

A review on photodegradation of various dyes using photocatalysts

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Abstract

Photocatalytic degradation is a recent capable technique for reducing the effects of various dyes and pesticides. The response of the spectroscopic data at the ultraviolet range is 200-350nm; whereas, researchers have attempted to raise the spectral range to 350-800nm, which is a visible light range of the spectrum. Therefore, photodegradation of the effluents can happen efficiently in the visible light range of the spectrum using doped or undoped photocatalysts. Photocatalytic degradation of many dyes has been investigated in the earlier and present times based on many photocatalysts, which is reviewed in this paper. The effects have been examined using spectroscopic and analytical methods of modern technology.

Keywords: *Dyes, Pesticides, Photodegradation, Photocatalysts.*

1. Introduction

The most available profuse energy source which is renewable is the solar energy. It's enormous potential can sustain and improve lives. Photosynthetic process is a universal process where the energy of the light is converted to chemical energy. Decrease of intensity of a substance or a dye solution can be obtained by exposure of radiation towards that substance. This can also include change in the properties of the substance or a solution such as change in color, density, oxygen demand and vice versa. The process can be assisted by the addition of photocatalytic suspension. Light emitted can have unequal

intensities due to environmental or atmospheric factors that will have an influence on the dye solution or any other substances to be degraded with it. Artificial light sources can be used to maintain stable intensities away from clouding and other environmental factors. Thus, solar lights and artificial lights have been used in the photodegradation process of many dyes in the industries.

Dyes are broadly used in commercial industries and they are found as waste products in run off disposal water [1]. Dyes are colored and can be harmful for organisms and some of them can be noxious in nature. Methods such as chlorination, ozonation, flocculation etc., is used remove the toxicity. The unfavorable character of these dyes transfers their harmful effects to different places causing further pollution in the ecosystem. Thus treatments of these dyes are necessary, which can reduce the residual concentration of the dyes [2].

Photodegradation is the reaction or effect of the solar light on the surface of any substance, dye solution, industrial waste effluents. The energy of the light radiation can break down and dissociate certain parameters of the unwanted materials which are unfavorable to the human and aquatic lives. This can cause degradation over a prolonged or quick interval of time. Chemical reactions can happen during the photodegradation reducing harmful effects of the substance, pathogens, and wastes of industries. Intensity, concentration, pathogenic activity, hazardous effects on soils, oceans, well water can also be reduced by photodegradation. This sort of photodegradation can be more effective when a

catalyst is added to increase the rate of degradation. This emerges the concept of photocatalytic degradation. Degradation using photocatalysts a recent trend in scientific research which involves usage of non-metals, semiconductors, nanoparticles, polymers and other grafted copolymers to increase the effectiveness of the undergoing reactions.

2. Literature Survey

Acridine Orange

Solar light mediated Acridine orange dye degradation has been conducted successfully. The dopant tetraethylammonium tetrafluoroborate with titanium dioxide has led to carbon, nitrogen, fluorine, boron doped TiO₂, used as photocatalysts for the photodegradation of Acridine orange dye. The analysis with Scanning Electron Microscope was performed with a process called gold- palladium sputtering. The X-Ray diffraction observed a phase of Crystallinity. The X-Ray photoelectron spectroscopy has been observed with excitation of Al K α . Digital illumination meter has been used for the measurement of solar intensity [3].

Blue Methylene

Solar illumination and Ultraviolet light usage in degradation of Methylene blue dye has been conducted. Magnetite and H₂O₂ has been used as a photocatalyst because of its semiconducting ability. The properties of magnetite have been able to break Methylene blue bonds. Decolorization induced by photoreduction has been explained. Factors affecting the dye removal, parameters such as dye discoloration from deep color to light color, Catalytic dosage, the concentration, light intensity, pH, and temperature have been investigated [4].

Crocein Orange

Ultraviolet radiation was received from elevated pressure mercury lamp and the photodegradation was attempted with Crocein orange dye using anatase form of Titanium dioxide as photocatalyst. The experiment has been conducted in Pyrex reactors and involves total oxidization of the dye, possibility of total degradation and mineralization of carbon to carbon Dioxide. The results suggest that TiO₂ and UV mediated reaction not only allows decolorization of the dye but also detoxification of the dyes involved. COD, TOC, pH variations, mass balance has been investigated [5].

