



Comparison of TiO₂ catalysis and Fenton's treatment for rapid degradation of Remazol Red Dye in textile industry effluent

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Abstract

The contamination of water bodies by toxic industrial effluents is a serious threat to environment and the exposed organisms. The treatment of carcinogenic azo dyes in wastewater of grossly polluting textile industry is a major challenge considering the persistent nature of chemical dyes against biological treatment. The present study explores efficacy of advanced oxidation processes—photocatalysis and photo-Fenton, towards degradation of Remazol Red dye in the textile industry effluent. It was observed that both processes can completely remove the colour and approximately 85% mineralization of the dye within reaction time of 60 min and 8 min, respectively. The economic analysis placed photo-Fenton as a cost-effective method with treatment cost of approx. 0.0090 US \$/litre of wastewater containing Remazol Red dye. Although, Photocatalysis was relatively slow, it is substantially effective in removal/degradation of colour from textile effluent against the biological treatment. The study concludes that photo-Fenton and Photocatalysis are cost-effective and substantial treatment options for removal of toxicity arising from coloured textile effluents.

Keywords Remazol red · Photocatalysis · Photo-Fenton · Decolorization · Textile effluent

1 Introduction

The textile industry has become a significant contributor to water pollution, utilising millions of gallons of freshwater globally, and resulting in the generation of huge volumes of wastewater. The wastewater generated in washing, scouring, mercerizing, and bleaching during textile processing varies significantly, thus causing complex nature of textile effluent. As per an estimate, about 2 million litres of water are consumed to fabricate 10 tonnes of textiles (Yaseen and Scholz 2019). The composition of textile industry effluent varies with the scale of industry, manufacturing processes, type of technology used, and degree/type of treatment to wastewater. So, the industry has ended up as one of the most notorious water-polluting sector. The untreated or poorly treated textile effluent, released either on the land surface or a water body, could relocate a huge cost to the environment, disturbing the ecology and triggering human health problems

(Ho et al. 2017). The nature of pollutants released depends on the chemicals that are used in different processes, thus often differs in the values of BOD (biochemical oxygen demand), pH, acidity, turbidity, suspended solids, temperature, etc. The suspended solids in the effluent combine with oily scum and interfere with the oxygen transfer mechanism in the air–water interface. The textile effluents also contain heavy metals, such as Cu, As, Zn, and Cr, capable of harming the environment (Eswaramoorthi et al. 2008). The colorants in the effluent can also cause diseases, such as irritation of skin and dermatitis, haemorrhage, nausea, ulceration of skin (Jothi 2015) etc. The residual dyes in the effluent may increase the BOD of the receiving water body, reducing the DO and reoxygenation process, thus, obstructing the development of photoautotrophic organisms.

The textile industry effluent is characterized by high pH, salinity, intensive colour and persisting odour. The use of azo (N≡N) dyes as colouring pigments for fibres has been a practice for centuries. Although studies have confirmed the ecotoxicity of azo dyes to a number of aquatic species, dyeing process still depends on 60–70% stock of azo dyes against the share of other pigments (Rajkumar and Muthukumar 2012). Synthetic dyes used to colour the textiles end up in the effluent, thus making wastewater toxic and

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carcinogenic. The frequently used dye for cellulose textiles is reactive Remazol Red. Remazol dyes are comparatively less reactive than other dyes, thus making them more stable in water. Moreover, the subsequent aerobic degradation of these dyes does not occur, since the masking groups are provided to make them color-fast (Ghaly 2014).

Conventional treatment processes like flocculation, chemical coagulation, simple sedimentation, and biological processes such as aerobic–anaerobic treatment, aerated lagoons, aerobic activated sludge, etc. have been used in the textile industries; however, these do not achieve complete degradation of the dyes (Ho et al. 2017). The implementation and selection of treatment method depends upon the operational skills, technological aids, knowledge, maintenance, and environmental concern as well. Whereas the photothermal dissociation under ambient conditions results in formation of aromatic amines which enhance toxicity and carcinogenicity (Saggiaro et al. 2011), the dyes are resistant to aerobic microbial breakdown. Although anaerobic process is used to treat textile effluents, slow rate and incomplete degradation of the dyes result in residual toxicity in treated wastewater. Moreover, phase transfer of toxic dyes takes place into the sludge produced during biological treatment (Maia et al. 2014). On the other hand, physical processes like adsorption, reverse osmosis, etc. are cost/energy-intensive and produce toxic sludge (Rajkumar and Muthukumar 2012). Since there are limitations associated with physical and biological processes, advanced oxidation processes (AOPs) like Photocatalysis and Fenton's treatment have come-up as potential treatment options for rapid chemical oxidation of persistent organic pollutants. AOPs aim at producing highly oxidising reactive hydroxyl radicals (OH^\bullet) which can oxidise organic compounds, particularly unsaturated molecules like azo dyes, non-selectively and rapidly (Saatci 2010). Therefore, Advanced Oxidation Process (AOP) has become a potential treatment method to decolourize and degrade dyes from textile industry.

