6] may help in managing only a few of the contaminants in wastewater from textile and dyeing industry.

Thus, the traditional methods of treatment are inadequate in that they cannot handle volumetric shock loads of effluent and the heterogenous nature of incoming wastewater. Moreover, these methods need different coagulants to treat different effluents; are not particularly efficient in removing colour; and generate large quantities of sludge, thereby creating secondary pollution [1,6–9]. Besides, the oxidation mechanisms used in these traditional methods fail to degrade or detoxify extremely persistent hazardous substances [10–14].

Biological methods of treating wastewater have proved to be more popular and have been adopted on a commercial scale because they are simple in design, cost effective, and user friendly. These methods include the activated sludge process, extended aeration, a moving-bed biofilm reactor or fluidized bed reactor, membrane bioreactors, a sequential batch reactor, and a submerged aerated fixed film [1,6,15–17]. Such methods have been earlier worked on pilot scale and proven effective in treating effluent from textile units include sequential batch reactor [16],

* Corresponding author at: Environment and Waste Management Division, The Energy and Resources Institute (TERI), Darbari Lal Seth Complex, Core 6C, India Habitat Centre, Lodhi Road, New Delhi 110 003, India.
E-mail address: nupur.bahadur@teri.res.in (N. Bahadur).

https://doi.org/10.1016/j.jwpe.2023.104302
Received 13 May 2023; Received in revised form 7 September 2023; Accepted 13 September 2023
Available online 16 September 2023

anaerobic- fluidized bed reactor [18], and activated sludge process [19,20]. As the effluent from textile units contains complex dyes and other toxic compounds which inhibit the growth of microbes, hence biologically treated water is not free of dissolved organics and unsuitable for further processing [21–24]. Furthermore, these microbial-treatment-based methods are slow with around 12–24 h of average hydraulic retention time of treatment, require large area and generate huge volumes of toxic slurry [25,26], which raises secondary pollution concerns.

Given these shortcomings, advanced oxidation processes (AOPs) such as UV photolysis [27–29], UV photolysis of peroxide [30], UV photo Fenton [31–41], and UV photocatalysis [7,42–46] maybe beneficial. These processes produce highly oxidizing reactive hydroxyl radicals (OH·) that have a greater ability to destroy their targets and can oxidize and degrade organic compounds, rapidly and indiscriminately [13,29,47].

Therefore, combination of biological treatment system and AOPs has the potential to treat heterogenous effluents and improve the health of treatment plants, augment capacities and promote use of treated water. Many studies have explored the integrated approach using AOPs to treat even particularly challenging streams [8,20,43,48–80]. Some of the recent studies from India, have integrated Photocatalysis with conventional biological treatment for treating mixed sewage effluent containing oils, solvents causing COD, BOD with other Persistent Organic Pollutants (POPs) and Contaminants of Emerging concern (CEC). The results show a significantly improved treated water quality as compared to conventional treatment alone [81]. Similar improvement has been reported in a recent study of photocatalysis as a standalone approach for treating heterogenous polluted open drain [81,82].

It is against this background that the present paper attempts to resolve the fundamental inadequacies in conventional practices by integrating photochemical AOPs with downstream conventional biological treatment for treating effluent from textile and dyeing units. To the best of our knowledge, no single study has compared the degradation of COD, Colour, and other regulated parameters with a detailed techno-economic analysis for various AOPs. More specifically, we assessed four methods (all based on various photochemical AOPs), namely UV-assisted photolysis, UV photolysis of peroxide, UV photo Fenton, and UV photocatalysis, for their feasibility as a pre biological treatment technology in terms of (a) their efficiency in eliminating colour, COD, and BOD, (b) their ability to meet regulatory norms, (c) their capacity to make the treated water more biodegradable so as to make the process compatible with further biological treatment downstream, (d) electrical energy consumption, and (e) cost effectiveness. The results of this study will help governments, regulatory bodies, and industries that such integration can benefit old centralized effluent treatment plants (ETPs). This will help to meet the growing demand for water treatment in developing countries as their economies continue to grow.

2. Materials and methods

2.1. Site conditions and sample collection

A common effluent treatment plant (CETP) with a capacity to handle 1 million litres of wastewater a day (MLD) was chosen for the present study. The effluent came from multiple cotton, hosiery, and polyester dyeing units and was being treated and discharged onto nearby fields in the Ganga River basin catchment area of the state of Uttar Pradesh, India. The site houses 11 textile and dyeing units which collectively contribute to a 1.55 MLD (million litres per day) influent to the common effluent treatment plant wherein the trials of various photochemical AOPs have been done.

The existing treatment system starts with a screen chamber and collection sump followed by an equalization tank. The effluent is thereafter pumped at a controlled rate to a conventional primary treatment consisting of three flash mixer units, one each to add lime, ferrous salts, and alum, followed by adding polyaluminium chloride. Thereafter, effluent is sent to a tube settler, which separates the effluent into the supernatant and primary sludge. The primary sludge contains about 20 %–30 % water and is stored in drums of high-density polypropylene (HDPE) in a waste shed for eventual disposal at a landfill. The supernatant, on the other hand, is sent for further treatment to a biological treatment plant based on extended aeration. The biologically treated water is filtered through a multigrade filter and activated-carbon filtration system. The residue (the sludge that remains) from the biological treatment plant is stored in a holding tank and dewatered in a filter press system which feeds the filtered water back to the treatment plant. This dried sludge is sold as manure whereas the clear water from the carbon filtration unit is stored in a separate tank connected to a pipeline that directs the overflow to an irrigation canal.

In this study, equalization tank outlet was chosen as the ideal location for sampling to ensure homogeneity of the effluent characteristics. From here, the samples were drawn using a submerged pump into four polypropylene jars each with a capacity of 50 L. The jars were filled to the brim, sealed, and then transported within 16 h in an air-conditioned vehicle to TADOX® wastewater treatment plant in Gurugram, in the state of Haryana [7,9,17,43,83]. After taking the samples for laboratory studies, the samples were immediately refrigerated at 4 °C to avoid any degradation of organic pollutants. A portion of these samples was sent to an accredited testing laboratory to assess the quality of wastewater in terms of the norms laid down by the regulatory authority in India for textile and dyeing units.

2.2. Treatment of samples subjected to photochemical advanced oxidation processes

For any treatment involving ultraviolet (UV) radiation to be effective, it is essential to remove any colloidal and suspended particles from the liquid to be treated. The particles were removed through coagulation and flocculation: once they had settled down following sedimentation, the supernatant was used for further investigation. For the study, the samples from the equalization tank were decanted in a 200 L tank fitted with a 0.5 HP AC motor to operate a steel agitator to mix the added coagulant and flocculants with water thoroughly for 30–45 min. After agitation, the mix was left undisturbed to allow the particles to settle, and the supernatant was used to carry out the rest of the studies. Full details of the coagulation and flocculation treatment are reported elsewhere [7,9]. The supernatant was stored in a 200 L polypropylene tank – the primary treatment tank – referred to as PT from now on. The four methods mentioned in Section 1 were tested, as described below. Complete information of the UV system employed for the studies has been earlier published elsewhere [7,9].

2.2.1. Ultraviolet-assisted photolysis

Ultraviolet-assisted photolysis for the experiment to test UV photolysis as an AOP, 10 L water from the PT was stored in a 10 L polypropylene beaker and connected to a submersible DC pump capable of circulating the water into the patented UV system. The treatment in recirculation mode lasted 120 min. The treated water was stored in another 10 L beaker.

2.2.2. Ultraviolet photolysis of peroxide

Ultraviolet photolysis of peroxide to 10 L water from the PT was added 10 mL of 30 % H_2O_2, which gave a solution of 9.97 mM. The solution was stirred for 30 min and then subjected to 120 min of UV light.

2.2.3. Ultraviolet photo Fenton

Ultraviolet photo Fenton to another 10 L water from the PT were added 2.78 g of $FeSO_4.7H_2O$ and 10 mL of 30 % H_2O_2 (30 %), giving a solution of 1 mM $FeSO_4$ and 9.97 mM hydrogen peroxide. The solution was stirred for 60 min and then subjected to 120 min of UV irradiation;

this process allowed proper mixing of ferrous salts and to achieve equilibrium of Fenton reactions.

2.2.4. Ultraviolet photocatalysis

Ultraviolet photocatalysis the last set involved heterogenous semiconductor photocatalysis (PC) using nanoparticles of titanium and UV light. A simplified process flow diagram of the TERI advanced oxidation technology (TADOX) is shown in Fig. 1. Technical information and detailed methodology of the TADOX® Technology based pilot scale plant treating 100 L per day (LPD) and its operation has been published in another recent article. Details of plant operation, analysis of the wastewater quality parameters, computation of energy requirements and evaluation of the figures of merit has been already given in the earlier publication of this series of case studies [9,17,43,84–88]. It involves UV-TiO_2 Photocatalysis as the secondary treatment followed by nanomaterial recovery at source. Such a photocatalytic treatment has been established to be useful in Dye intermediates, Basic organics, Dye molecules, Synthetic textile effluent, Real textile and dyeing wastewater treatment systems and has been successful in eliminating need of biological treatment at any stage [17,42,43,83,84,86–94].

During the TADOX® treatment, the treated water was transferred via a built-and-developed mechanism equipped with suitable membrane filters to remove the spent nanoparticles. Clean water was thus obtained, and the used nano catalyst recovered. For other three processes illustrated earlier, there was no need for separation of nano catalysts. Hence, to explore whether the nano catalyst from TADOX® can be reused for treating the next batch, all reject material from the nanomaterials recovery unit was stored in a reject-collection tank. Reject water from this tank was oven-dried repeatedly and regenerated after adequate washing and air drying to remove inorganic salts. To ascertain any loss in crystallinity or other properties after one cycle of TADOX treatment, crystallographic analysis was carried out using a Bruker D-8 Advanced X-ray Diffractometer with a CuKα wavelength of 1.54059 Å and 2θ scanning between 20° to 70° of fresh and reused TiO_2 particles [95,96]. These recovered nanomaterials were then reused for photocatalytic treatment in place of fresh nanomaterials as above.

