Textile wastewater: What benefits does the photocatalytic degradation of dye offer for the removal of synthetic dyes from wastewater?

Environmental science research project: Group 16B

ABSTRACT

Advanced oxidation processes (AOPs) have been developed to overcome the drawbacks of traditional conventional processes in treatment of textile wastewater. Photocatalytic degradation of synthetic dyes and organic pollutants in wastewater using TiO2/UV and using Nano photocatalysts have been discussed.

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1. INTRODUCTION

Water is the most abundant natural resource available on the earth, but only 1% of the available water is suitable for human consumption [1]. With the gradual increase in the global population and accompanying industrialisation, the impact of environmental pollution on human health has also increased. Water pollution is causing deaths of almost 14,000 people daily [2]. Dyes belonging to the class of synthetic organic compounds are a main constituents of this pollution which are mainly released by food, plastic, textile, paper and pharmaceutical industries [3]. Large group of organic compounds are carried by industrial and textile dyes, which account more than 7,00,000 ton per year [4]. The precise amount of dyes produced on the planet are not known, also the amount of dyes discharged in the environment is also not known. It is a mere estimation that above 10,000 ton per year are produced [5]. If dye wastewater is once discharged into a particular waterbody, it can kill almost all the living bodies which include organisms, algae, fishes [2]. Synthetic dyes have a wide applications in industries which result in very large production, also the environmental pollution caused due to them cannot be ignored [5].

2. STATE OF ART

The main reason that supply of fresh water become unsuitable for consumption is constant contamination of natural water sources by organic and inorganic pollutants [1]. Some traditional physical and chemical processes such as usage of active carbon, filtration, coagulation [4], electrocoagulation, chemical precipitation, separation of pollutants [3] are used for the degradation and discoloration on modern dyes, which prove to be ineffective due to high composition of aromatic groups in the dye molecules, also bearing high operational costs. Moreover due to their non-destructive nature these methods do not degrade the dyes, but it just transfers the pollution from one phase to the other [3], [4]. Forgacs et al. [5] state that the these traditional degradation techniques are ineffective as these inorganic azo dyes are chemically stable. Out of the 18 azo dyes studied, 11 passed through the activated sludge process totally untreated, waste activated sludge adsorbed 4 of them and 3 were biodegraded. Majority of the synthetic dyes are resistant to the biodegradation and also are toxic, highly coloured, carcinogenic or mutagenic. So it is important to rectify these discharge before they are exposed to the environment [6].

Advanced oxidation processes (AOPs) have been developed in the past years [4], which have a potential of mineralizing most of the contaminants. Conventional oxidation process chemically attack the pollutants resulting in change of the chemical structure of the specific molecules, in comparison to these, the AOPs provide hydroxyl radicals having oxidation potential. Solar energy is used as an advanced natural source for oxidation [7], from which photocatalytic degradation is considered to be the most favoured and a greener technology as there are no wastewater problems and also the process is favoured by mild pressure and temperature conditions [4], [3]. Commercial dies can resist photodegradation, so optimal process conditions have to be selected for photocatalysis [5].

3. PHOTOCATALYTIC DEGRADATION OF SYNTHETIC TEXTILE DYES

Photocatalysis is being used in environmental fields such as demolition of aqueous pollutants, purification of air, metal recovery [8]. Photocatalytic degradation is an advanced oxidation process (AOP) that uses ultraviolet light (UV) from the sun or nano catalysts that react with the different organic pollutants [1]. Due to the efficiency of this process and also the ability to operate at normal temperature and pressure conditions it is gaining importance all over the world. After the failure of all conventional technologies used for decolouration or degradation of toxic synthetic dye effluents from textile waste water, there was a need for a new reliable and efficient dye degradation process. Semiconductor based photocatalytic degradation is a technique developed in 1972, receiving much importance as far as wastewater treatment and terminating the deterioration of the environment is considered [9]. Figure 1 shows graphical abstract of how photocatalytic degradation takes place (data from [10]).