The Photocatalytic process relies on excitation of semi-conducting oxides (TiO_2 , ZnO , Fe_2O_3 , ZnS and CdS) thereby promoting the movement of an electron and hole towards the semiconductor surface, where they take part in electron transfer reactions with solvent and the adsorbed species (Balzani et al. 2019). The semiconductor oxide acts as catalyst to generate holes and free radicals (OH^\bullet) for degradation of complex organic contaminants (Verma and Haritash 2020). TiO_2 is frequently used as an efficient photocatalyst for oxidation of wide range of organic compounds. Studies have reported that ZnO and TiO_2 were the most effective photocatalysts for the decolourization of dyes with slightly higher efficiency of ZnO (Palak et al. 2019; Akyol et al. 2004). The use of commercial grade TiO_2 report complete degradation of Remazol dye under photo-irradiation in a period of approximately 2 h (Saatci 2010), while the use of

nano- TiO_2 (P25) reports complete degradation with higher reaction rate. As compared to the traditional chemical oxidation like chlorination, photocatalysis process is more effective for treatment of wastewater (Balzani et al. 2019). Similarly, the Fenton's process has also gained more attention (Asghar 2015) towards degradation of organic compounds. A mixture of ferrous (II) ions and hydrogen peroxide (H_2O_2) produces hydroxyl radicals in the acidic medium, reducing a significant amount of COD and total organic carbon TOC content. Ferrous (II) and hydrogen peroxide can be used for wastewater treatment owing to easy availability and non-toxic nature of iron, and easy to handle nature of 30% hydrogen peroxide (Modirshahla et al. 2007), respectively. Photo-Fenton, on the other hand, combines the Fenton reaction with UV radiation causing photochemical decomposition of hydrogen peroxide. Photo-Fenton is the preferred technique to generate hydroxyl radicals, resulting in an increased rate of degradation (da Rocha Santana 2017). According to a study (Saatci 2010), the photo-Fenton's process has higher oxidation rate than the Fenton's process with reported efficiency of 90% degradation of COD in a reaction time of 20 min. Low cost, simple use and rapid degradation make this process suitable for the treatment of textile wastewater. The other advantages of AOPs over conventional treatment methods are—non-selective and destructive action, and complete mineralization of organic pollutants. AOPs generate low to zero waste and use short-lived chemical species with high oxidizing power to degrade complex molecules. Therefore, the current study aims to evaluate and compare the performance of Photocatalysis, Solar-Photocatalysis, and Photo-Fenton's process to find an appropriate treatment method to decolourise/degrade textile industry effluent containing Remazol Red dye.

2 Materials and methods

2.1 Collection and characterisation of textile effluent

The effluent samples (20 in number) were collected from different textile industries located in Ghaziabad and Gautam Buddha Nagar districts, Uttar Pradesh (UP), India. The samples were collected in pre-rinsed virgin polypropylene plastic bottles of 1.0 L capacity during September to October, 2020 immediately after the first phase of COVID-19 lockdown in India. The samples were characterised for pH, electrical conductivity (EC), Total dissolved solids (TDS), using Labman make (LMMP 30 model) bench-top multiparameter; Total suspended solids (TSS) were determined gravimetrically; analysis for nitrate (NO_3^{2-}), was carried out spectrophotometrically (Lab India make UV 3092 Model) at a wavelength of 220 nm; and Biological Oxygen Demand (BOD_5),

Chemical Oxygen Demand (COD), Total Sulphides, and Ammonia (NH₃) were determined using standard methods as prescribed by APHA (2012). All the samples were analysed in triplicates and intra-lab comparison of analysis was performed to ensure the accuracy of analysis ($\geq 95\%$).

2.2 Chemicals/reagents and experimental setup for dye degradation

The reactive textile dye Remazol Red obtained from Gayatri Dye Chem Industries, Gujarat, India was used to prepare synthetic wastewater (100 mg/l) using ultrapure (Type-1) water. The absorption spectrum of Remazol red dye was plotted in the wavelength range from 190 to 800 nm over a double beam UV–Vis spectrophotometer. The wavelength of maximum absorption (λ_{max}) was obtained at 520 nm; and standard curve of Remazol red dye was plotted in concentration range of 10 to 100 mg/l. Analytical grade (AR) TiO₂ (P25) was obtained from Evonik Industries, Germany; and Ferrous sulphate (FeSO₄·7H₂O) (99.5%) and hydrogen peroxide (H₂O₂) (30% w/v) were obtained from Central Drug House (CDH), India. The degree of mineralisation was measured over the TOC Analyser (TOC-L Shimadzu Make, Japan).

The experiments for dye degradation were performed using 200 ml extract of synthetic stock solution (100 mg/l), in triplicates, at room temperature (25°C) with continuous stirring at 150 rpm and air-sparging. The experiments were conducted to study the effect of varying concentrations of TiO₂ (0.1 g/l to 20.0 g/l) and H₂O₂ at pH 7.0 for photocatalytic treatment. Photo-Fenton experiments were studied to examine the effect of varying Fe²⁺ concentration (0.33 mM to 1 mM); effect of H₂O₂ (1 mM to 10 mM); and effect of varying pH (1.0–4.0) and optimized values were recorded from the same. Since Fenton's process operates in acidic pH range only, the experiments were performed in pH range of 1.0–4.0. A sample volume of 5 ml was extracted for analysis at a regular time interval varying from 5 to 15 min depending

upon the treatment pace until the process got stabilized. The Photocatalytic and Photo-Fenton experiments were carried out in a fabricated UV-chamber having 8 UV tubes (Philips 36 W each), whereas solar-photocatalytic treatment was conducted under sunlight. The aggregated source intensity of the UV-chamber was 672 W/m² as explained by Verma and Haritash (2019). The results of different processes were compared and their efficiency towards complete removal of Remazol was evaluated. To study the mineralization of dye, initial and final values of TOC were determined. The percent removal/ degradation of dye was calculated using the following equation:

$$\text{Efficiency (\%)} = [(C_i - C_t) / C_i] \times 100 \quad (1)$$

where C_i is the initial dye TOC concentration; and C_t is the dye TOC concentration at time 't'.