2.3. Analysis of wastewater quality

Water quality parameters of all the samples were analysed at a laboratory accredited by the National Accreditation Board for Testing and Calibration Laboratories, India, in accordance with ISO/IEC 17025:2017 using the prescribed methods [97]. Such physicochemical parameters as pH, electrical conductivity, and total dissolved solids (TDS) were determined using a Pocket Pro+ Multi 2 tester (Hach Company, Loveland, Colorado). A spectrophotometer (DR6000, also by Hach) was used for recording the UV–Vis spectra. All samples were tested in triplicate. The mean values are reported here, and the coefficient of variation was 8 %–20 %.

2.4. Estimation of figures of merit

Energy efficiency is compared in terms of electrical energy per order of magnitude of removal (E_{EO}) in the photocatalytic method used in TADOX: E_{EO} was introduced as a figure of merit by IUPAC and is defined as electrical energy units in kilowatt hours (kWh) essential for breaking down any pollutant C by an order of magnitude in a unit volume (1 m^3) [96,98]. As seen in Eqs. (1) and (2), respectively, E_{EO} was computed with respect to order of removal of COD and colour unit (CU). This parameter is critical in estimating the overall cost of treatment and for upscaling AOP to field applications. The similar approach has been earlier applied in previous publications by the authors [9].

$$E_{EO,COD} = \frac{Pt1000}{Vlog\left(COD_i/COD_f\right)} \tag{1}$$

$$E_{EO,CU} = \frac{Pt1000}{Vlog\left(CU_i/CU_f\right)} \tag{2}$$

where P is the electrical power consumption (in kWh), t denotes the time of treatment in hours, and V is the volume of wastewater treated; COD_i, COD_f, CU_i, and CU_f denote the initial and final COD (mg/L) and colour unit values in Pt—Co units of the water sample, as expressed earlier.

2.5. Estimation of overall cost of integration

The overall cost of the treatment was estimated by adding up all the key expenses in wastewater treatment, namely electrical energy consumption and the cost of chemicals and catalysts. Electrical energy consumed includes that used for all relevant operations including mixing, aeration, UV irradiation, and nanomaterial recovery for an end-to-end treatment. Similarly, it incorporates cost of consumption of all chemicals such as coagulants, flocculants, and nano catalysts. Full details of the method of calculating the cost have been published by our group elsewhere [9].

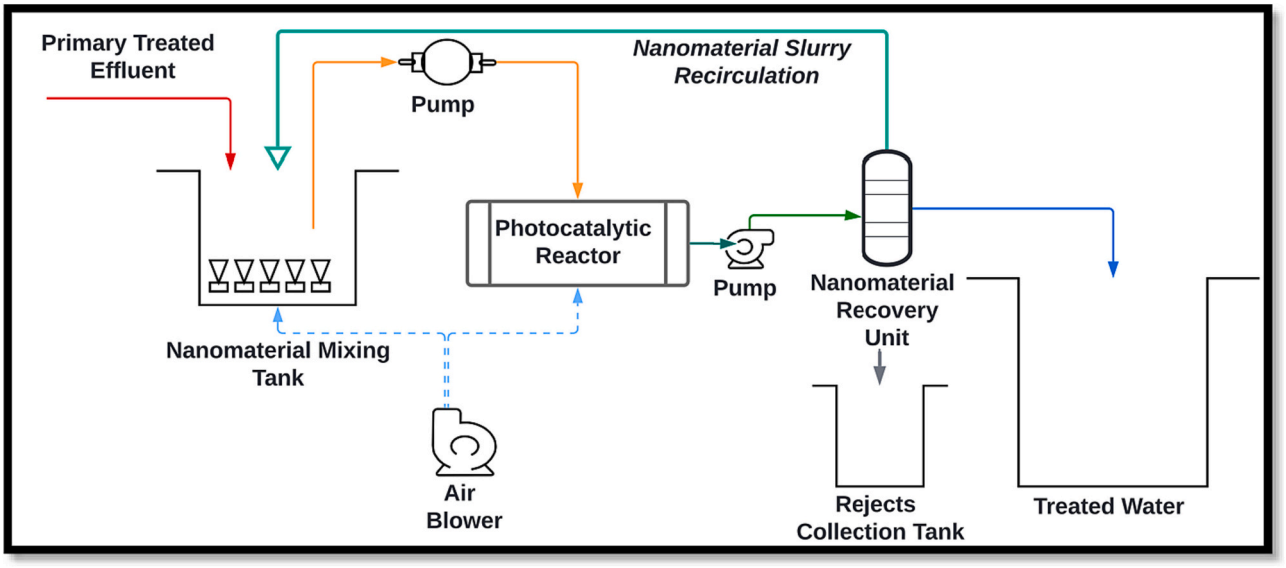

Fig. 1. Flow diagram of the heterogenous photocatalysis system based on TERI advanced oxidation technology (TADOX®) [7,9].

3. Results and discussion

3.1. Appearance of treated water

Raw effluent was treated using different methods, and Fig. 2 shows photos of raw effluent and of its samples after each of the four treatments.

It is evident from Fig. 3 that the UV–Vis spectra of all AOP-treated water samples are substantially different from those of the raw (untreated) sample, indicating that all the four AOPs were effective in removing organic matter and colour from wastewater; Fig. 3 also shows that the UV Vis spectra of primary-treated water (PT) were markedly lower than those of raw water (R), which shows that the primary treatment is effective to some extent in removing suspended solids and colour. It is clearly seen from Fig. 2 that water subjected to any of the four AOPs appears markedly different, and that water subjected to the UV photocatalysis treatment is aesthetically the most pleasing.

Water subjected to UV photolysis is darker than that subjected to PT and, to some extent, to photo Fenton, whereas water subjected to UV photolysis of peroxide and UV photocatalysis is clearer than that subjected only to PT. The UV–Vis spectra also show clearly that the absorbance between 250 nm and 300 nm is the lowest in the case of UV photolysis of peroxide and UV photocatalysis, the two processes most effective in removing colour. Therefore, based on the appearance of the treated water (Fig. 2) and on UV–Vis spectra (Fig. 3), UV photolysis of peroxide and UV photocatalysis seem the most promising for removal of colour or further downstream biological treatment system. The absorbance in the 250–300 nm range suggests the presence of organic contaminants, UV-absorbable organic compounds, and oxidizable and non-oxidizable organic compounds typically represented as total organic carbon (TOC) in these samples [99]. The lower absorbance in all AOPs around 280 nm and the flattening of the peak in the case of UV photocatalysis supports the inference that the greater transparency of the treated water was mainly due to removal of organic compounds or TOC.

3.2. Physicochemical characteristics and removal of organic pollutants

Table 1 gives the physical, chemical, and organic parameters of the raw effluent, primary-treated effluent, and effluent treated with each of the four AOPs. The parameters are also compared with the norms laid down by the Central Pollution Control Board (CPCB), Government of India. Although such treated water is not meant to be discharged directly after either PT or after treatment using any of the four methods, the extent and the efficiency of the treatments compared to the CPCB standards show the advantages and disadvantages of integrating such treatments with the conventional biological treatment downstream.

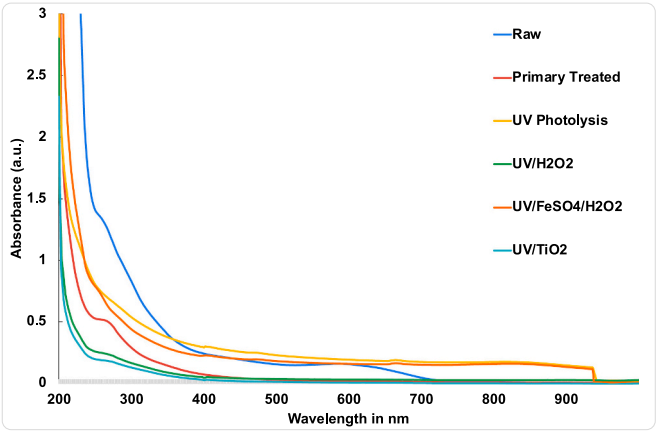

Fig. 3. UV Vis spectra of raw (untreated) sample (R), primary-treated water (PT), four photochemical AOP treatments.

3.2.1. Physical parameters

In terms of pH, all the AOPs except UV photolysis produced water that met the CPCB norms. For removing total dissolved solids (TDS), UV/TiO_2 proved the most effective, followed, in that order, by UV/H_2O_2, UV Fenton, and UV photocatalysis; this is because adding H_2O_2 increased the content of TDS significantly. In terms of total soluble solids (TSS), however, only UV/TiO_2 met the norms. Water treated using UV/TiO_2 meets the norms, with respect to physical characteristics for feeding to the downstream biological treatment downstream.

3.2.2. Organic parameters and organic compounds

This section compares the treatments in terms of several organic parameters such as colour, BOD, COD (Fig. 4), and oil and grease content. Although PT is effective to some extent in removing colour (Table 1), it takes the AOPs, especially UV/TiO_2 and UV/H_2O_2, for photo-oxidative degradation of pollutants resulting in clearer water that meets the norms.