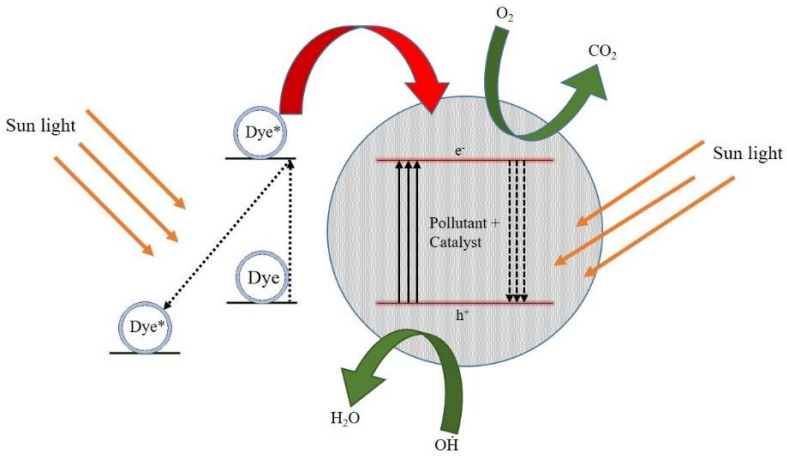


Figure 1: Graphical abstract of photocatalytic degradation technique (data from [10]).

3.1 Photocatalytic degradation of textile dyes using TiO_2/UV

AOPs includes heterogeneous photocatalysis of organic compounds using semiconductor oxides such as TiO_2, ZnO, WO_3, ZnS, SnO_2, etc. [8] out of which nano-titanium dioxide (TiO_2) is widely used due to optical and electrical properties, low cost, high photocatalytic activity, high chemical stability, ability to work at ambient pressure and temperature conditions, resistance to chemical corrosion [4], [8]. The crystalline structure of TiO_2 can gradually affect its photocatalytic activity. Also it was observed that the catalytic ability of TiO_2 was hampered by its particle size, increase in the degradation was seen as the particle size of TiO_2 decreased [6]. The photocatalytic activity of TiO_2 emerges from its electronic structure and photoelectric properties. This technique can be explained by the band theory which consists of two separate bands, valence band and conduction band. It has a band gap energy of 3.2 eV. When UV light is irradiated over the surface of TiO_2, with an equal or greater value of the band gap energy of TiO_2, its surface is stimulated and it creates a hole-electronic pair, having the properties of oxidation as well as reduction [9].

According to Yasmina et al. [8] the process of photocatalytic degradation can be summarized in the following stages of reactions:

Stage A - Activation of TiO_2

Irradiation of light on photocatalysts to boost the formation of electron-hole pair in metal oxide

$$TiO_2 + h\nu \rightarrow TiO_2 + e_{bc}^{-} + h_{bv}^{+}$$

Reaction 1: Activation of TiO_2 by UV

Stage B – Separating electrons and holes

$$TiO_2 (e_{bc}^{-} + h_{bv}^{+}) \rightarrow \text{Release of heat}$$

Reaction 2: Release of heat

Stage C – Oxidation and Reduction

$$O_{2,ads} + e_{BC}^{-} \rightarrow O_{2,ads}^{-}$$

$$A + e_{BC}^{-} \rightarrow \text{Reduction}$$

Reaction 3: Reduction reaction in photocatalysis

$$H_2O + h_{bv}^{+} \rightarrow OH^{\circ}_{ads} + H^{+}$$

$$OH_{ads}^{-} + h_{bv}^{+} \rightarrow OH^{\circ}_{ads}$$

$$R_{ads} + h_{bv}^{+} \rightarrow R^{\circ}_{ads}$$

Reaction 4: Oxidation during photocatalysis

Stage D – Photocatalytic degradation of organic molecules

$$O\dot{H} + \text{Pollutants} + O_2 \rightarrow CO_2 + H_2O + \text{Product intermediates}$$

Reaction 5: photocatalytic degradation of pollutants

A UV/visible spectrophotometry test was carried out by Yasmina et al. [8], where they followed the photocatalytic technique, hence determining different pollutant concentrations at different reaction times in UV by spectrophotometry. A spectrophotometer of type (Scan Spectro 80DVUV/Vis) spectral range of 190 to 1100 nm was used. Two tests were carried out, one with direct photolysis under UV and other with UV and glass plates treated with TiO_2/UV. Figure 2 shows the experimental setup of photocatalytic reactor [6], and graph 1 shows the result of the tests.