3 Results and discussion

3.1 Characteristics of textile industry effluent

The physico-chemical characteristics of textile effluent are given in Table 1. The average pH of untreated influent from was 7.5 against pH of 7.2 for treated effluent. It is reported that acidic conditions (low pH) or alkaline conditions (high pH) can alter the enzymatic structure and development of microorganisms in the receiving water-body, while pH > 8.5 can affect fish production (Edmund 1998). The average value of EC in textile effluent before and after treatment was 5.2 mS/cm and 4.3 mS/cm, respectively. High EC of the sample indicates the presence of ions like sodium, potassium, iron, etc. which are present in surfactants, detergents, and other chemicals used during the scouring process to remove natural impurities (Holkar et al. 2016). The average TDS of the treated effluent was 2147 mg/l. The high TDS has the potential to deteriorate the quality of surface water

Table 1 Characteristics of industrial wastewater from medium scale textile industries

Parameter	Unit	Influent		Effluent	
		Range	Mean ± SD	Range	Mean ± SD
pH	–	3.5–11.3	7.5 ± 1.79	3.1–9.7	7.2 ± 1.31
EC	mS/cm	1–11	5.2 ± 2.9	1–13	4.3 ± 3.3
TDS	mg/l	640–5505	2721 ± 1500.8	464–6660	2147 ± 1701
TSS	mg/l	8–698	179.9 ± 169.2	2–176	31.2 ± 40.4
BOD ₅	mg/l	40–240	141.0 ± 80.4	20–200	79 ± 54
COD	mg/l	240–2400	835.0 ± 741.1	80–640	320 ± 175
Nitrate	mg/l	2–62	28.0 ± 16.9	0–16	5.7 ± 3.8
Total Sulphides	mg/l	1.2–88	13.7 ± 18.7	0–56	6.8 ± 12.5

EC electrical conductivity, TDS total dissolved solids, TSS total suspended solids, BOD₅ 5-day biochemical oxygen demand, COD chemical oxygen demand, SD standard deviation

as a consequence of which the aquatic life gets adversely affected. The average TSS of effluent was 180 mg/l, nitrates were 28 mg/l, total sulphides as 13.7 mg/l, average BOD was 141 mg/l and COD was 850 mg/l. Due to the high BOD, the dissolved oxygen in receiving water may reduce significantly causing septic conditions that leads to death of fishes and other aquatic species. Chemical oxygen demand (COD) indicate the occurrence of organic as well as inorganic matter in the textile dyeing industry effluents. It comprises both the biodegradable and non-biodegradable portions of live bacterial attack, but average BOD/COD ratio <0.3 indicates that it can be oxidized by strong chemical oxidants (Abbasi 1998; Tan et al. 2000; Chiron et al. 2000) thus indicating that treatment by chemical oxidation (AOPs) is a preferred method.

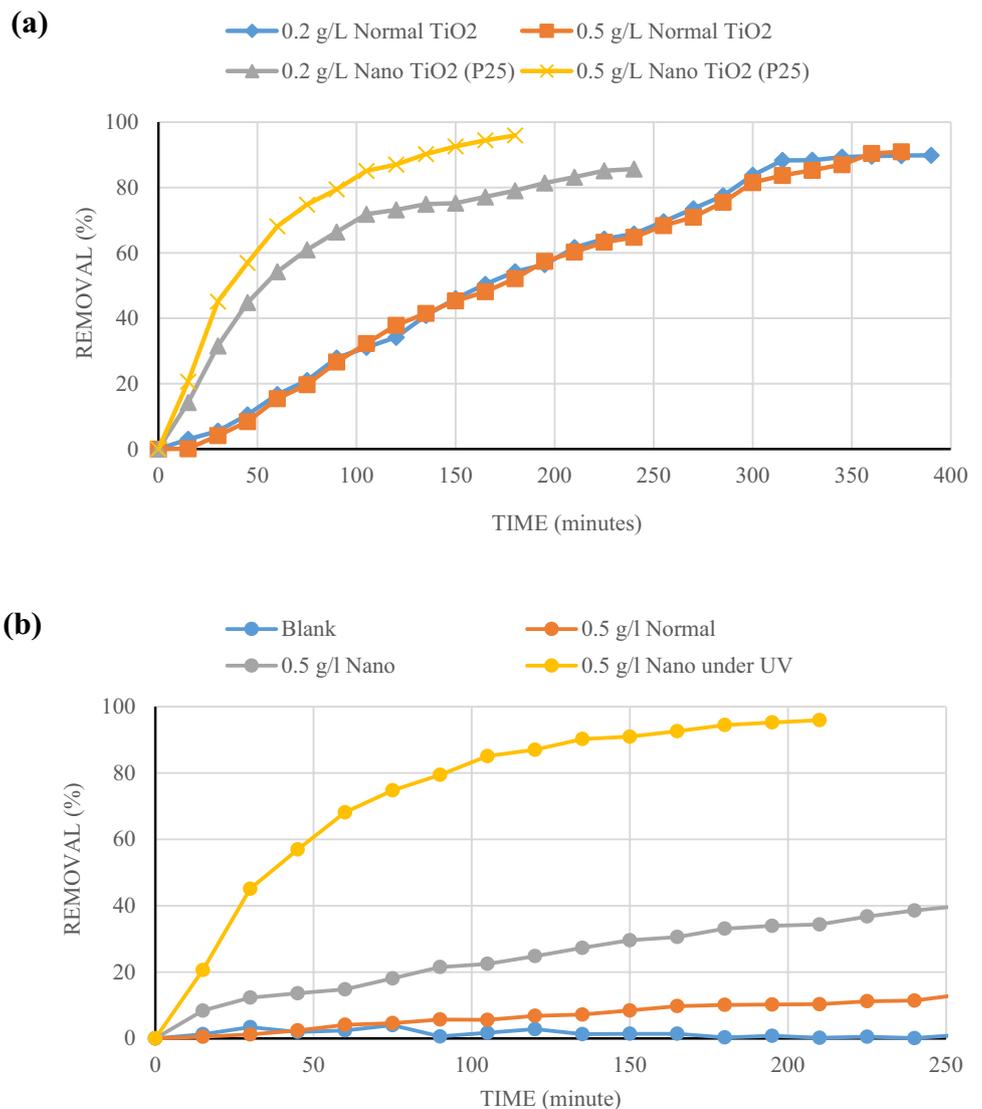
3.2 Photocatalytic degradation of Remazol Red dye