For removing COD and BOD, UV Fenton and UV/H_2O_2, respectively, proved the most efficient. It is noteworthy that UV/TiO_2 in fact

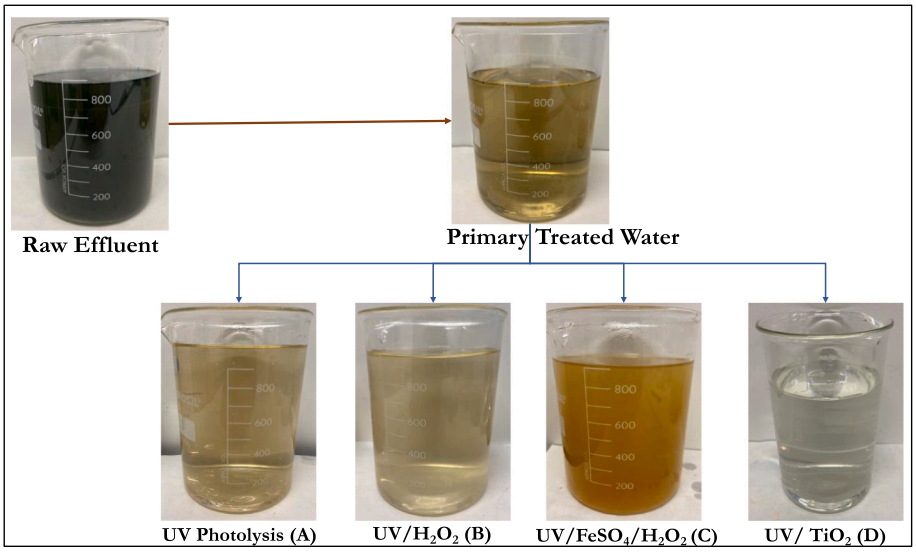

Fig. 2. Untreated Raw effluent, Primary treated water and treated after each of the four treatments, all based on advanced oxidation processes.

Table 1
Physicochemical parameters of raw (untreated) effluent from textile units, primary-treated effluent, and primary-treated effluent further subjected to each of four advanced oxidation processes (AOPs).

Parameter	Unit	Mean values (CV%)						Standards notified By CPCB for treated effluents from integrated textile units
		Raw effluent	Effluent after primary treatment	Primary-treated effluent subjected to UV photolysis	Primary-treated effluent subjected to UV/H_2O_2	Primary-treated effluent subjected to UV/$FeSO_4$/H_2O_2	Primary-treated effluent subjected to UV/TiO_2	
pH	–	7.8 (1.1)	**9.2 (1.3)**	**8.6 (1.4)**	7.8 (0.89)	8.1 (1.4)	7.6 (1.9)	6.5–8.5
Conductivity[a]	μS	7386.0 (4.4)	4042.0 (4.1)	4407.0 (5.2)	3941.0 (4.7)	5287.0 (4.5)	2471.0 (2.3)	–
Total dissolved solids	mg/L	**3685.0 (5.5)**	2011.0 (5.7)	2017.0 (8.6)	**2666.0 (9.1)**	**2686.0 (7.6)**	1944.0 (5.7)	2100.0
Total suspended solids	mg/L	**1214.0 (7.8)**	**204.0 (11.1)**	**191.0 (12.1)**	**131.0 (14.3)**	**102.0 (12.1)**	21.0 (11.5)	100.0
Colour	Pt-Co units	**656.0 (1.3)**	**305.0 (0.7)**	**303.7 (1.2)**	79.0 (2.3)	**156.7 (2.5)**	45.0 (4.8)	150.0
Oil and grease	mg/L	**124.3 (12.4)**	**118.3 (11.2)**	**117.2 (13.4)**	**40.5 (14.3)**	1.3 (11.3)	3.2 (12.3)	10.0
Total chromium	mg/L	0.5 (1.9)	0.4 (1.2)	0.4 (1.3)	0.2 (1.6)	0.2 (1.4)	0.2 (1.2)	1.0
Sulphide	mg/L	**3.4 (8.1)**	**3.3 (9.0)**	**3.1 (8.2)**	ND	ND	ND	2.0
Phenolic compounds	mg/L	ND	ND	ND	ND	ND	ND	1.0
Sodium absorption ratio (SAR)		**365.0**	**315.8**	**378.6**	**570.8**	**423.6**	**110.3**	26.0
Total Kjeldahl nitrogen[a,b]	mg/L	11.2 (9.1)	10.5 (12.3)	3.1 (4.5)	5.6 (7.8)	1.9 (12.1)	1.5 (10.9)	50
Biological oxygen demand (BOD)	mg/L	**105.8 (15.1)**	**84.5 (19.1)**	**103.7 (10.1)**	**55.0 (19.4)**	**103.1 (17.5)**	**166.1 (15.1)**	30.0
Chemical oxygen demand (COD)	mg/L	**720.0 (8.5)**	**650.0 (8.3)**	**290.5 (7.7)**	160.0 (8.1)	144.0 (10.2)	200.0 (9.3)	250.0
BOD: COD ratio[a]	–	0.1	0.1	0.4	0.3	0.7	0.8	–
Nitrate[a]	mg/L	42.3 (2.3)	7.3 (1.9)	6.5 (2.5)	6.3 (3.4)	6.0 (4.1)	11.4 (2.3)	–
Nitrite[a]	mg/L	10.3 (1.1)	0.3 (3.2)	0.1 (4.5)	0.1 (4.2)	0.1 (4.1)	4.0 (3.4)	–
Chloride[a]	mg/L	1595.3 (5.1)	1302.4 (3.2)	957.2 (10.2)	850.8 (2.1)	1169.9 (7.1)	283.6 (8.1)	–
Phosphate[a]	mg/L	0.9 (9.2)	0.1 (9.0)	0.1 (8.9)	0.2 (11.3)	0.1 (7.8)	0.1 (8.4)	–
Total hardness[a]	mg/L	520.0 (8.1)	420.0 (6.4)	140.0 (9.4)	80.0 (17.3)	200.0 (12.5)	360.0 (11)	–
Calcium[a]	mg/L	112.0 (8.8)	52.0 (7.2)	28.8 (14.3)	14.4 (16.2)	40.0 (8.9)	49.6 (7.2)	–
Magnesium[a]	mg/L	58.3 (8.2)	18.1 (7.0)	16.5 (12.3)	10.7 (16.9)	24.3 (11.2)	57.4 (9.8)	–
Sodium[a]	mg/L	1684.0 (0.8)	935.0 (1.1)	901.0 (0.98)	1011.0 (1.3)	1201.0 (0.6)	403.4 (0.7)	–
Iron[a]	mg/L	7.2 (6.1)	6.5 (3.2)	4.6 (2.3)	5.6 (7.2)	10.1 (3.1)	1.3 (4.5)	–
Sulphate[a]	mg/L	201.3 (2.3)	10.1 (12.4)	15.6 (8.3)	20.3 (3.5)	10.82 (5.1)	3.4 (8.1)	

Notes: Numbers in bold indicate values greater than the permissible limits stipulated by India's Central Pollution Control Board.
Experiments were conducted in triplicate and above are the mean values and the relative standard deviation (RSD) computed is less than 10 % in reported values.
[a] Standard not notified by the regulator for textile sector.
[b] Ammonical nitrogen has been notified in the prescribed standard.

increased BOD, an observation related to the treatment of wastewater reported by several earlier studies [7,8,17]. The increase in BOD is possibly because the treatment converts some residual or recalcitrant organics to biodegradable components, thereby making the biological treatment downstream more effective [6]. This explanation is supported by the observation that the UV/TiO_2 treatment shows highest biodegradability of the treated water [8]. The integrated approach – using one of the AOPs together with biological treatment – was evaluated by Gil-Pavas et al. (2020), who showed that using PC and electro Fenton in conjunction with biological treatment systems produced high-quality treated water that met the norms prescribed for reuse [100,101].

It is also noteworthy that a great deal of variation in residual BOD was observed in the case of these AOPs. This variation could be attributed to the generation of hydroxyl ions and other reactive oxygen species (ROS) [102], which have their own oxidative potential and kinetics of reaction, thereby differentiating the reaction pathway of the oxidative degradation of dyestuff present in the raw effluent. Another important observation is that UV photolysis lowered COD significantly but had no effect on BOD: it is possible that whereas UV can degrade some of the light-sensitive dyestuff directly, UV alone cannot degrade other compounds in wastewater such as organic constituents of dye baths including oils and solvents. UV/H_2O_2 was more effective than UV photolysis was in degrading such substances because adding H_2O_2 resulted in higher rate of generation of ROS; these oxidative species lead to oxidative cleavage of molecules and, in turn, to removal of COD. Similar reactions are also expected in the photo Fenton treatment: in this reaction, the presence of iron salts catalyses the reaction and makes the treatment more effective in terms of oxidative potential and generation of ROS. However, the side reactions and the presence of iron salts in treated water and the resultant dark colour make the photo Fenton treatment unsuitable for treating water for reuse in textile units. Photocatalysis showed the highest BOD:COD ratio with minimal residual colour and lowest residual ions, which makes the process the most suitable among the AOPs for treating wastewater from textile units and for integrating the process with the existing conventional systems, a recommendation supported by our earlier studies [43].

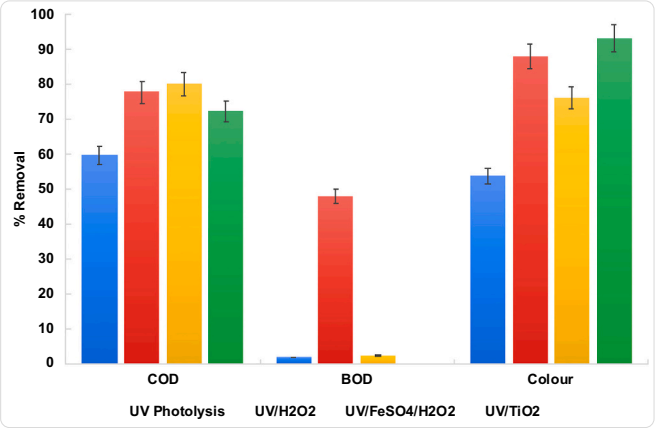

Fig. 4. Comparison of COD, BOD and Colour removal by various photochemical AOPs.
Note: UV/TiO_2 treatment, instead of lowering BOD level, *increased* it instead.