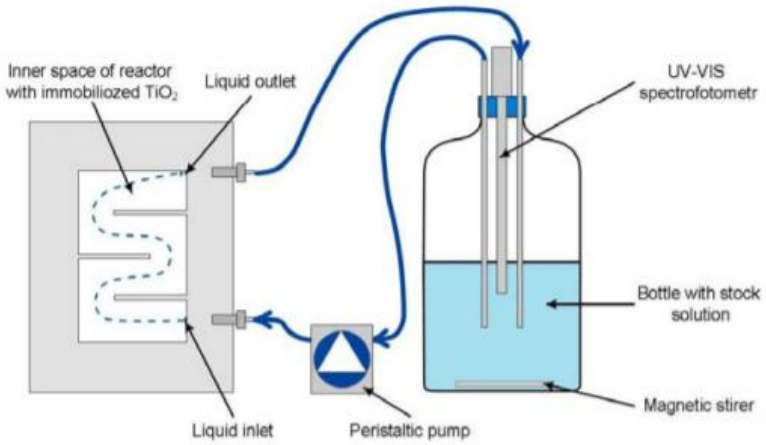


Figure 2: Experimental setup of photocatalytic reactor [6].

According to the studies, TiO_2 photodegradation technique can degrade up to 3000 organic compounds that are difficult to degrade.[9] Table 1 shows different applications of TiO_2 based photocatalytic degradation for treatment of organic pollutants in wastewater treatment.[9]

Wastewater type	Pollutant	Catalyst	Reference
Dye wastewater	Methyl orange Alkaline red dye Rhodamine 6G Anthraquinone dye	Y-TiO_2-HPW TiO_2-Fenton TiO_2 N-TiO_2	[11] [12] [13] [14]
Pharmaceutical wastewater	Amoxicillin Penbritin	TiO_2	[15]
	Cloxacillin Oxolinic acid	TiO_2	[16]
Pesticide wastewater	Kappa furan pesticides Armour mix phosphorous Alon Organophosphorus pesticide	TiO_2 TiO_2 TiO_2-SBA TiO_2	[17] [18] [19] [20]
Explosives wastewater	TNT RDX HMX	TiO_2	[21]
Chlorine hydrobenzene wastewater	Chlorinated Phenol	TiO_2	[22]
Nitrobenzene wastewater	Nitrobenzene	$H_3PW_{12}O_{40}/TiO_2$	[23]

Table 1: Different applications of TiO_2 based photocatalytic degradation for treatment of organic pollutants in wastewater treatment

3.2 Photocatalytic degradation of textile dyes using Nano photocatalysts

Nanotechnology in the field of nanoscience, which uses nanometer as a scale level is an emerging technology in the field of wastewater treatment and also with respect to various environmental problems. Nanoparticles are those that have size of at least less than 100nm of one dimension, various nanomaterials developed are in the form of nanowires, nanotubes, particles, films, etc[1]. Nanopowder particles show a noticeable increase in the photocatalytic action, hardness, as they have a combination of high surface area to volume ratio, small particle size[24].

Loghman K et al[4] investigated the degradation of direct green 6 and reactive orange 72 using Nano-strontium titanate under 20 and 400 W UV irradiation.

Nano-strontium titanate powder (P.N.517011) and nano-titania (p25) were provided by Sigma Aldrich and Degussa company and commercially available direct green 6 and reactive orange 72 were obtained from Alvan Sabet company, Iran.

Dye solution was first prepared by distilled water and then the Nano materials were added in different compositions. For the first 15 minutes the solution was stirred without UV irradiation so as to achieve dye adsorption equilibrium. The solution was radiated under two lamps of 20W and 400W for a total for 3 hours with continuous stirring at 200 rpm and temperature of 25°C, with dyes having pH of 6.6 for Reactive orange dye and 6.4 for direct green dye. The photocatalytic degradation and decolourisation efficiency were calculated as follows:

Efficiency (%) = $\frac{C0-Ce}{C0} * 100$

C_0 and C_e are initial and final concentrations of dye before and after photo-irradiation.