The TiO_2 -assisted photocatalytic degradation confirmed significant removal of Remazol Red dye from the textile effluent. The effect of regulating factors (TiO_2 , H_2O_2 , and light) on efficiency of the process is as discussed below.

3.2.1 Effect of catalyst size, type of light, and Irradiation time

To optimize the effect of catalyst on degradation of Remazol Red dye, commercially available normal TiO_2 and nano- TiO_2 (P25) were used in the present study. The comparison of normal TiO_2 against nano- TiO_2 , revealed that nano- TiO_2 has got better potential towards treatment of textile dyes (Fig. 1a). Since nano- TiO_2 has more surface area, absorption of energy (UV-associated) is more and so is the production of OH^\bullet radicals. The nano- TiO_2 resulted in almost complete

Fig. 1 **a** Photocatalytic treatment of Remazol dye against Normal TiO_2 and Nano TiO_2 (P25); **b** Photocatalytic treatment of Remazol Red dye under sunlight and UV source



removal of colour (at a dose 0.5 g/l) within 3.0 h, whereas normal TiO₂ could remove only 80% of the colour even after 5.0 h. Considering the edge of nano-TiO₂ over normal TiO₂, rest of the experiments were conducted using nano-TiO₂ for treatment of textile effluent.

Since, sunlight only consists of 3–5% UV light, degradation occurs slower (Davis and Huang 1990). The solar-photocatalytic experiment set of 0.5 g/l using normal TiO₂/H₂O₂/Sunlight and nanoTiO₂/H₂O₂/Sunlight showed 13% and 40% degradation efficiency in 255 min, respectively (Fig. 1b). Poor degradation rate could be attributed to the ambient conditions as the experiment was carried out in winters when intensity of sunlight was lower. Moreover, the lower fraction of UV (~5%) in total solar terrestrial radiation results in lower energy and weak activation of TiO₂. Since the energy associated with UV light is high, it can easily activate TiO₂ resulting in formation of OH• radicals. It is observed that higher light intensity is directly proportional to generation of OH• radicals thus facilitating the faster dye degradation.

Under the optimized concentration of TiO₂ (1.0 g/l), 98% of the Remazol dye was degraded in 60 min of the irradiation time. The photodegradation of the dye promoted by photocatalyst via the direct photolysis in 60 min of the irradiation time is responsible for degradation of only the molecules adsorbed on the surface of TiO₂. Increasing the catalyst concentration increases the turbidity of the solution hence strongly inhibiting the light penetration resulting in less degradation.

3.2.2 Effect of H₂O₂

To inhibit the problem of electron–hole recombination is to add another electron acceptor, i.e., H₂O₂, to the reaction. It

enhances the degradation of compounds due to a more efficient generation of hydroxyl radical and inhibition of electron–hole recombination (Mahmoodi et al. 2006). The colour degradation was faster in the presence of H₂O₂ as it is a powerful oxidizing agent; and it increased the photodegradation efficiency. The experiment conducted with nano TiO₂ dose of 0.10 g/l, 0.20 g/l, and 0.50 g/l, and constant concentration of 5 mM H₂O₂ in the dye solution exhibited a faster rate than the experiment in the absence of H₂O₂. Dye degradation efficiency achieved in both the experiments were though similar (90% and 94%); however, it was acquired in 210 min in the presence of H₂O₂ compared to 315 min in its absence (Fig. 2). The addition of H₂O₂ with TiO₂/UV has a synergistic effect. The UV irradiation causes H₂O₂ to photolyze, generating two hydroxyl radicals (2OH•) (6) or hydrogen ions (7) for the production of hydroperoxyl radicals (5) (Konstantinou & Albanis 2004). Since, electron–hole recombination is hampered, the hydroxyl radicals are induced either directly (2) or indirectly (4) (Sam-sudin et al. 2015). Similar findings showing synergistic effect between photocatalytic activity from nano TiO₂ and H₂O₂ been reported by Karimi et al. (2014):