In summary, the data shows that UV photolysis removed 59.72 % of COD and had no significant effect on BOD. However, it also increased the colour from 656 to 903.7 units, likely due to the presence of UV-sensitive dye components in the sample. Treatment C (photo-Fenton) removed 76.1 % of colour and 80 % of COD, but it also increased the residual Fe content by 40 %, which could reduce the reusability of the treated water. Photolysis of H_2O_2) showed similar COD, BOD, and colour removal as photo-Fenton, but it had better colour removal. The colour was degraded to an overall PCU removal of 88 %, which is higher than treatment photo-Fenton. This is likely because photo-Fenton is a powerful oxidative reaction, but the requirement of ferrous salts as a catalyst result in discolouring the treated water and reducing its reusability. The poor removal of colour and increase in Fe content in treated water are the main reasons why photo-Fenton has not been widely adopted in the textile wastewater treatment sector. Photolysis of H_2O_2, on the other hand, has the drawback that the residual colour in the treated water is still higher than the desired levels of 50 PCU.

In terms of removing oil and grease (suspended and emulsified), their content in the water from primary treated water was less than that in raw, or untreated, effluent owing to the high adsorptive capacity of alkali earth metal oxide coagulants used in the primary treatment [5]. However, even after primary treatment, the treated water contained significant amounts of oil and grease. These emulsified oils cannot be removed using physical processes or chemical coagulation—only AOPs can degrade such long-chain saturated or unsaturated oils. All the AOPs were able to lower the oil and grease content (Table 1); their removal efficiencies are consistent with the kinetics of hydroxyl ions generation of each AOP [3,4]. UV photolysis and UV/H_2O_2 had little effect on oils and grease whereas photo Fenton and UV photocatalysis were far more effective in removing oils and grease, probably because of hydroxyl radicals and ROS produced in both the treatments, which show higher kinetics of ROS generation and higher oxidative potential than do other photochemical AOPs [3,29,47,103]. Streams containing emulsified oils are particularly amenable to being treated with sophisticated AOPs: simple AOPs may not be as effective with such streams. Moreover, the reduction in oil content and the increase in BOD in treated water also indicate that the long-chain saturated or unsaturated alkanes or polyols or di-ols are converted into simpler compounds, which are easily biodegradable. This difference is probably the main reason for the high BOD:COD ratio (biodegradability) seen in the case of treatments involving photo Fenton and UV photocatalysis; we have already reported such degradation of oils into smaller compounds [7–9]. Effective degradation of oil and grease makes the downstream biological treatment more effective, and water obtained following such treatment is safe enough for reuse in dye bath or washing processes during dyeing or textile production. Such water is also safe enough to be discharged into surface water bodies provided it meets the CPCB norms for discharge into surface water [104].

3.2.3. *Inorganic parameters*

All the four AOPs removed sulphides in significant quantities, which is directly attributable to the oxygen requirements of sulphides and the fact that the hydroxyl radicals oxidized this sulphide to sulphates—the sulphides in the effluent thus worked as scavenging ions for the AOPs. This inference was confirmed from the fact that the weaker AOPs, namely UV photolysis and UV/H_2O_2, resulted in lesser removal in sulphides possibly because the two processes did not generate enough radicals to serve as scavengers. On the other hand, the stronger AOPs, namely photo Fenton and photocatalysis, removed all the sulphides, possibly because these two processes generated significant quantities of ROS, resulting in the oxidation of even those sulphides, oils, etc. that were not the primary targets of the reaction.

None of the AOPs was effective in removing significant quantities of other inorganic compounds such as calcium and magnesium and, in turn, total hardness. This inability lies in the very nature of AOP-based treatment: the ROS mainly target oxidizable compounds in water. It is important to note that even after any of the treatments, the residual levels of sodium, calcium, and magnesium levels result in a higher sodium absorption ratio (SAR), which is a regulated parameter for the textile and dyeing industry. The higher SAR value after the treatment shows the inability of the AOPs to degrade inorganic pollutants and related contamination [102]. If this treated water with high SAR is discharged onto land or used for irrigation, the soil will turn sodic (excessively rich in sodium) and unfit for cultivation [105].

3.3. *Reusability of catalysts*

To understand the economics of the treatment, the cost of replacement of catalysts needs to be computed for all the AOPs. However, UV/H_2O_2, UV/$FeSO_4$, or UV H_2O_2 involve no catalyst, eliminating the matter of its reusability; only UV/TiO_2 generates spent nanomaterials: to assess its economic viability, we need to evaluate its operational expenses in terms of the consumption and regeneration of the nanomaterial and the reuse and replacement needs [9].

The reusability potential of titanium nanoparticles has been evaluated in two ways, namely by evaluating the characteristics of used nanomaterials using X-ray diffraction studies or by evaluating the associated changes in treatment efficiency following one-time reuse of the spent nanomaterials. The differences between the X-ray diffraction (XRD) spectra of titanium nanoparticles used only once and those reused are shown in Fig. 5.

The markedly sharp and intense peaks seen in Fig. 5 depicting crystalline TiO_2 nanoparticles used only once or reused confirm that the catalyst TiO_2 remains intact. Both kinds of samples show the occurrence of the anatase phase of titanium, as verified by the International Centre for Diffraction Data File No. 21–1486. The marginal and insignificant peaks observed in the reused sample could be due to surface moisture in the material, the moisture probably originating in washing the spent nanoparticles after their first photocatalytic reaction and before their reuse for the next cycle; moreover, the catalyst was neither heated nor annealed prior to regeneration [9,88]. This also explains the reduction in the intensity of peaks in the XRD spectra. Therefore, as no significant visible difference was seen either in the crystallinity or in the XRD pattern between the freshly used and the reused catalyst, it should be possible to reuse the nanomaterials for another batch of UV/TiO_2. This discussed in the next section.

3.4. *Appearance of treated water from fresh and reused titanium nanoparticles*

UV Vis spectra for photocatalysis treatment using fresh or reused

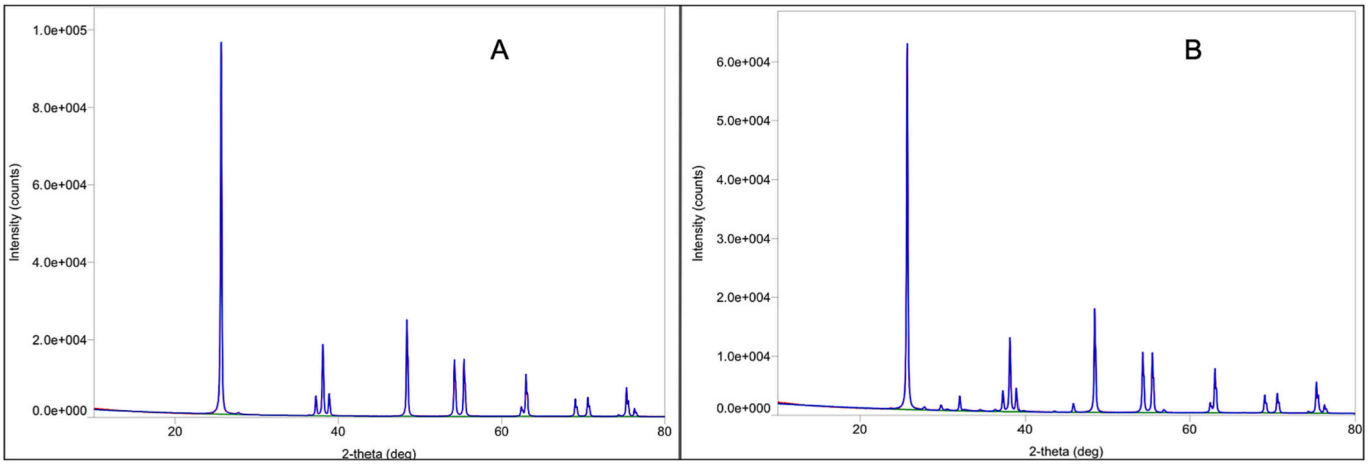

Fig. 5. X-ray diffraction spectra of titanium nanoparticles used only once (A) and those reused (B) as part of a UV/TiO_2 treatment following a primary treatment of effluent from textile units.

titanium along with those for raw (untreated) and primary-treated effluent are shown in Fig. 6.

The significantly lowered absorbance at 220–300 nm clearly indicates removal of UV-absorbable organics and other organic compounds in significant quantities, and that at 270–300 nm, of TOC [99]. Thus, photochemical oxidation using either fresh or reused catalyst followed a similar degradation pathway and reaction mechanism. This may be examined further through detailed characterization of quality parameters of wastewater and comparison with CPCB standards.

3.5. Quality of treated water resulting from reused catalyst

Table 2 shows the physical, organic, cationic, and anionic parameters of water obtained from UV photocatalysis treatments using reused titanium nanoparticles.

As can be seen from Table 2, treatment that deployed reused catalyst also resulted in water compliant with the norms of CPCB except in the case of BOD and SAR, the values of which exceeded the permissible limits (the reasons are explained earlier). It is important to note that the efficiency in terms of removing colour, COD, and BOD remained the same irrespective of whether the catalyst was fresh or reused, which indicates that the reused nanomaterials still had enough active sites on their surface capable of adsorbing organic contaminants and generating enough ROS through UV light activation to yield results comparable to those from fresh nanoparticles. Therefore, it could be concluded that this nanomaterial could be reused over several cycles [43].

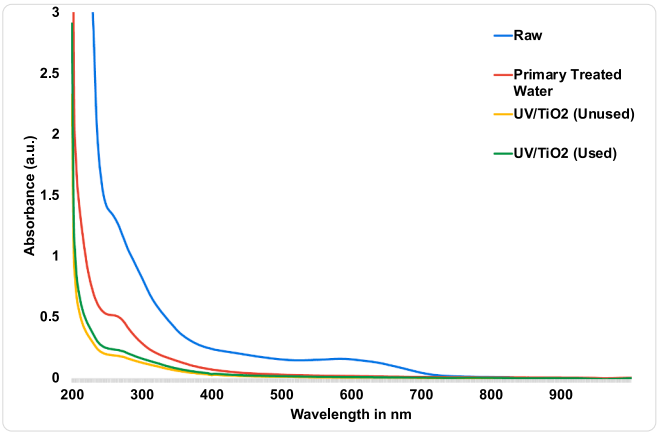

Fig. 6. UV Vis spectra for photocatalysis treatment using fresh (D1) or reused (D2) titanium along with those for raw (R, untreated) and primary-treated (PT) effluent from a textile unit.