The efficiencies of different nanocatalysts for photocatalytic degradation of organic pollutants in wastewater are listed in table 2 [1].

Table 2 Photocatalytic efficiency of various nano-catalysts for removal of organic pollutants from wastewater.

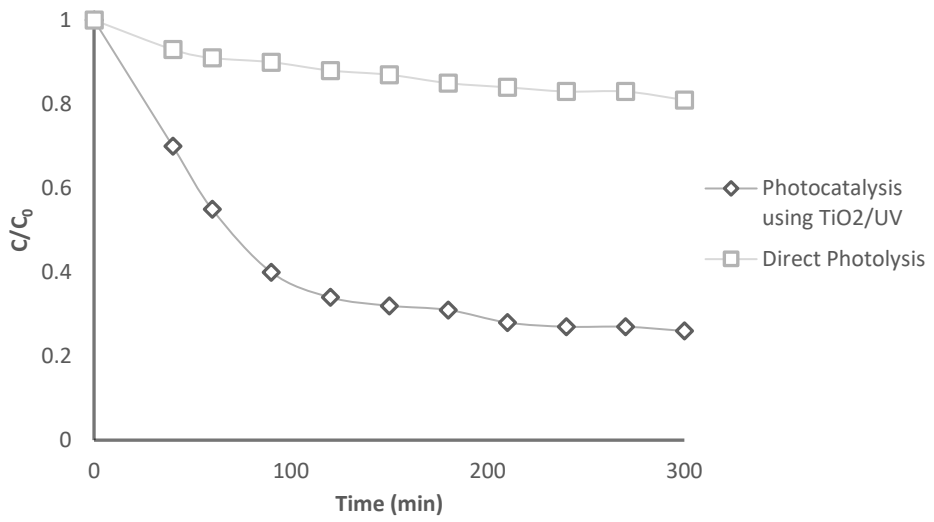
Catalyst	Light region	Conditions	Pollutant	Results	Reference
$Y_2O_3:Eu^{3+}$	350–400 nm (UV)	Cat. Dose = 0.24 g/L, Duration = 120 min	Methylene blue	Up to 90% degradation efficiency of methylene blue was observed	Kumar et al. (2015)
Ti_2CO coatings	420 nm (Vis)	Duration = 3 h	Methylene blue	Removal of Methylene blue form 10 μ mol/L to around 8.5 μ mol/L was observed	Guan et al. (2016)
TiO_2/trititanate	UV–Vis region	Cat. Dose = 1 g/L, Duration = 2 h	Rhodamine B	The degradation efficiency of Rhodamine B of >91% was achieved	Chen et al. (2015)
AgBr/ZnO	410 nm (Vis)	Cat. Dose 1 g/L, pH = 6.86 Duration = 4 h	Methylene blue	Up to 87% of methylene blue was decomposed by AgBr/ZnO after 240 min	Dai et al. (2014)
3D SnO	365 nm (UV)	Cat. Dose = 2 g/L, Duration = 2.5 h	Methyl orange	Photocatalytic degradation of methyl orange was 83% after 150 min	Cui et al. (2015)
ZnO nanorods	365 nm (UV)	Cat. Dose = 1 g/L, Duration = 42 min	Rhodamine B	The quenched catalyzed greatly improved the photocatalytic degradation of Rhodamine B	Fang et al. (2015)
Zero-valent nano-copper	Visible region	Cat. Dose = 0.16 g/L, Duration = 80 min	Methyl orange	Up to 35% degradation of methyl orange was achieved with in 80 min.	Liu et al. (2016)
Biomorphic TiO_2 photonic crystal	>420 nm (Vis)	Cat. Dose = 1 g/L, Duration = 4 h	Methyl orange	Up to 30% degradation of methyl orange was achieved with in 4 h.	Wang et al. (2016)
$CuFe_2O_4@C_3N_4$	>420 nm (Vis)	Poll. Cone. 0.04 mM, Duration = 3.5 h	Orange II	Nearly 98% of Orange II is degraded within 210 min photocatalysis	Yao et al. (2015)
$Ag_3PO_4/BiPO_4/Cu$ (tpa).grapheme	⩾420 nm (Vis)	Duration = 2 h	Atrazine herbicide	The nano composite showed more 80% photocatalytic degradation of Atrazine herbicide	Mohaghegh et al. (2015)