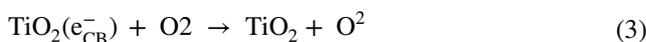
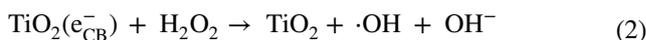
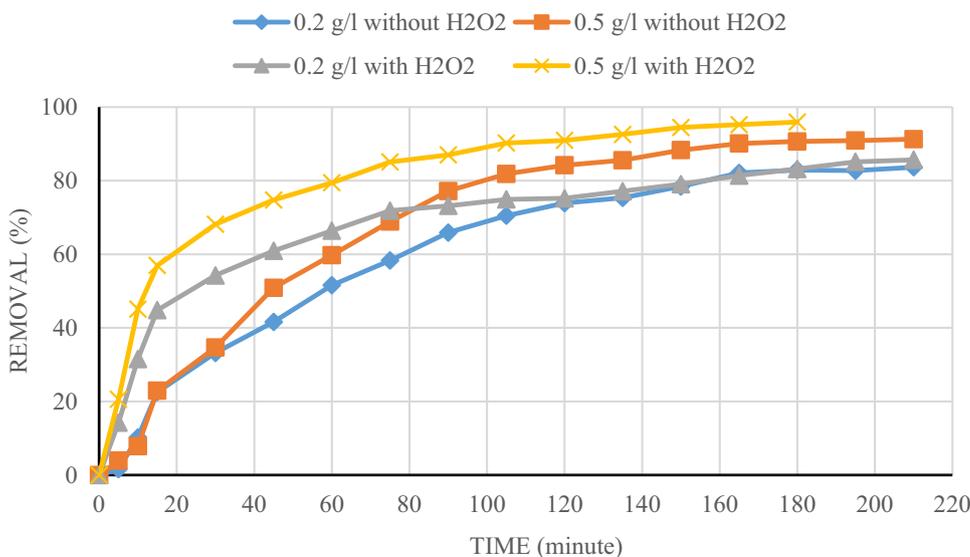


Fig. 2 Photocatalytic (TiO₂) treatment of dye in the presence and absence of H₂O₂





where e_{CB}^- represents the electron in conduction band.

3.2.3 Effect of catalyst loading

It was observed that dye degradation rate was slower when the catalyst dose was less because of the lesser availability of active sites, thus, less surface area of the photocatalyst. In addition, the limited generation of hydroxyl radicals and superoxide ions demands a longer irradiation time to degrade the high-strength dye (100 mg/l). The degradation rate increased with an increase in the TiO_2 dose as more surface area was available for adsorption. Similar observations have been made in other studies too (Neppolian et al. 2002; Kaur and Singh 2007). It was noted that at 1.0 g/l TiO_2 almost complete degradation (~98%) was achieved in 60 min (Fig. 3). The results are in good agreement with the results of Maia et al. (2014), where 1.0 g/l of TiO_2 completely degraded Remazol Blue RGB and Remazol Carbon RGB and nearly 90% for the Remazol Yellow Gold RGB, in 120 min of photodegradation. Complete degradation of reactive dye, RB4 dye (anthraquinone dye) was achieved with TiO_2 dose of 1.0 g/l in 40 min of irradiation time as reported by Samsudin et al. (2015). At a higher dose, scattering of light caused by the opacity of the solution (cloudy suspension) affects the degradation efficiency (Carp et al. 2004). It, thus, reduces the number of photons absorbed resulting in fewer hydroxyl radicals generation from TiO_2 to oxidise the dye. The phenomena was observed while augmenting TiO_2 dose from 1.5 g/l to 20.0 g/l in the current study. While attaining the maximum degradation efficiency, the turbid solution formed decreased the efficiency with increased TiO_2

dose. This cloudy suspension was also reported in degradation of dyes like Reactive Red 180, Reactive Red 2 and Reactive Blue 19 (Hamlin et al. 1999; Lee and Pavlostathis 2004). Though the degradation efficiency was maximum with TiO_2 dose of 1.0 g/l in the current study, the rate kinetics was, however, higher with TiO_2 dose 10.0 g/l and 20.0 g/l also contributing to maximum degree of mineralisation of the order of 80% and 85%, respectively. The higher degradation efficiency while increasing TiO_2 dose may be because electron–hole pairs are generated when photons, the energy packets, are absorbed by the photocatalyst, exciting the electrons to jump from valence band to conduction band. These electron–hole pairs either react with the dye molecule directly or react with the surface-bound water to generate hydroxyl radicals. More the loading of TiO_2 , more will be the availability of active sites for adsorption, hence, more electron–hole pair to bind with water resulting in more OH^\bullet radicals. The typical mechanism is represented by the following reaction equations:

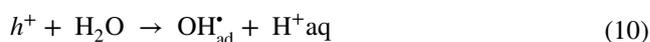
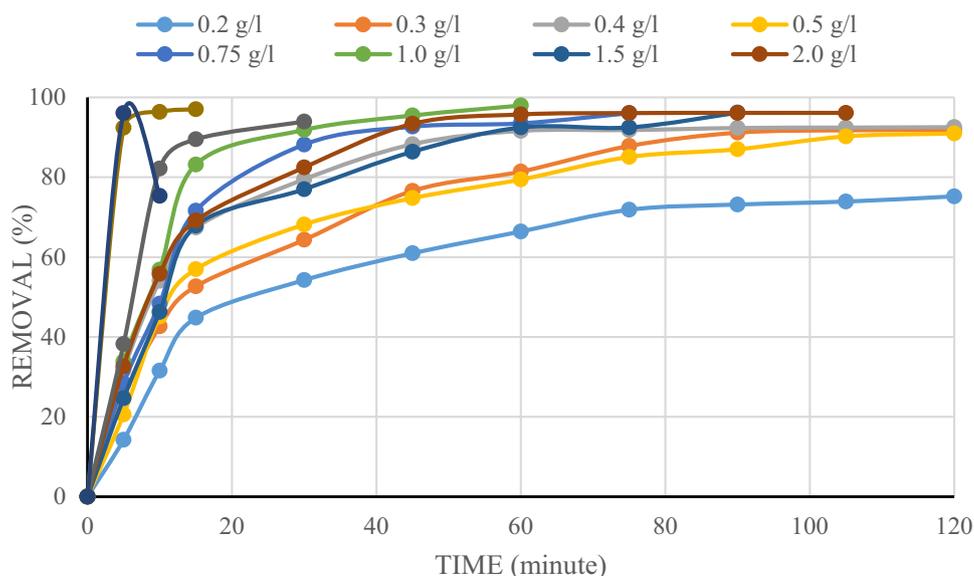
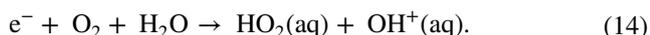


Fig. 3 Photocatalytic treatment of Remazol Red dye at varying doses (g/l) of Nano TiO_2





3.3 Photo-Fenton experiment

The degradation of Remazol Red dye during Fenton's treatment was observed to be higher compared to photocatalysis. The regulating parameters of Fenton's treatment (Fe^{2+} , H_2O_2 , pH etc.) were optimized to arrive at better efficiency towards dye degradation.

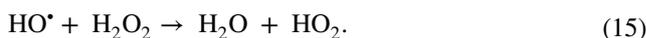
3.3.1 Influence of Fe^{2+} concentration

In Fenton's and Photo-Fenton's processes, ferrous ion (Fe^{2+}) is a significant factor determining the rate of the reaction. In the current study, the influence of variable concentrations of Fe^{2+} (0.33 mM; 0.5 mM; 1.0 mM) on decolorisation of Remazol Red dye was studied at pH 3.0. The concentration of H_2O_2 was kept constant at 5.0 mM, while the Fe^{2+} concentration was varied to maintain the ratio of 1:5, 1:10, and 1:15 for Fe^{2+} : H_2O_2 . It was observed that Fe^{2+} at concentration of 0.5 mM (ratio 1:10 with H_2O_2), achieved complete decolourization in 8 min, while it was 87% and 96% for the Fe^{2+} dose at ratio of 1:5 and 1:15 which stabilized in the reaction time of 6 min and 11 min, respectively (Fig. 4). A similar study (Punzi et al. 2012) reported complete colour removal of Remazol Red RR at 0.25 mM iron concentration in less than 30 min. At lower iron concentration, the degradation is less because of limited availability of OH^{\bullet} radicals to carry out oxidation. More iron concentration in the sample causes a slight reduction in the degradation rate of Remazol

dye. $FeSO_4$ dissociates as Fe^{2+} which acts as the catalyst to dissociate H_2O_2 generating OH radicals but the high iron concentration has a scavenging effect on hydroxyl radicals (Verma and Haritash 2019).

3.3.2 Influence of H_2O_2 concentration

It was observed that degradation efficiency increased from 61 to 100% when H_2O_2 concentration was increased from 1.0 to 5.0 mM fixed iron concentration of 0.5 mM and pH 3.0. At maximal concentration of 10.0 mM, complete decolourisation was observed in about 10 min against the reaction time of 8.0 min at optimized H_2O_2 level of 5.0 mM (Fig. 5). Hence, the H_2O_2 concentration of 5.0 mM was considered as the optimized dose. Several studies on various textile dyes have also reported that decolourization after reaching its maximum efficiency, later stabilizes and has no effect even after increasing H_2O_2 concentration. This is due to the scavenging effect of hydroxyl radicals and generation of OH_2 (15) radicals at higher concentration of H_2O_2 (Chacó et al. 2006):



The TOC analysis also reported the highest mineralisation of about 85% in the experiment with Fe^{2+} concentration of 0.5 mM and H_2O_2 concentration of 5.0 mM as compared to others.

Fig. 4 Effect of Fe^{2+} concentration (mM) on degradation of Remazol Red dye during Photo-Fenton treatment