3.6. Consumption of electrical energy

Whether a given AOP is suitable for large-scale deployment depends a great deal on its energy efficiency as measured in terms of energy consumption per unit volume of effluent treated; the lower the order of magnitude of the quantum of undesirable substances removed from the effluent (the E_{EO} value), the higher the direct energy consumption, leading to higher cost of the treatment and greater capital expenditure in terms of the design of the UV reactor and hydraulic residence time of the treatment [7,8,17]. Table 3 shows the estimated E_{EO} to lower the COD for each of the four treatments.

Of the four AOPs, energy value was the highest for photocatalysis, followed, in that order, by photolysis of peroxide and photo Fenton. These values are much lower than the values in literature for the $E_{EO,\ COD}$, 1–100 kWh/m^3 being regarded as efficient [2,7]. Moreover, the estimated values are better than those reported recently by Khorram et al., who estimated the $E_{EO,\ COD}$ to be 178.61 kWh/m^3 in treating a similar effluent using UV/TiO_2 [106]. Even compared to the values from some recent work by our research group (98.5–161 kWh/m^3), the values shown in Table 3 are much lower irrespective of the process. These lower $E_{EO,\ COD}$ values were due to the efficient design of the UV reactor, optimized arrangement of the UV lamp, and specialized low-energy lamps.

It is noteworthy that photocatalysis consumed maximum energy whereas photo Fenton was far more energy efficient. However, it is important to note that the aim of any AOP is not merely to remove COD but also to improve the appearance of treated water and to make the treated effluent more easily biodegradable. This is why Table 4 relates the E_{EO} to colour removal.

As can be seen from Table 4, the $E_{EO,\ CU}$ value for photocatalysis is much lower than that for photo Fenton whereas the opposite trend is seen in the case of $E_{EO,\ COD}$. This is because photocatalysis was better not only in eliminating colour and COD but also improved BOD of the final treated water; photo Fenton, on the other hand, could only remove COD and increased the biodegradability—with little impact on colour, although the degree of transparency is a crucial determinant of the suitability and feasibility of any AOP. To the best of our knowledge, such $E_{EO,\ CU}$ values, shown in the Table 4, have not been reported so far in any research on a variety of photochemical AOPs.

3.7. Operational expenses

To determine the economic feasibility of any of the four AOP-based

Table 2
Physicochemical parameters of primary-treated effluent and primary-treated effluent further subjected to an advanced oxidation process involving fresh or reused TiO_2.

Parameter	Unit	Primary-treated[a] (PT)	UV/TiO_2 (fresh TiO_2)	UV/TiO_2 (reused TiO_2)	Standards notified By CPCB for treated effluents from integrated textile units [51]
pH	–	**9.2 (1.3)**	7.6 (1.9)	7.8 (1.7)	6.5–8.5
Conductivity	mS	4042.0 (4.1)	2471.0 (2.3)	2971.0 (4.2)	–
Total dissolved solids	mg/L	2011.0 (5.7)	1944.0 (5.7)	2001.0 (4.2)	2100.0
Total suspended solids	mg/L	**204.0 (11.1)**	21.0 (11.5)	23.0 (12.1)	100.0
Colour	Pt-Co units	**305.0 (0.7)**	45.0 (4.8)	46.0 (4.9)	150.0
Oil and grease	mg/L	**118.3 (11.2)**	3.2 (12.3)	3.5 (14.2)	10.0
Total chromium	mg/L	0.4 (1.2)	0.2 (1.2)	0.2 (2.0)	1.0
Sulphide	mg/L	**3.3 (9.0)**	Not detected (ND)	ND	2.0
Phenolic compounds	mg/L	ND	ND	ND	1.0
Sodium absorption ratio		**315.8**	**110.3**	**175.3**	26.0
Total Kjeldahl nitrogen	mg/L	10.5 (12.3)	1.5 (10.9)	1.7 (9.1)	50[b]
Biological oxygen demand	mg/L	**84.5 (19.1)**	**166.1 (15.1)**	**109.1 (18.2)**	30.0
Chemical oxygen demand	mg/L	**650.0 (8.3)**	200.0 (9.3)	204.0 (10.1)	250.0
BOD: COD ratio[b]	–	0.1	0.8	0.5	–
Nitrate[b]	mg/L	7.3 (1.9)	11.4 (2.3)	17.4 (5.2)	–
Nitrite[b]	mg/L	0.3 (3.2)	4.0 (3.4)	0.7 (3.7)	–
Chloride[b]	mg/L	1302.4 (3.2)	283.6 (8.1)	567.2 (10.2)	–
Phosphate[b]	mg/L	0.1 (9.0)	0.1 (8.4)	0.02 (12.1)	–
Total hardness[b]	mg/L	420.0 (6.4)	360.0 (11)	200.0 (10.7)	–
Calcium[b]	mg/L	52.0 (7.2)	49.6 (7.2)	36.8 (7.8)	–
Magnesium[b]	mg/L	18.1 (7.0)	57.4 (9.8)	26.2 (11.2)	–
Sodium[b]	mg/L	935.0 (1.1)	403.4 (0.7)	492.0 (0.9)	–
Iron[b]	mg/L	6.5 (3.2)	1.3 (4.5)	1.3 (4.7)	–
Sulphate[b]	mg/L	10.1 (12.4)	3.4 (8.1)	3.6 (8.1)	

Note: Numbers in bold indicate values greater than the permissible limits stipulated by India's Central Pollution Control Board; values in parenthesis show the coefficient of variation (%).

[a] Includes conventional coagulation flocculation at the common effluent treatment plant.

[b] Standards not notified by regulator for textile sector.

systems, the overall cost of each is presented in Table 5.

Photolysis of H_2O_2 and photo Fenton were the most expensive, the cost of treating 1000 L of pre-treated water being INR 126 and INR 155, respectively, whereas UV/TiO_2 was the most cost effective, at INR 59.75 ($0.8), a figure that compares favourably to that by GilPavas et al. (2020), who estimated the cost of treating 1000 L of effluent from textile units, using electrocoagulation and photo Fenton, at $2.3/$m^3$

Table 3
Computation of estimated E_{EO} to lower chemical oxygen demand by integrating four advanced oxidation processes with the conventional treatment system in treating effluent from textile units.

Treatment parameter	Unit	UV/ Photolysis	UV/ H_2O_2	UV/ $FeSO_4$/ H_2O_2	UV/ TiO_2
Overall lamp requirement	Watts	30	30	30	30
Duration	Hours	2	2	2	2
Electrical energy consumed	kWh/L per batch	0.06	0.06	0.06	0.06
Volume of water treated	L per batch	10	10	10	10
Electrical energy consumed per unit volume treated	kWh/m^3	6	6	6	6
Ratio of initial and final chemical oxygen demand (Ci/Cf)	–	2.48	4.5	5	3.6
$E_{EO,\ COD}$	kWh/m^3/ order-COD	15.2	9.19	8.58	10.79

Table 4
Estimated electrical energy in terms of colour removal for four advanced oxidation processes to treat effluent from textile units.

Treatment parameter	Unit	UV photolysis	UV/ H_2O_2	UV/ $FeSO_4$/ H_2O_2	UV/ TiO_2
Overall lamp requirement	Watts	30	30	30	30
Duration	Hours	2	2	2	2
Electrical energy consumed	kWh//L per batch	0.06	0.06	0.06	0.06
Volume of water treated	L per batch	10	10	10	10
Electrical energy consumed per unit volume treated	kWh/m^3	6	6	6	6
Ratio of initial colour and final colour (CU_i/ CU_f)	–	2.16	8.3	4.19	14.58
$E_{EO,\ CU}$	kWh/m^3/ order colour	18	6.53	9.65	5.16

[100,101]. UV/TiO_2 proved cheaper in the present study because we reused titanium nanoparticles multiple times. The cost was also lower than that reported earlier by our research group ($1.55–$2.0/m^3) for a study that also assessed the UV/TiO_2 method but involved smaller textile dyeing units [7]. The cost estimated in the present study for proposed integration in cluster-level effluent treatment systems is in line with the requirements of such developing countries as India in which centralized treatment plants are not feasible given the scattered distribution of units with significant adverse impacts on the environment unless the effluent from such units is treated at the level of a cluster [8,107,108].

4. Conclusion

The study showed that effluent treatment based on AOPs alone presents tremendous potential in treating textile wastewater. Moreover, integration with the prevalent conventional biological treatment

Table 5
Computation of the overall cost of integrating each of the four advanced oxidation processes in treating effluent from textile units.

	Aspect	Unit	UV photolysis	UV/ H_2O_2	UV/ $FeSO_4$/ H_2O_2	UV/ TiO_2
A1	Total electrical power (P)	Watts	30.00	30.00	30.00	30.00
A2	Duration (t)	Hours per batch	2.00	2.00	2.00	2.00
A3	Electrical energy consumed (P × t)	kWh per batch	0.06	0.06	0.06	0.06
A4	Cost per unit energy consumed (R)	INR per kWh	8.00	8.00	8.00	8.00
A	Cost of energy consumption (P × t × R)	INR per batch	0.48	0.48	0.48	0.48
B	Cost of chemicals	INR per batch	0.00	0.68	0.97	0.02
C	Cost of maintenance	INR per batch	0.10	0.10	0.10	0.10
D	Overall cost of treatment per batch (A + B + C)	INR per batch	0.58	1.26	1.55	0.60
E	Volume of water treated per batch	L	10.00	10.00	10.00	10.00
F	Cost of treatment in rupees (D/ E × 1000)	INR/ m^3	**58.00**	**126.00**	**155.00**	**59.75**
G	Cost of treatment in US dollars ($1 = INR 79.83; June 2022)	$/$m^3$	0.75	1.62	2.00	0.77

systems may even be beneficial for meeting the compliances of the industry. It is evident from the characteristics of the raw effluent and primary treated effluent that biological treatment alone cannot meet to regulatory norms. Therefore, textile units should deploy further treatment for reuse of water for their internal processes instead of discharging it, directly or indirectly, into drainage or irrigation networks. Comparison of various photochemical AOPs shows that UV photolysis is not effective at removing colour, while photo-Fenton has the drawback of increasing the residual Fe content. Photolysis of H2O2 has better colour removal than Photo Fenton, but the residual colour is still higher than the desired levels. Treated water from Photocatalysis met the norms for colour removal. Hence, the best treatment among the four AOPs evaluated was UV/TiO_2 photocatalysis, which removed 80 % of COD and increased the BOD:COD ratio by 8 times compared to the conventional treatment plant. it consumed the least energy (10.79 kWh/m^3 per order COD and EEO, CU = 5.16 kWh/m^3 per order CU), which also made it the most cost effective (0.77 USD to treat 1000 L of effluent). It is also important to note that photocatalysis-based systems can be fully automated and can work in dual mode (the electricity can be from the grid or from solar panels)—the process is thus economical, widely applicable, and easily adaptable. Such studies shall benefit in achieving sustainable growth in the textile and dyeing industry and tremendous scope for future research studies. Further studies may include a field pilot plant of sufficient scale to operate in a continuous manner to accurately assess techno economic feasibility in terms of energy and chemical consumption.