Carbon nanorods-TiO_2	⩾420 nm (Vis)	Cat. Dose = 0.2 g/L, Duration = 4 h	2,4-dichlorophenol	Up to 96% of photocatalytic degradation of 2,4-dichlorophenol was achieved with in 8 h	Ortega-Liebana et al. (2016)
Fe–TiO_2 coated with side-glowing optical fibers	Visible region	Duration = 8 h	Rhodamine B	Up to 90% of Rhodamine b removal can be achieved with in 8 h of photocatalysis	Lin et al. (2015)
Polyaniline/ZnO	Visible region	Catalyst dose = 0.4 g/L, Duration = 5 h	Methylene blue and malachite green dyes	Dyes removal with 99% efficiency was achieved under natural sunlight	Eskizeybek et al. (2012)
Immobilized TiO_2	300–800 nm	Duration = 96 h, Shaking = 75 rpm, Pollutant conc. = 5 mg/L	Pharmaceutically active compounds (propranolol, diclofenac, and carbamazepine)	Photocatalytic efficiency of 100% for propranolol, 100% for diclofenac, and 76% for carbamazepine was achieved	He et al. (2016)
ZnO/Zn	365 nm (UV)	pH = 6–8, Duration = 4.5 h	Methylene blue	Complete degradation of methylene blue was achieved (98%)	Lin et al. (2014)
ZnO–FeO-clinoptilolite	Solar light	pH = 8.3, Catalyst Dose = 0.1 g/L	Real Fish pond wastewater	More than 80% degradation efficiency was achieved	Bahrami and Nezamzadeh-Ejhieh (2014)
Ag–TiO_2/Ag/a-TiO_2	425 nm (Vis)	Duration = 90–110 min, *E. coli* population = 10^5 cfu	Escherichia coli bacteria	The relative rate of reduction in the bacteria was improved to 4.7×10^{-2}/min corresponding to 110 min in the visible	Akhavan (2009)
CuO/ZnO	Visible region	pH = 6.0, Duration = 1 h	Acid Red 88 dye	In the presence of external electron acceptors such as peroxomonosulfate, peroxodisulfate and H_2O_2, CuO-ZnO shows approximately 2 times higher photocatalytic degradation of Acid Red 88 compared to that ZnO	Sathishkumar et al. (2011)
Graphene-	Visible region	Duration = 1 h, Methylene	Methylene blue	The Graphene-$Co_xZn_{1-x}Fe_2O_4$ heterostructures showed more	Nazim et al.