Disperse Dye

UV-C light emitted by low pressure mercury arc lamp in a plexiglass reactor confined in a quartz sleeve has been used in the experiment. Photochemical reductive cleavage with silicadodecatungstic acid along with the solvent isopropanol initiates re-oxidation potentiality. Dispersants, leveling agents, buffer solutions were altered to observe change in the photodegradation parameters and how that would influence the kinetic properties of the Disperse dye. Kinetics of decolorization was first ordered and photodegradation rate of kinetics was limited to zero order in spite of the UV light penetration [6].

Eosin Y

Visible light irradiation using tungsten filament lamp was a source of power for degrading of Eosin Y dye and the photodegradation was attempted using prepared Silver Bromide and Zinc Oxide nanocomposites and separately with Zinc Oxide. Photo mineralization, dosage of photocatalyst, concentration of the dye, existence of inorganic salt, observation of the activity of the photocatalysts was studied. XRD pattern observed using Cu-K α excitation, Field Emission SEM, HRTEM was characterized for the samples and the photocatalytic performance was credited towards light generated electron-hole pairs [7].

Fuchsin Basic

Visible light irradiation of Basic Fuchsin dye using iron zinc cuprate photocatalyst made by ceramic technique and was observed spectrophotometrically. Pseudo-first order kinetics was followed during the degradation of the dye. The effect of concentration of the dye was studied during the process. The light intensity was varied by changing the light source distance and the surface of exposure of radiation. Conductivity measures the concentration of ions, pH variations are analyzed, chemical oxygen demand decreases after the exposure of radiation, total dissolved solid and dissolved oxygen were investigated [8].

Gentian Violet

Ultraviolet light irradiation of Gentian Violet dye using Titanium dioxide P25 Degussa as a photocatalytic source has been investigated. Aqueous dispersion of Titanium dioxide photocatalyst has an effect on the method of degradation and mineralization process. Adsorption quantity of semiconductor, number of carbon atoms and the

functional group influences the photodegradation process. UV spectrum has given sufficient information about the degradation through the wavelength and absorbance criteria. Adsorption effect, light intensity and pH have been studied in this work [9].

Hazardous Dye- Tartrazine

Ultraviolet light irradiation of hazardous dye Tartrazine using Titanium dioxide as photocatalyst placed in a Quartz glass photoreactor has been investigated. COD determination was done by open reflux method. The decolorization rate constant was determined. The rate of dye degradation followed Pseudo- first order and degradation efficiency has been high on addition of H₂O₂ with TiO₂ particle. Experiment with different pH, catalytic dosage, changing the dye concentration of the solution and effects of electron acceptor H₂O₂ were studied [10].

Indigo Carmine

Solar light on the dye named Indigo Carmine using neodymium doped Titanium dioxide on graphene oxide nanocomposites as photocatalyst has been investigated. The spherical nanocrystalline size of the prepared photocatalyst has stimulated high photodegradation. TiO₂-GO and different concentrated Nd-TiO₂-GO were observed to have more light absorption in the visible light range compared with TiO₂ alone. FTIR, SEM, TEM, Raman spectroscopy, UV-Vis spectroscopy of the nanocomposites were characterized. The band gap was measured for the synthesized nanocomposites [11].

Janus Green

Ultraviolet light irradiation of Janus Green dye using silver modified Titanium dioxide as a photocatalytic source has been investigated. Surface enhanced Raman spectroscopy and vibrational spectral studies has been employed to study the photodegradation of the dye. UV-VIS-NIR spectrum has been recorded for solid Janus Green dye. Photocatalytic studies and electrochemical studies have been compared, also includes the similarity between reduction and photodegraded product. Comparison between electrochemically degraded product and photochemically degraded product has been compared [12].

K Brilliant Red

UV lamp radiation with wavelength 228 to 400nm on Brilliant Red K-2BP dye using Titanium dioxide supported with activated Carbon surface has been investigated. The experiment was conducted in BFBPR reactor which is a double cylinder like reactor. Addition of Na₂SO₄, pH value and initial dye concentration, alkaline suspension influenced photodegradation of K-2BP. Langmuir- Hinshelwood model was applied; isotherm absorption and correlation plots were based on Beer-Lambert's law. The mechanism of adsorption was explored and FTIR spectrum was taken for proof [13].