CRediT authorship contribution statement

Nipun Bhargava Conceptualization, Methodology, Investigation, Formal Analysis, Writing: original draft.

Nupur Bahadur Conceptualization, Investigation, Writing: review and editing, Visualization, Resources, Project Administration and Funding Acquisition.

Arun Kansal Supervision, Writing: review and editing, Project Administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Authors gratefully acknowledge the support of Perfact Researchers Pvt. Ltd., New Delhi, New Delhi in collection, preservation, transportation, and analysis of all wastewater samples. National Mission for Clean Ganga (NMCG), Ministry of Jal Shakti, Government of India, is acknowledged for funding such studies on pollution abatement under the NMCG-TERI Centre of Excellence (CoE) on Water Reuse [Ref. No: Mi/31/2021-PMC-NMCG].

Funding

National Mission for Clean Ganga (NMCG), Ministry of Jal Shakti, Government of India, is acknowledged for funding such studies on pollution abatement under the NMCG-TERI Centre of Excellence (CoE) on Water Reuse [Ref. No: Mi/31/2021-PMC-NMCG].

References

[1] C.R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit, A critical review on textile wastewater treatments: possible approaches, J. Environ. Manag. 182 (2016) 351–366, https://doi.org/10.1016/j.jenvman.2016.07.090.
[2] D.B. Miklos, C. Remy, M. Jekel, K.G. Linden, J.E. Drewes, U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment – a critical review, Water Res. 139 (2018) 118–131, https://doi.org/10.1016/j.watres.2018.03.042.
[3] M.A. Oturan, N. Oturan, C. Lahitte, S. Trevin, Production of hydroxyl radicals by electrochemically assisted Fenton's reagent, J. Electroanal. Chem. 507 (2001) 96–102.
[4] M.A. Oturan, N. Oturan, C. Lahitte, S. Trevin, Production of hydroxyl radicals by electrochemically assisted Fenton's reagent, J. Electroanal. Chem. 507 (2001) 96–102, https://doi.org/10.1016/S0022-0728(01)00369-2.
[5] E. Brillas, I. Sirés, M.A. Oturan, I. Sire, M.A. Oturan, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton 's reaction chemistry, Chem. Rev. 109 (2009) 6570–6631, https://doi.org/10.1021/cr900136g.
[6] M. Mostafa, Waste water treatment in textile industries-the concept and current removal technologies, Mostafa 501 (2015) 501–525. http://www.innspub.net.
[7] N. Bahadur, N. Bhargava, Novel pilot scale photocatalytic treatment of textile & dyeing industry wastewater to achieve process water quality and enabling zero liquid discharge, J. Water Process Eng. 32 (2019), https://doi.org/10.1016/j.jwpe.2019.100934.
[8] N. Bahadur, N. Bhargava, TERI Advanced Oxidation Technology (TADOX®) to treat industrial wastewater with integration at pre-and post-biological stage: case studies from India, Water Pract Technol. 17 (2022), https://doi.org/10.2166/wpt.2022.065.
[9] N. Bahadur, P. Das, N. Bhargava, Improving energy efficiency and economic feasibility of photocatalytic treatment of synthetic and real textile wastewater using bagasse fly ash modified TiO2, Chem. Eng. J. Adv. 2 (2020), https://doi.org/10.1016/j.ceja.2020.100012.
[10] A. Al Mayyahi, H. Ali Abed Al-Asadi, Advanced Oxidation Processes (AOPs) for Wastewater Treatment and Reuse: A Brief Review, n.d. www.ajast.net.
[11] P. Mani, M. Madhusudanan, Zero Liquid Discharge Scheme in a Common Effluent Treatment Plant for Textile Industries in Tamilnadu, India, Nat. Environ. Pollut. Technol. 13 (2014) 769–774.
[12] S. Ullah, M. Noman, M. Siddique, K. Sahak, K. Saba Ali, F. Khan, Treatment of Industrial Wastewater (IWW) and Reuse through Advanced Oxidation Processes (AOPs): a comprehensive overview a comprehensive overview of climate change