Table 2: Photocatalytic efficiency of various Nano-catalysts for removal of organic pollutants from wastewater (data from [1]).

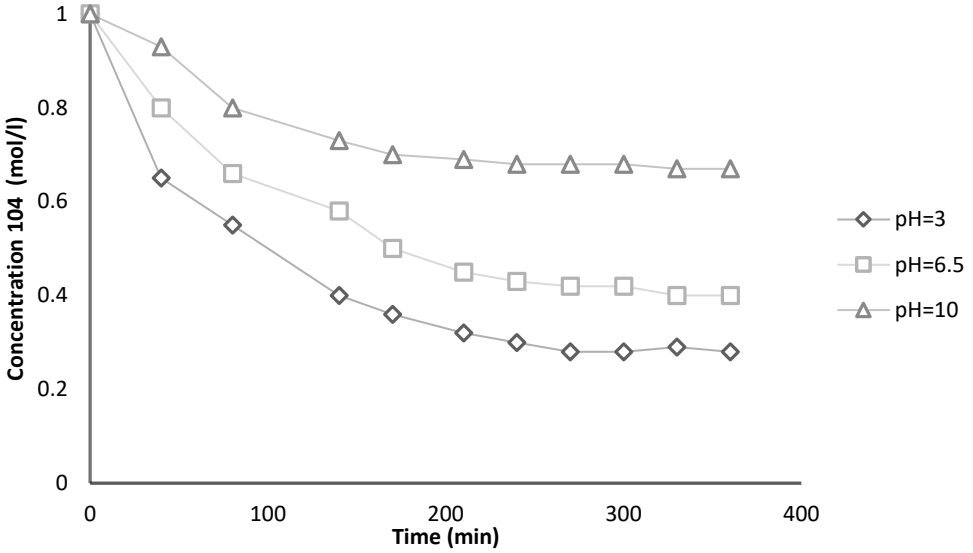
4. RESULTS AND DISCUSSIONS

4.1 Photocatalytic degradation of textile dyes using TiO_2/UV

From the report by Yasmina et al. [8], from graph 1 we can clearly see that the degradation of pollutants by TiO_2/UV is much faster than by UV Photolysis (Reaction time of 6 hours was considered). Graph 2 shows the degradation rate for different pH values of the solution. We can see that the degradation is accelerated for aqueous pH value (pH=3).



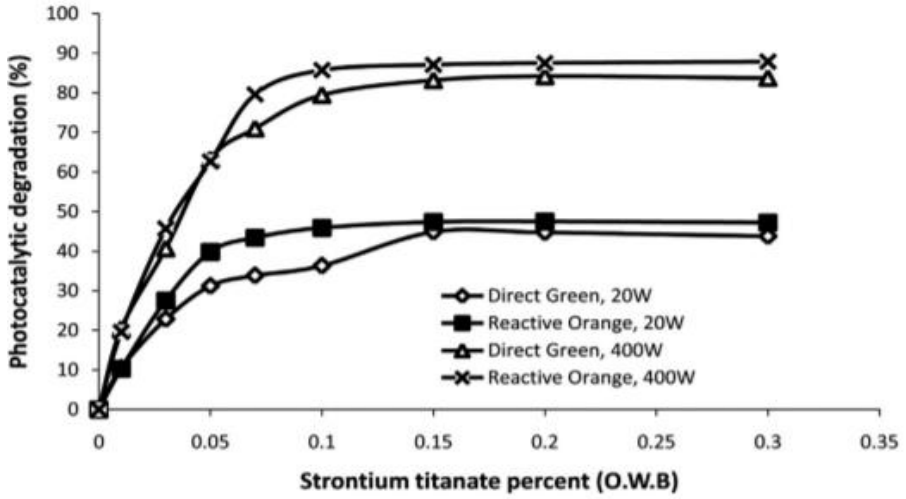
Graph 1: Comparison between the degradation of pollutant by direct photolysis (365 nm) and degradation by TiO2 / UV (λ = 365 nm) (data from [8])



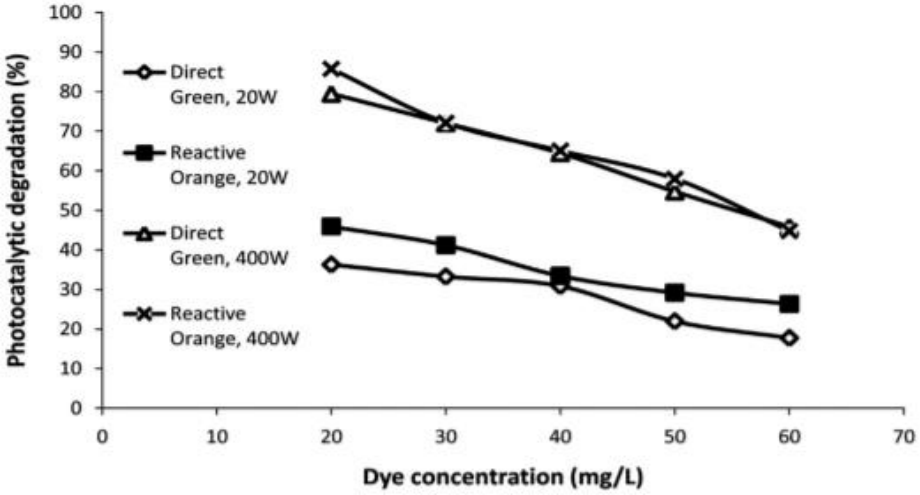
Graph 2: Degradation depending on different pH values. (data from [8])