Lissamine fast Yellow

Halogen lamp irradiation almost comparable to sunlight surrounded with aluminum reflectors in a slurry type batch reactor with thermostatic water circulation was used for the investigation of the dye Lissamine fast yellow. The photocatalyst Zinc oxide along with H₂O₂, FeCl₃, O₂, Na₂CO₃ has been employed to study the degradation of the dye. The pH of the prepared samples has an important effect on the reaction rate. Mineralization of the dye in aqueous phase has been observed at the end of the process. Removal of COD, NO₃⁻ and SO₄²⁻ release of ions and UV-Vis spectrum were investigated. Comparative study with both artificial and solar light was done on the dye. Thermometer, conductivity and pH meters were incorporated in the reactor [14].

Methyl Green

UV lamp radiation on Methyl Green with ZnO-TiO₂ photocatalyst supported with natural Tunisian clay as support was investigated. These were characterized by SEM, HRTEM, EDX micro analysis was performed and the experiment was conducted in a quartz reactor. COD was determined by digestion method in the reactor. TEM images confirm the morphology of the materials involved. Catalytic dosage, pH, dye concentration, UV intensity, varied oxidants was evaluated. Complete dye mineralization was obtained on photodegradation with the catalysts [15].

Naphthol Blue Black

Sunlight mediated Naphthol blue black degradation of dye has been conducted successfully with Ce_{1-x}Mn_xO₂ [x= 0, 0.1, 0.3, 1] as photocatalyst. The samples were characterized by XRD, FTIR, surface area and thermal techniques. Cerium oxide had low activity in degradation compared to Mn⁴⁺ in Cerium oxide crystal lattice on degradation on Naphthol blue

black degradation. Thermal analysis of cerium-manganese hydroxide co-precipitate for the reaction of diffusion of solid state and decomposition temperature were analyzed. Experimental conditions like catalytic variation without radiation, without aeration, changing pH conditions were studied [16].

Orange G

Ultraviolet mercury vapor lamp radiation on Orange G dye with Copper and Aluminium Oxide photocatalyst in a quartz photoreactor was investigated. Reduction of total organic carbon was analyzed using TOC analyzer. The efficiency of decolorization was observed to be almost 85% in the Orange G dye. Degradation was performed at low and high pH with the dye. Effect on flow rate of ozone were analyzed and showed advantages in reduction of organic wastes. Catalyst loading was increased to increase the photon quantity absorption in turn the degradation rates too and the amount of catalyst used was optimized for better degradation process [17].

Para-Phenylenediamine

Para-Phenylenediamine (PPM) is an important ingredient of hair dye. Low pressure lamp of mercury radiation on para-phenylenediamine with magnetic poly methylmethacrylate coated on Titanium dioxide as photocatalyst was investigated. The experiment was conducted in an air tight reactor of Pyrex glass with features to maintain temperature. Durability of the catalyst has been demonstrated. The samples have been characterized by SEM, TEM and EDS. BET surface area has been observed and the conditions of experiment were varied to present the relatability between COD reduction and PPM reduction [18].

Quinoline Yellow

Tungsten lamp UV light radiation of Quinoline Yellow dye using powdered Titanium dioxide as a photocatalyst in a photoreactor has been investigated. Concentration of dye and photocatalyst, pH change, concentration of substrate and electron acceptor parameters were examined. The rate of degradation of Quinoline Yellow along with COD removal and decolorization of the dye was observed. Titanium dioxide in the presence and absence of UV light, with and without oxidation process on the dye were experimented. Degradation with Hydrogen peroxide was performed and compared to other degradation rates [19].

R Bismarck Brown

UV light irradiation of Bismarck Brown R using Titanium dioxide as photocatalyst in a batch reactor made up of Pyrex glass has been investigated and characterized by SEM, EDS and FTIR. Percentage of degradation, pH change from 3 to 7, concentration of dye and photocatalyst were examined. Sol gel method was used to synthesize Titanium dioxide. Ultraviolet spectrum was taken for the degrading dyes at various concentrations. The rate of dye degradation followed Pseudo first order. Langmuir Hinshelwood equation was applied and efficiency of degradation was observed at pH 3. Organic Contaminations can be degraded by this [20].

S Alizarin Red

UV light irradiation on Alizarin Red S with Zinc oxide nanoparticle as photocatalyst in a double walled reaction container has been investigated and characterized by FESEM, TEM, XRD, EDS and UV spectroscopy. Zinc oxide photocatalyst was prepared using low temperature analytical tools. The photocatalyst performance compared to commercial photocatalyst. Compositional properties, structural properties and morphology of the photocatalyst were also characterized in this [21].