impacts on water resources, a global perspective view project treatment of industrial wastewater (IWW) and reuse through Advanced Oxidation Processes (AOPs): a comprehensive overview, IOSR J. Environ. Sci., Toxicol. Food Technol. 15 (2021) 4–14. doi:https://doi.org/10.9790/2402-1501010414.
[13] Yadav, Advanced techniques for wastewater treatment: a review, Open Access J. Waste Manag. Xenobiot. 2 (2019) 1–11.
[14] C. Gadipelly, A. Pérez-González, G.D. Yadav, I. Ortiz, R. Ibáñez, V.K. Rathod, K. V. Marathe, Pharmaceutical industry wastewater: review of the technologies for water treatment and reuse, Ind. Eng. Chem. Res. 53 (2014) 11571–11592, https://doi.org/10.1021/ie501210j.
[15] T. Adane, A.T. Adugna, E. Alemayehu, Textile industry effluent treatment techniques, J. Chem. 2021 (2021), https://doi.org/10.1155/2021/5314404.
[16] P. Pattnaik, G.S. Dangayach, A.K. Bhardwaj, A review on the sustainability of textile industries wastewater with and without treatment methodologies, Rev. Environ. Health 33 (2018) 163–203.
[17] N. Bahadur, TERI Advanced Oxidation Technology (TADOX) to Treat Textile and Dyeing Wastewater, Achieve Zero Liquid Discharge, and Enhance Water Reuse: R&D-Based Policy Recommendations, the Energy and Resources Institute Policy Brief, 2021.
[18] S. Sen, G.N. Demirer, Anaerobic treatment of real textile wastewater with a fluidized bed reactor, Water Res. 37 (2003) 1868–1878.
[19] M. Gavrilescu, M. Macoveanu, Attached-growth process engineering in wastewater treatment, Bioprocess Biosyst. Eng. 23 (2000) 95–106.
[20] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination–a review, Sci. Total Environ. 409 (2011) 4141–4166.
[21] B. Sengupta, Advance Methods for Treatment of Textile Industry Effleunts, 2007.
[22] D.S. Kharat, Treatment of textile industry effluents: limitations and scope, J. Environ. Res. Dev. 9 (2015) 1210–11213.
[23] J.K. Vyas, For Challenges Against Implementation of ZLD in Textile Processing Industries and Clusters in India, 2016.
[24] S.H. Mehta, D.S. Vyas, S.M. Patel, H. Pamnani Arti, Mehta, Optimization of treatability by FACCO for treatment of chemical industry effluent, Int. J. Sci. Technol. Eng. 3 (2017) 328–336.
[25] S. Mani, R.N. Bharagava, Textile industry wastewater: environmental and health hazards and treatment approaches, in: Unknown, 2018.
[26] P. Mani, M. Madhusudanan, Zero liquid discharge scheme in a common effluent treatment plant for textile industries in Tamilnadu, India, Nat. Environ. Pollut. Technol. 13 (2014) 769–774.
[27] P.A. Soares, R. Souza, J. Soler, T.F.C.V. Silva, S.M.A.G.U. Souza, R.A. R. Boaventura, V.J.P. Vilar, Remediation of a synthetic textile wastewater from polyester-cotton dyeing combining biological and photochemical oxidation processes, Sep. Purif. Technol. (2017), https://doi.org/10.1016/j.seppur.2016.08.036.
[28] K. Paździor, L. Bilińska, S. Ledakowicz, A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment, Chem. Eng. J. 376 (2019) 120597.
[29] J. Wang, S. Wang, Reactive species in advanced oxidation processes: formation, identification and reaction mechanism, Chem. Eng. J. 401 (2020) 126158.
[30] J.J. Rueda-Marquez, I. Levchuk, P. Fernández Ibañez, M. Sillanpää, A critical review on application of photocatalysis for toxicity reduction of real wastewaters, J. Clean. Prod. 258 (2020) 120694.
[31] M.A. Sheikh, A. Kumar, M. Paliwal, R. Ameta, R.C. Khandelwal, Degradation of organic effluents containing wastewater by photo-Fenton oxidation process, Indian J. Chem., Sect. A: Inorg., Phys., Theor. Anal. Chem. 47 (2008) 1681–1684.
[32] E.S. Elmolla, M. Chaudhuri, Combined photo-Fenton–SBR process for antibiotic wastewater treatment, J. Hazard. Mater. 192 (2011) 1418–1426, https://doi.org/10.1016/j.jhazmat.2011.06.057.
[33] R.P. Cavalcante, L. da Rocha Sandim, D. Bogo, A.M.J. Barbosa, M.E. Osugi, M. Blanco, S.C. de Oliveira, M. de Fatima Cepa Matos, A. Machulek Jr., V. S. Ferreira, Application of Fenton, photo-Fenton, solar photo-Fenton, and UV/H2O2 to degradation of the antineoplastic agent mitoxantrone and toxicological evaluation, Environ. Sci. Pollut. Res. Int. 20 (2013) 2352–2361.
[34] P. Asaithambi, R. Saravanathamizhan, M. Matheswaran, Comparison of treatment and energy efficiency of advanced oxidation processes for the distillery wastewater, Int. J. Environ. Sci. Technol. 12 (2015) 2213–2220, https://doi.org/10.1007/s13762-014-0589-9.
[35] P. Asaithambi, D. Beyene, E. Alemayehu, Treatment of landfill leachate waste using sono (US) and photo (UV) based advanced oxidation processes: studies on various operating parameters, Desalin. Water Treat. 94 (2017) 147–155, https://doi.org/10.5004/dwt.2017.21583.
[36] P. Asaithambi, R. Saravanathamizhan, M. Matheswaran, Comparison of treatment and energy efficiency of advanced oxidation processes for the distillery wastewater, Int. J. Environ. Sci. Technol. 12 (2015) 2213–2220.
[37] P. Asaithambi, R. Saravanathamizhan, M. Matheswaran, Comparison of treatment and energy efficiency of advanced oxidation processes for the distillery wastewater, Int. J. Environ. Sci. Technol. 12 (2015) 2213–2220, https://doi.org/10.1007/s13762-014-0589-9.
[38] A. Arka, P. Asaithambi, S. Kebede Debela, Development of solar photo-fenton process for the removal of color, COD, and turbidity from institutional wastewater, J. Energy Environ. Chem. Eng. 7 (2022) 26, https://doi.org/10.11648/j.jeece.20220702.12.
[39] P. Asaithambi, B. Sajjadi, A.R.A. Aziz, Integrated ozone–photo–Fenton process for the removal of pollutant from industrial wastewater, Chin. J. Chem. Eng. 25 (2017) 516–522, https://doi.org/10.1016/J.CJCHE.2016.10.005.
[40] P. Asaithambi, E. Alemayehu, B. Sajjadi, A.R.A. Aziz, Electrical energy per order determination for the removal pollutant from industrial wastewater using UV/Fe2+/H2O2 process: optimization by response surface methodology, Water Resour Ind. 18 (2017) 17–32, https://doi.org/10.1016/j.wri.2017.06.002.
[41] P. Asaithambi, M.B. Yesuf, R. Govindarajan, N.M. Hariharan, P. Thangavelu, E. Alemayehu, A review of hybrid process development based on electrochemical and advanced oxidation processes for the treatment of industrial wastewater, Int. J. Chem. Eng. 2022 (2022), https://doi.org/10.1155/2022/1105376.
[42] N. Bahadur, P. Das, N. Bhargava, Improving energy efficiency and economic feasibility of photocatalytic treatment of synthetic and real textile wastewater using bagasse fly ash modified TiO2, Chem. Eng. J. Adv. 2 (2020), https://doi.org/10.1016/j.ceja.2020.100012.
[43] N. Bahadur, N. Bhargava, TERI Advanced Oxidation Technology (TADOX®) to treat industrial wastewater with integration at pre- and post-biological stage: case studies from India, Water Pract. Technol. 17 (8) (2022) 1692–1705, https://doi.org/10.2166/wpt.2022.065.
[44] P. Kumari, N. Bahadur, L.F. Dumée, Photo-catalytic membrane reactors for the remediation of persistent organic pollutants – a review, Sep. Purif. Technol. 230 (2020) 115878.
[45] S. Horikoshi, N. Serpone, Can the photocatalyst TiO2 be incorporated into a wastewater treatment method? Background and prospects, Catal. Today 340 (2020) 334–346.
[46] T. Fazal, A. Razzaq, F. Javed, N. Hafeez Ainy, U.S. Amjad Rashid, M.S. Ur Rehman, A. Faisal, F. Rehman, Integrating adsorption and photocatalysis: a cost effective strategy for textile wastewater treatment using hybrid biochar-TiO2 composite, J. Hazard. Mater. 390 (2020), 121623.
[47] Y. Nosaka, A.Y. Nosaka, Generation and detection of reactive oxygen species in photocatalysis, Chem. Rev. 117 (2017) 11302–11336.
[48] O. Ganzenko, C. Trellu, N. Papirio Stefano, Oturan, D. Huguenot, G. van Hullebusch Eric, D. Esposito, M.A. Oturan, Bioelectro-Fenton: evaluation of a combined biological-advanced oxidation treatment for pharmaceutical wastewater, Environ. Sci. Pollut. Res. Int. 25 (2018) 20283–20292.
[49] P. Aravind, V. Subramanyan, S. Ferro, R. Gopalakrishnan, Eco-friendly and facile integrated biological-cum-photo assisted electrooxidation process for degradation of textile wastewater, Water Res. 93 (2016) 230–241.
[50] H. Md Anawar, R. Chowdhury, Remediation of polluted river water by biological, chemical, ecological and engineering processes, Sustainability. 12 (2020) 7017.
[51] K. Nadeem, G.T. Guyer, N. Dizge, Polishing of biologically treated textile wastewater through AOPs and recycling for wet processing, J. Water Process Eng. 20 (2017) 29–39.
[52] P. Xu, H. Han, B. Hou, H. Zhuang, S. Jia, D. Wang, K. Li, Q. Zhao, The feasibility of using combined TiO2photocatalysis oxidation and MBBR process for advanced treatment of biologically pretreated coal gasification wastewater, Bioresour. Technol. (2015), https://doi.org/10.1016/j.biortech.2015.04.051.
[53] M. Henze, P. Harremoes, E. Arvin, J.L. Jansen, Wastewater Treatment: Biological and Chemical Processes, 2nd ed., Springer, Berlin, Germany, 1997.
[54] P. Xu, H. Han, B. Hou, H. Zhuang, S. Jia, D. Wang, K. Li, Q. Zhao, The feasibility of using combined TiO2 photocatalysis oxidation and MBBR process for advanced treatment of biologically pretreated coal gasification wastewater, Bioresour. Technol. 189 (2015) 417–420.
[55] J.Q. Cui, X.J. Wang, X.L. Lin, Treatment of textile wastewater using facultative contact reactor-biological contact oxidation and ozone biological aerated filter, Adv. Mater. Res. 777 (2013) 318–325, https://doi.org/10.4028/www.scientific.net/amr.777.318.
[56] J.J. Rueda-Márquez, M. Sillanpää, P. Pocostales, A. Acevedo, M.A. Manzano, Post-treatment of biologically treated wastewater containing organic contaminants using a sequence of H2O2based advanced oxidation processes: photolysis and catalytic wet oxidation, Water Res. 71 (2015) 85–96, https://doi.org/10.1016/j.watres.2014.12.054.
[57] L. Rizzo, D. Sannino, V. Vaiano, O. Sacco, A. Scarpa, D. Pietrogiacomi, Effect of solar simulated N-doped TiO2photocatalysis on the inactivation and antibiotic resistance of an *E. coli* strain in biologically treated urban wastewater, Appl. Catal. B (2014), https://doi.org/10.1016/j.apcatb.2013.07.033.
[58] J.J. Rueda-Márquez, M. Sillanpää, A. Pocostales, P. Acevedo, M.A. Manzano, Post-treatment of biologically treated wastewater containing organic contaminants using a sequence of H2O2 based advanced oxidation processes: photolysis and catalytic wet oxidation, Water Res. 71 (2015) 85–96.
[59] I.A. Alaton, S. Dogruel, E. Baykal, G. Gerone, Combined chemical and biological oxidation of penicillin formulation effluent, J. Environ. Manag. 73 (2004) 155–163.
[60] L.S. da Silva, M.M.M. Gonçalves, L.R. Raddi de Araujo, Combined photocatalytic and biological process for textile wastewater treatments, Water Environ. Res. (2019) 1–8, https://doi.org/10.1002/wer.1143.
[61] I.A. Alaton, S. Dogruel, E. Baykal, G. Gerone, Combined chemical and biological oxidation of penicillin formulation effluent, J. Environ. Manag. 73 (2004) 155–163, https://doi.org/10.1016/j.jenvman.2004.06.007.
[62] L. Rizzo, D. Sannino, V. Vaiano, O. Sacco, D. Scarpa, A. Pietrogiacomi, Effect of solar simulated N-doped TiO2 photocatalysis on the inactivation and antibiotic resistance of an *E. coli* strain in biologically treated urban wastewater, Appl. Catal. B. 144 (2014) 369–378.
[63] N.K. Sharma, L. Philip, Combined biological and photocatalytic treatment of real coke oven wastewater, Chem. Eng. J. 295 (2016) 20–28.
[64] R. Shoukat, S.J. Khan, Y. Jamal, Hybrid anaerobic-aerobic biological treatment for real textile wastewater, J. Water Process Eng. 29 (2019) 100804.

[65] N.K. Sharma, L. Philip, Combined biological and photocatalytic treatment of real coke oven wastewater, Chem. Eng. J. (2016), https://doi.org/10.1016/j.cej.2016.03.031.

[66] J.J. Milledge, E.P. Thompson, A. Sauvêtre, P. Schroeder, P.J. Harvey, Chapter 8 - novel developments in biological technologies for wastewater processing, in: C. M. Galanakis, E. Agrafioti (Eds.), Sustainable Water and Wastewater Processing, Elsevier, 2019, pp. 239–278.

[67] R. Aless, V. Cesaro, V. Belgiorno Naddeo, Wastewater treatment by combination of advanced oxidation processes and conventional biological systems, J. Bioremediat. Biodegrad. 4 (2013) 1–8.

[68] R. Chemlal, L. Azzouz, R. Kernani, N. Abdi, H. Lounici, H. Grib, N. Mameri, N. Drouiche, Combination of advanced oxidation and biological processes for the landfill leachate treatment, Ecol. Eng. 73 (2014) 281–289.

[69] Y. Lester, H. Mamane, I. Zucker, D. Avisar, Treating wastewater from a pharmaceutical formulation facility by biological process and ozone, Water Res. 47 (2013) 4349–4356.