4.2 Photocatalytic degradation of textile dyes using Nano photocatalysts

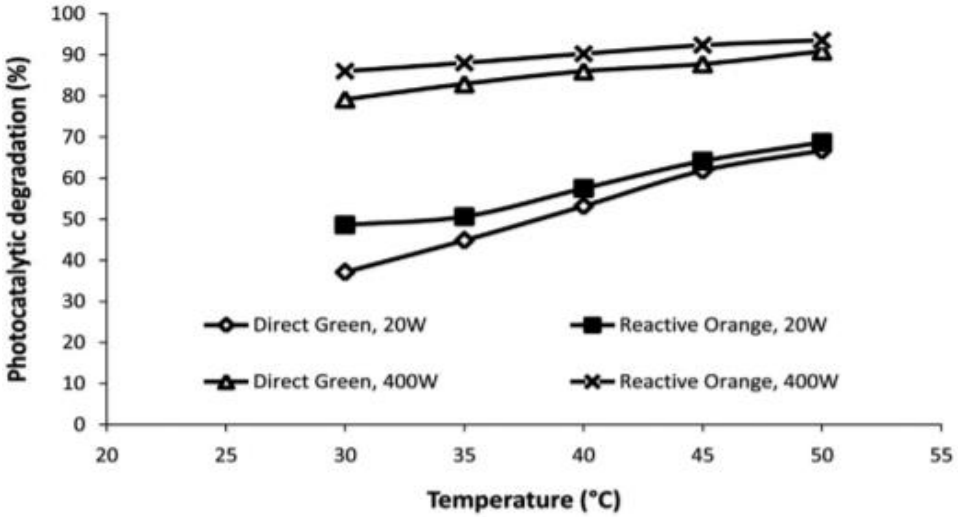
Loghman K et al. [4] observed the percentage dye degradation in presence of a nanocatalyst strontium titanate with direct dye degradation and photocatalytic degradation, graph 3 shows that by increasing nano-strontium titanate concentration, the degradation of dye increases for irradiation of 400W UV lamp compared to 20W UV lamp. Graph 4 shows that by increasing the dye concentration, the photocatalyst degradation decreases rapidly. At high dye concentrations, the UV light is absorbed by the nanocatalyst $SrTiO_3$ instead of the dyes, which decreases its efficiency. According to the results of Loghman K et at. [4], graph 5 shows that with increasing temperature the dye degradation efficiency also increases. The reaction completes more efficiently and also the oxidation rate increases with increase in temperature.



Graph 3: Comparison diagram of photocatalytic reactive and direct dye degradation with different percent of Nano-strontium titanate based on weight of bath [4].



Graph 4: Comparison diagram of photocatalytic dye degradation with different dye concentrations [4].



Graph 5: Comparison diagram of photocatalytic dye degradation in temperature range of 30–50 °C [4].

5. CONCLUSION

Water being the most essential need of all the living beings on this planet, it is necessary to prevent pollution of waterbodies. Today it is possible to treat the household, industrial and commercial wastewater more efficiently than with older conventional technologies, thanks to the upcoming advanced wastewater treatment techniques. Photocatalytic degradation being one of them, it is a highly efficient, reliable, having low cost and environment friendly technique. Major drawback is that it degrades and decolorizes the textile wastewater only by absorbing the UV light which is just 4% of the natural sunlight. The research in photocatalysis is required on catalysts with higher photo catalysis ability and also high response to light range for photocatalysis. Nano catalysts have a high surface area to volume ratio which increase the photon absorption ability on photocatalyst surface. It is mostly applied to small processes where less nanoparticles are required as they are not yet cost-effective as compared to conventional material like activated carbon. Further research is required to develop cost-effective methods for nanoparticles synthesizing and also increasing their efficiency for large scale industrial applications.

6. References

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