Toluidine Blue

UV light irradiation of Toluidine Blue dye using Magnesium Oxide as photocatalyst in a closed semi-batch reactor made up of Pyrex glass was investigated. Operating parameters like catalytic dosage from 10 to 70 mg, dye concentration, pH of the solutions were studied. Nitric acid and sodium carbonate were used to adjust the pH of the solution. Degradation was in aqueous solution. The dye removal was favored in high acidic medium and pseudo first order was followed. Visible spectrometer has been used to analyze the samples collected. Percentage of dye removal has been studied at various conditions [22].

Violet Crystal dye

Visible and UV light irradiation of Crystal Violet dye using Gold doped Titanium dioxide in solution which is aqueous has been investigated. Undoped and doped Titanium dioxide as colloidal suspension made by sol gel process has been done. The photocatalysts have been characterized by TEM, XRD and UV spectral analysis. UV exposure accelerates the degradation. XRD and TEM determine the particle size. The intensity of absorption peak decreases on degradation. Excitation from valence band to

conduction band has been observed. Superoxide radical anion formed by the combination of molecular oxygen has been observed [23].

Xanthene Dye

UV light irradiation of Xanthene dye using Titanium dioxide as photocatalyst in a photoreactor was investigated. The pH values show the dependence of pH in the process. Acidic conditions revealed better results because of the opposite charges between TiO₂ which is positive and the dye which is negative. The toxicity has been reduced in the process. Anaerobic process was implied in the experiment. The photoreactor ensured oxygenation process in it. Methanogenic activities were performed followed by respiratory inhibition analysis. Dissolved oxygen was measured using probe polarographic oxygen connected to DO meter. COD removal was studied in the experiment [24].

Y Chrysoidine

UV light irradiation of Chrysoidine Y using Zinc Oxide, Titanium dioxide as photocatalyst in a photoreactor made up of Pyrex glass with a molecular oxygen supply was investigated. Total organic carbon was measured in turn measuring the mineralization process of the dye. Control experiments were performed in blank solution in all cases of solutions of degradation. The rate of degradation for depleting total organic carbon and dye decomposition on basis of pH change was revealed. Absorption intensity was measured for the dye degradation. Optimum conditions of degradation were determined in the experiment [25].

3. Conclusion

The photodegradation and adsorption of various dyes using different catalysts have been investigated by researchers. Efficiency of adsorption of dyes onto the photocatalysts was achieved as per various factors influencing the degradation process. Ultraviolet light illumination helped in achieving the efficiency of adsorption high by the activity of photocatalyst. Changes in pH had an influence on the adsorption efficiency of the dyes at the right pH. Pretreatments along with the combination photocatalytic treatments of dye and waste water could work wonder for degradation of pollutants.

References

[1] Khalek and Mahmoud, Visible light assisted photocatalytic degradation of crystal violet, bromophenol

blue and eosin Y dyes using AgBr-ZnO nanocomposites. *Environmental Nanotechnology, Monitoring & Management*, Vol 9: 164-173, (2018).

[2] Mandavgane and Mohabansi, Photocatalytic removal of Eosin Y by TiO₂ and ZnO catalysts, *Emerging Materials Research*, Vol 3 (Issue EMR3): 144-148, (2014).

[3] Lee and Kim, Anion co-doped Titania for Solar Photocatalytic Degradation of Dyes, *Carbon Letters*, Vol 9 (No.2): 131-136, (2008).

[4] Reza and Kurny, Photocatalytic Degradation of Methylene Blue by Magnetite+H₂O₂+UV Process, *International Journal of Environmental Science and Development*, Vol.7 (No.5): 325-329, (2016).

[5] Lachheb and Puzenat, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, *Applied Catalysis B: Environmental* 39, 75-90, (2002).

[6] Alaton, Homogenous photocatalytic degradation of a disperse dye and its dye bath analogue by silicadodecatungstic acid, *Dyes and Pigments*, 60, 167-176, (2004).

[7] Khalek and Mahmoud, Visible light assisted photocatalytic degradation of crystal violet, bromophenol blue and eosin Y dyes using AgBr-ZnO nanocomposites. *Environmental Nanotechnology, Monitoring & Management*, Vol 9: 164-173, (2018).