[70] H. Hayat, Q. Mahmood, A. Pervez, Z.A. Bhatti, S.A. Baig, Comparative decolorization of dyes in textile wastewater using biological and chemical treatment, Sep. Purif. Technol. 154 (2015) 149–153.

[71] M. Vilaseca, M.-C. Gutiérrez, V. López-Grimau, M. López-Mesas, M. Crespi, Biological treatment of a textile effluent after electrochemical oxidation of reactive dyes, Water Environ. Res. 82 (2010) 176–182.

[72] M. Shireesha, A. Group, A Review on Effluent Treatment of Textile by Biological and Chemical Methods 4, 2017, pp. 961–968.

[73] A.C. Vincenzo Naddeo, Wastewater treatment by combination of advanced oxidation processes and conventional biological systems, J. Bioremediat. Biodegrad. (2013), https://doi.org/10.4172/2155-6199.1000208.

[74] R. Chemlal, L. Azzouz, R. Kernani, N. Abdi, H. Lounici, H. Grib, N. Mameri, N. Drouiche, Combination of advanced oxidation and biological processes for the landfill leachate treatment, Ecol. Eng. (2014), https://doi.org/10.1016/j.ecoleng.2014.09.043.

[75] M. Bahri, A. Mahdavi, A. Mirzaei, A. Mansouri, F. Haghighat, Integrated oxidation process and biological treatment for highly concentrated petrochemical effluents: a review, Chem. Eng. Process. Process Intensif. 125 (2018) 183–196.

[76] I.A. Saleh, N. Zouari, M.A. Al-Ghouti, Removal of pesticides from water and wastewater: chemical, physical and biological treatment approaches, Environ. Technol. Innov. 19 (2020) 101026.

[77] L. Bilińska, K. Blus, M. Foszpańczyk, M. Gmurek, S. Ledakowicz, Catalytic ozonation of textile wastewater as a polishing step after industrial scale electrocoagulation, J. Environ. Manag. 265 (2020) 110502.

[78] Z. Al-Qodah, Y. Al-Qudah, E. Assirey, Combined biological wastewater treatment with electrocoagulation as a post-polishing process: a review, Sep. Sci. Technol. 55 (2020) 2334–2352.

[79] D. Chebli, F. Fourcade, S. Brosillon, S. Nacef, A. Amrane, Supported photocatalysis as a pre-treatment prior to biological degradation for the removal of some dyes from aqueous solutions; Acid Red 183, Biebrich Scarlet, Methyl Red Sodium Salt, Orange II, J. Chem. Technol. Biotechnol. 53 (2010).

[80] L.P. Ramteke, P.R. Gogate, Improved treatment approach for the removal of aromatic compounds using polymeric beads in Fenton pretreatment and biological oxidation, Environ. Sci. Pollut. Res. Int. 23 (2016) 20281–20296.

[81] N. Bahadur, N. Bhargava, S.K. Sarkar, V. Dhawan, Breakthrough in treatment of sewage using TADOX®, by-passing biological treatment with removal of micropollutants to enable high end water reuse, J. Inst. Eng. (India): A. (2023), https://doi.org/10.1007/s40030-023-00738-5.

[82] N. Bahadur, N. Bhargava, S.K. Sarkar, V. Dhawan, TERI advanced oxidation technology (TADOX®) for treatment and rejuvenation of open drains and surface water bodies: making habitats sustainable, Water Pract Technol. 18 (2023) 1357–1365, https://doi.org/10.2166/wpt.2023.087.

[83] N. Bahadur, Design and development of photocatalytic reactor for treatment of industrial effluent as well as sludge using recently patented technology, in: Proceedings of the India International Science Festival- Young Scientists' Meet Department of Science and Technology, Government of India, 2015, p. 71, 1–5.

[84] N. Bahadur, Design and development of photocatalytic reactor for treatment of industrial effluent as well as sludge using recently patented technology, in: Proceedings of the India International Science Festival- Young' Meet Department of Science and Technology, Government of India, 2015, pp. 1–5, 71.

[85] A. Kumar, N. Mathur, Photocatalytic oxidation of aniline using Ag^{+}-loaded TiO_2 suspensions, Appl. Catal. A. 275 (2004) 189–197.

[86] A. Kumar, N. Mathur, Photocatalytic degradation of aniline at the interface of TiO_2 suspensions containing carbonate ions, J. Colloid Interface Sci. 300 (2006) 244–252.

[87] N. Bahadur, N. Bhargava, Novel pilot scale photocatalytic treatment of textile & dyeing industry wastewater to achieve process water quality and enabling zero liquid discharge, J. Water Process Eng. 32 (2019) 100934.

[88] P. Das, N. Bahadur, V. Dhawan, Surfactant-modified titania for cadmium removal and textile effluent treatment together being environmentally safe for seed germination and growth of Vigna radiata, Environ. Sci. Pollut. Res. Int. 27 (2020) 7795–7811.

[89] A. Kumar, N. Mathur, Photocatalytic degradation of aniline at the interface of TiO_2 suspensions containing carbonate ions, J. Colloid Interface Sci. 300 (2006) 244–252, https://doi.org/10.1016/j.jcis.2006.03.046.

[90] A. Kumar, N. Mathur, Photocatalytic oxidation of aniline using Ag^{+}-loaded TiO_2 suspensions, Appl. Catal. A Gen. 275 (2004) 189–197, https://doi.org/10.1016/j.apcata.2004.07.033.

[91] R. George, N. Bahadur, N. Singh, R. Singh, A. Verma, A.K. Shukla, Environmentally benign TiO_2 nanomaterials for removal of heavy metal ions with interfering ions present in tap water, Mater Today Proc. 3 (2016) 162–166.

[92] V. Kumar, N. Bahadur, D. Sachdev, S. Gupta, G.B. Reddy, R. Pasricha, Restructural confirmation and photocatalytic applications of graphene oxide–gold composites synthesized by Langmuir–Blodgett method, Carbon N. Y. 80 (2014) 290–304.

[93] V. Kumar, N. Bahadur, D. Sachdev, S. Gupta, G.B. Reddy, R. Pasricha, Restructural confirmation and photocatalytic applications of graphene oxide-gold composites synthesized by Langmuir-Blodgett method, Carbon N Y. 80 (2014) 290–304, https://doi.org/10.1016/j.carbon.2014.08.067.

[94] N. Bahadur, K. Jain, A.K. Srivastava, Govind, R. Gakhar, D. Haranath, M.S. Dulat, Effect of nominal doping of Ag and Ni on the crystalline structure and photocatalytic properties of mesoporous titania, Mater. Chem. Phys. 124 (2010) 600–608, https://doi.org/10.1016/j.matchemphys.2010.07.020.

[95] O. Keen, J. Bolton, M. Litter, K. Bircher, T. Oppenländer, Standard reporting of electrical energy per order (EEO) for UV/H2O2 reactors (IUPAC technical report), J. Macromol. Sci. Part A Pure Appl. Chem. 90 (2018) 1487–1499.

[96] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Technologies for Both Electric-and Solar-driven Systems † (IUPAC Technical Report), 2001.

[97] A. Rice, E.W. Baird, R.B. Eaton, APHA 2017 Standard Methods for Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation ISBN, Washington, 2017.

[98] O. Keen, J. Bolton, M. Litter, K. Bircher, T. Oppenländer, Standard reporting of Electrical Energy per Order (EEO) for UV/H2O2 reactors (IUPAC technical report), in: De Gruyter (Ed.), Pure and Applied Chemistry, 2018, pp. 1487–1499, https://doi.org/10.1515/pac-2017-0603.

[99] D. Li, X.S. He, B.D. Xi, Z.M. Wei, H.W. Pan, D.Y. Cui, Study on UV–visible spectra characteristic of dissolved organic matter during municipal solid waste composting, Adv. Mater. Res. 878 (2014) 840–849.

[100] E. GilPavas, I. Dobrosz-Gómez, M.-Á. Gómez-García, Optimization and toxicity assessment of a combined electrocoagulation, H_2O_2/Fe^{2+}/UV and activated carbon adsorption for textile wastewater treatment, Sci. Total Environ. 651 (2019) 551–560, https://doi.org/10.1016/j.scitotenv.2018.09.125.

[101] E. GilPavas, I. Dobrosz-Gómez, M.-Á. Gómez-Garcia, Optimization and toxicity assessment of a combined electrocoagulation, H_2O_2/Fe^2+/UV and activated carbon adsorption for textile wastewater treatment, Sci. Total Environ. 651 (2019) 551–560.

[102] M.I. Stefan, Advanced Oxidation Processes for Water Treatment, 2018.

[103] D. Zhang, S. Yan, W. Song, Photochemically induced formation of reactive oxygen species (ROS) from effluent organic matter, Environ. Sci. Technol. 48 (2014) 12645–12653.

[104] T. Schellenberg, V. Subramanian, G. Ganeshan, D. Tompkins, R. Pradeep, Wastewater discharge standards in the evolving context of urban sustainability–the case of India, Front. Environ. Sci. Eng. China 8 (2020) 30.

[105] A. Shinde, V.P. Deshpande, 7 Impact of sodium absorption ratio on Kharun river basin, Raipur, Chhattisgarh, in: De Gruyter (Ed.), Water Resource Technology, 2021, pp. 77–84.

[106] A. Ghaffarian Khorram, N. Fallah, Comparison of electrocoagulation and photocatalytic process for treatment of industrial dyeing wastewater: energy consumption analysis, Environ. Prog. Sustain. Energy 39 (2020) 13288.

[107] A. Chavan, M.H. Fulekar, Integration of photocatalytic oxidation and biodegradation treatment processes to enhance degradation efficiency of CETP wastewater contaminants, Bionanoscience 8 (2018) 761–768.

[108] A.V. Padalkar, R. Kumar, Common effluent treatment plant (CETP): reliability analysis and performance evaluation, Water Sci. Eng. 11 (2018) 205–213, https://doi.org/10.1016/j.wse.2018.10.002.