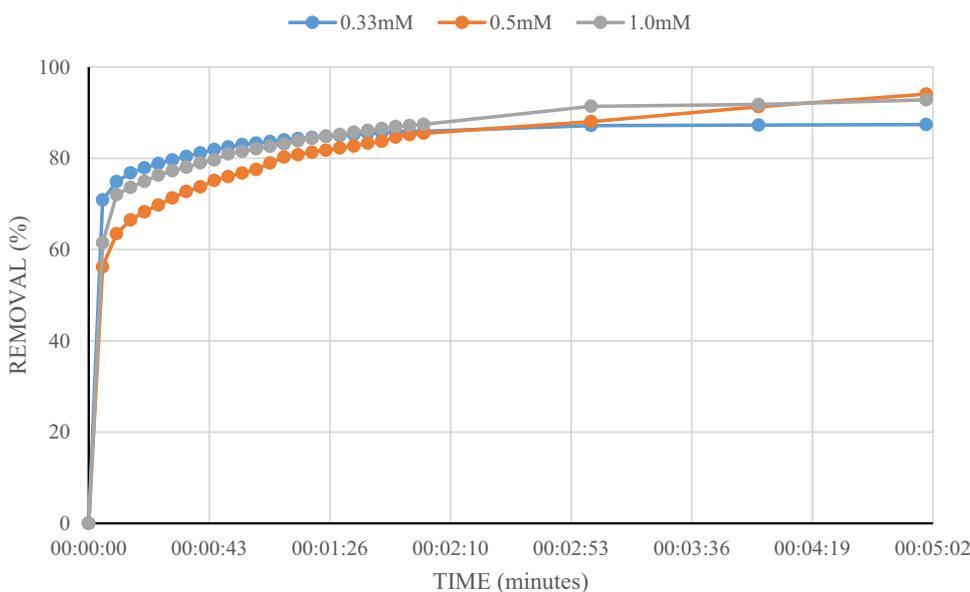
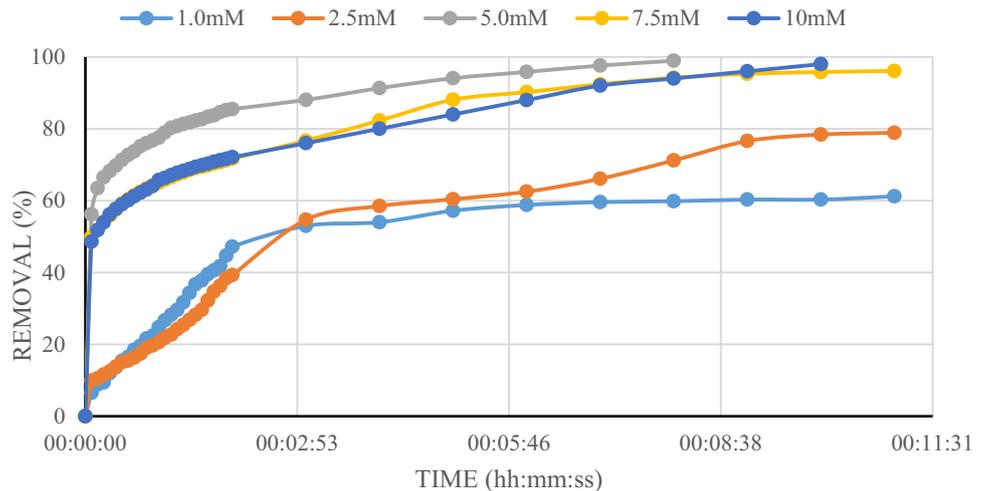


Fig. 5 Photo-Fenton treatment of dye at varying H_2O_2 concentration (mM) and pH 3.0



3.3.3 Influence of pH

The pH of the textile industry effluent governs the oxidation of organic impurities. Since the generation of $\bullet\text{OH}$ radicals is also pH dependent, under acidic conditions (2.0–4.0), maximum hydroxyl radicals are generated to carry out effective degradation. The current study considered the effect of pH values in the range of 1.0–5.0 with an optimized dose of Fe^{2+} and H_2O_2 ratio of 1:10. Quicker and complete decolorization (100%) of the dye was observed at pH 3.0 within 8 min of the reaction time. The complete degradation at pH 3.0 took almost half the time for maximum degradation than

at pH 2.5 and 3.5 as indicated in Fig. 6. The results were in strong agreement with the optimum degradation of organic pollutants, azo dyes like AO7 (acid orange 7) (Sharma et al. 2016), Mordant red 73 dye, Amoxicillin (AMX) (Verma and Haritash 2019), and several other studies at pH 3.0. It is reported that the stability of H_2O_2 and Fe^{2+} is also more at pH 3.0 (Kwon et al. 1999). Moreover, the degree of mineralisation was also found maximum (~85%) at pH 3.0.

As the pH of the dye solution increased from 1.0 to 3.0, decolorization also increased; however, it decreased at pH 3.5 and 5.0. Degradation was minimum (93%) at pH 1.0 achieved in 40 min of reaction time. Complex iron

Fig. 6 Effect of pH on degradation of Remazol Red dye during Photo-Fenton treatment