[8] Kumawat and Joshi, Photocatalytic degradation of basic Fuchsin over quaternary oxide iron zinc cuprate (FeZn₂Cu₃O_{6.5}), *Advances in Applied Science Research*, Vol.6 (Issue 7): 209-215, (2015).

[9] Bendjabeur and Zouaghi, DFT and TD-DFT insights, Photolysis and Photocatalysis investigation of three dyes with

similar structure under UV irradiation with and without TiO₂ as a catalyst: effect of adsorption, pH and light intensity, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 190, 494-505, (2018).

[10] Gupta and Jain, Removal of the hazardous dye-Tartrazine by photodegradation on titanium dioxide surface, *Materials Science and Engineering C* 31, 1062-1067, (2011).

[11] Oppong and Anku, Photocatalytic degradation of indigo carmine using Nd-doped TiO₂-decorated graphene oxide nanocomposites, *Journal of Sol-Gel Science and Technology*, 1-12, (2016).

[12] Bonancea and Nascimento, Surface-enhanced Raman study of electrochemical and photocatalytic degradation of the azo dye Janus Green B, *Applied Catalysis B: Environmental* 77, 339-345, (2008).

[13] Geng and Cui, Adsorption and Photocatalytic Degradation of Reactive Brilliant Red K-2BP by TiO₂/AC in Bubbling Fluidized Bed Photocatalytic Reactor, *Journal of Industrial and Engineering Chemistry* 49, 11321-11330, (2010).

[14] Pare and Singh, Artificial light assisted photocatalytic degradation of lissamine fast yellow dye in ZnO suspension in a slurry batch reactor, *Indian Journal of Chemistry*, Vol.48A, 1364-1369, (2009).

- [15] Hadjltaief and Zina, Photocatalytic degradation of methyl green dye in aqueous solution over natural clay-supported ZnO-TiO₂ catalysts, *Journal of Photochemistry and Photobiology A: Chemistry* 315, 25-33, (2015).
- [16] Borker and Salker, Solar assisted photocatalytic degradation of Naphthol Blue Black dye using Ce_{1-x}Mn_xO₂, *Materials Chemistry and Physics* 103, 366-370, (2007).
- [17] Pawar and Pednekar, Photocatalytic Degradation of Orange-G dye using Cu/Al₂O₃ photocatalyst, *International Journal of Innovative Research in Science, Engineering and Technology*, Vol.6 (Issue 9): 18275-18282, (2017).
- [18] Chen and Liu, Photocatalytic degradation of *p*-phenylenediamine with TiO₂-coated magnetic PMMA microspheres in an aqueous solution, *Journal of Hazardous Materials* 163, 973-981, (2009).
- [19] Gupta and Jain, Photodegradation of hazardous dye quinoline yellow catalyzed by TiO₂, *Journal of Colloid and Interface Science* 366, 135-140, (2012).
- [20] Amalraj and Pius, Photocatalytic Degradation of Alizarin Red S and Bismarck Brown R Using TiO₂ Photocatalyst, Photocatalytic Degradation of Alizarin Red S and Bismarck Brown R Using TiO₂ Photocatalyst, *Journal of Chemistry & Applied Biochemistry*, Vol.1 (Issue 1): 105, (2014).
- [21] Kansal and Lamba, Photocatalytic degradation of Alizarin Red S using simply synthesized ZnO nanoparticles, *Materials Letters* 106, 385-389, (2013).
- [22] Salim and Salih, Photodegradation Study of Toluidine Blue Dye in Aqueous Solution using Magnesium Oxide as a Photocatalyst, *International Journal of Chemistry*, Vol.7 (Issue 2), 143-149, 2015.
- [23] Begum and Gogoi, Photocatalytic Degradation of Crystal Violet dye on the surface of Au doped TiO₂ nanoparticles, *Indian Journal of Chemical Technology*, Vol.24, 97-101, 2017.
- [24] Pereira and Pereira, UV/TiO₂ Photocatalytic Degradation of Xanthene Dyes, *Photochemistry and Photobiology*, 89: 33-39, (2013).
- [25] Qamar and Saquib, Semiconductor mediated photocatalytic degradation of an azo dye, chrysoidine Y in aqueous suspensions, *Desalination* 171, 185-193, (2004).