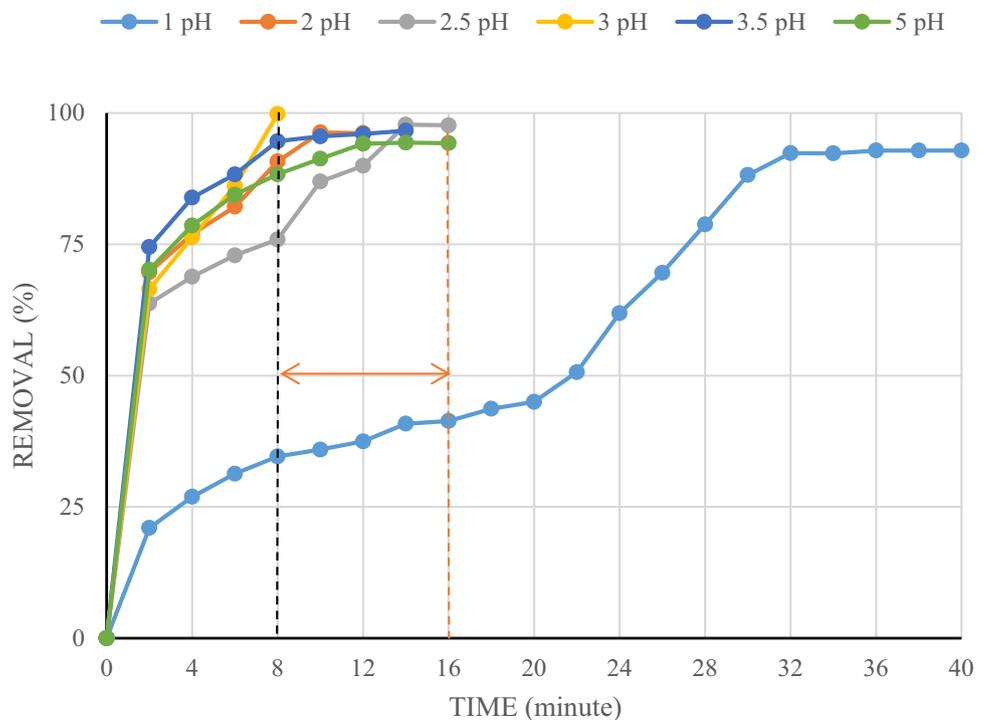


Table 2 Economic analysis of the operating cost of experiments

Treatment method	Energy per hour (kWh)	Time for treatment (minute)	Rate of Energy (per kWh) (INR)	Cost of electricity (INR)	Chemical consumed	Cost of chemical per litre (INR)	Cost of treatment in per litre (UD\$)
Photo-Fenton	0.3	8	8.50	0.34	FeSO ₄ ·7H ₂ O H ₂ O ₂ (30% w/v)	0.07 0.25	0.0090
Photocatalysis	0.3	60	8.50	2.55	TiO ₂ (P25) H ₂ O ₂ (30% w/v)	18.14* 0.25	0.29

*Calculated considering 92% recovery of TiO₂

species and oxonium (H₃O₂⁺) ions are formed and H⁺ ions scavenge the hydroxyl radicals at lower pH values (Kwon et al. 1999). In addition, with 2.0 > pH > 4.0, the oxidation potential of hydroxyl radicals decreases. On the contrary, the degradation efficiency at pH 5.0 was lesser (94%) than at pH 3.0, since both iron and H₂O₂ become unstable at alkaline conditions. Iron precipitates as hydroxide and does not react with H₂O₂ to form hydroxyl radicals, whereas hydrogen peroxide is destabilized to forms water and oxygen.

3.4 Recovery of TiO₂ and Economic Analysis

Since TiO₂ act as the catalyst in decolourization of dye, most of it can be recovered. However, some of the TiO₂ was lost during the experiments, while it goes through centrifuging before taking the observations over the spectrophotometer. A known amount of TiO₂ was added initially to the sample. After the sample got stabilised, it was oven dried at 105 °C. The recovery of TiO₂ was calculates as

$$\text{TiO}_2 \text{ recovered} = \frac{(w_1 - w_2)}{w_1} \times 100, \quad (16)$$

where, w₁ - initial weight of the TiO₂ added to sample, w₂ - final weight of the TiO₂ recovered post experiment.

Up to 70–97% of the TiO₂ added was recovered during the experiment under optimized conditions of photocatalysis. Therefore, optimization of TiO₂ contributes towards reducing the overall cost of treatment of the synthetic wastewater and making the process green and sustainable. Hence, recycling and recovery of TiO₂ could be foreseen as a sustainable approach for treating the wastewater.

The economic analysis of the operating cost of experiments for degradation of Remazol dye by photocatalysis and Photo-Fenton treatment was conducted. Since, Photo-Fenton and Photocatalytic degradation exhibited the maximum degradation efficiency; economic comparison of the respective methods was conducted with respect to reagents usage and energy consumption. The experiment were conducted under UV light (8 UV tubes) each having power rating of 36 W, magnetic stirrer of power rating 8.5 W; and air sparger of

power rating 3.5 W, thus, making a total power consumption of 300 W. The price of commercial electricity in Uttar Pradesh Province is INR 8.5 for 1KWh. In case of Photocatalytic treatment, the maximum colour removal efficiency (98%) was obtained in 60 min for 1.0 g/l TiO₂ dosage. The nano-sized TiO₂ used in the experiment costs INR 22,680 per 100 g; however, only 8% of the amount added was consumed (92% of it was recovered) during the process. The 8% of the TiO₂ consumed costs INR 3.63 per 200 ml (INR 18.14 per litre of the solution). Each litre of wastewater sample of strength 100 ppm with respect to Remazol Red consumed 0.3 KWh of power in 1 h while achieving the maximum efficiency making the energy cost approximately INR 2.55/-. Hence, the total cost is 0.29 US \$ per litre for 100 ppm synthetic dye solution of Remazol Red. In case of Photo-Fenton experiment, complete degradation (100%) was achieved in 8 min (~0.13 h). Hence, the total power of 0.04 KWh was consumed in 8 min, making the energy cost of 0.0090 US \$ per litre, which is the total cost for Photo-Fenton experiment (Table 2). Hence, it is observed that Photo-Fenton is a far cheaper and efficient method for colour removal from textile industry effluent.

4 Conclusion

Based on the results obtained in the present study, it is concluded that TiO₂-photocatalysis and photo-Fenton process are efficient and sustainable methods for removal of colour (dye) from the textile industry effluent. Since production of OH• radicals and their non-selective oxidative action is associated in both the processes, degradation of other organic impurities from industrial effluent is also expected. The optimization of regulating factors in both the processes can significantly enhance the efficiency towards degradation and reduce the treatment cost at the same time. The economic comparison based on the input of energy and materials revealed that photo-Fenton process is not only a rapid method for colour removal, but is also cost-effective, thus, making it a sustainable option for degradation of dyes in textile effluent.

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