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RESEARCH ARTICLE

OPTIMIZATION OF AZO-DYES TO REDUCE ENVIRONMENTAL IMPACT OF TEXTILE INDUSTRIES.

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Abstract

The dyes which are released into water bodies become detrimental, color is only the factor, the other fact is that under the action of anaerobic bacteria they form toxic compounds and they are also not easily degradable. Thus, before discharging them into water bodies the complete degradation of these organic compounds becomes necessary. Even by using well established techniques like adsorption, coagulation, membrane separation, flocculation, aerobic biological separation, precipitation is not possible to completely degrade such types of pollutant. In recent years an alternative method is developed, known as "Advance Oxidation Process" (AOPs). The AOP results in complete degradation as compared to other usual oxidants, in this process the radicals are greater oxidizing power. The later one is better technique for organic pollutant degradation however AOP's includes both heterogeneous and homogeneous photocatalytic processes. In present work Photo- catalytic degradation of Yellow 6 dye was performed in the photoreactor in which process takes place reaction vessel designed specially. In terms of change in dye concentration, pH concentration, radical quencher (propanol), catalyst loading, light intensity and change in terms of color by measuring the optical density. Initially pollutant's effects are analyzed by varying pollutant concentration. The result shows that chances for reusing the wastewater increases when recalcitrant organic pollutants degrade completely. The photo-catalytic degradation of dye and textile mill wastewater is environmental friendly techniques.

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Introduction:-

Essentially for sustaining life and environment water is most important natural resource. We have always thought that water is free gift of nature and is available in abundance and mostly is in sea. About 2.5% of water is fresh water that does not contain significant levels of dissolved minerals or salt $2/3^{\text{rd}}$ of that frozen ice caps and glaciers. In totally only 0.01% of the total water of the planet is accessible for consumption¹ (Central Pollution Control Board 2005). Clean drinking water is a basic human need. The major source of drinking water is ground water in both urban and rural areas.

But now water scarcity is becoming a global concern. Although the earth's surface is covered by water more than 70% and it is commonly viewed by people as a limitless resource. This view however, is quickly changing because of the fresh water sources being depleted at alarming rates. Through the increase of water usage and pollution, water scarcity is becoming a problem in which population and industrialization play a vital role. Population surge at a

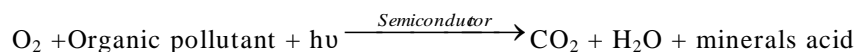
place tends to create stress on the local potable water and also the availability of water per capita is severely reduced. The industrialization is an important parameter for the advancement of any nation but an extensive industrialization aggravates fresh water sources scarcity because of the humungous amount of water required for infrastructure and manufacturing processes, also resulting in pollutants released as byproduct of manufacturing process which gets discharged in local water bodies or ground polluting there by fresh water resources.

Manufacturing and processing of dyes for textiles industry requires enormous amount of water and the generated liquid waste results in pollution. Numerous reports on the detrimental effects, of these activities cited above, on the environment have made the environmental impact a major issue and crucial parameter in the progress of industrial processes. Textile industry requires humungous volumes of water for the dyeing and finishing operations. Taking into consideration both the volume discharged and effluents composition, waste water generated as byproduct by this textile industry is rated as one of the major contributor for polluting, among all the industrial sectors. Given the scale of variety of dyes, fibers, finishing products in use and process aids, the textile industry produces waste water of great chemical complexity, volume and diversity. In the recent past few years, new and stringent regulation along with improved laws concerning waste water discharge has been established in several countries. Industrial waste byproducts comprise of both organic as well as inorganic substances. Organic waste consists of residue from vegetables and fruits which contains solvent and cleaning fluids, also includes pesticides residue and lignin from paper and pulp. Effluent consists inorganic wastes such as metals and brine salts.

Textiles dyes along with other common industrial dye stuffs are a major contributor towards largest groups of waste comprising of organic compound that poses danger to environment. Nearly 1 to 2 % of the global production of dyes remains unutilized during the dyeing process and is discharged textile effluents. Dyeing of fabrics in textile processing industries results dye from these waste water is undesirable, because of their color and also because they result in alarming rates of toxicity and carcinogenicity. Different physical methods, chemical treatment and biological techniques can be used to separate dyes from waste water. Each of these techniques has technical shortcomings and economic limitations. Most physiochemical dye separation methods have drawbacks of being too expensive, possess limited versatility, their removal encounters severe interference by other waste water compounds and generate further waste by-product that along with these must be handled²⁻⁵.

Origin of universe is also a transformation process. Due to uncountable reason chemistry is also known as subject of transformation. Organic molecules of industrial importance are transforming from one molecular species to other molecular species or reactant to product, many techniques are available for transformation of organic molecules. Many compounds are transforming from one molecular species to other molecular species in presence of direct irradiation of ultraviolet/visible radiations. But large number of molecules are remains un-reacted in presence of visible or ultraviolet radiation so catalyzed process are very good technique for molecular transformation, photo catalyzed technique is one of them has very good potential of transformation of industrial importance organic molecules like transformation of azo dyes. Transformation of industrial importance compounds (azo-dyes), the Resin Dowex-11 is immobilized by presence Methylene Blue, used as photo catalyst which is better than other transformation process which is carried out earlier for transformation of azo dyes.

The main application of the photo catalysis is to resolve issues of environmental interest like, it can be the depuration of air or water, using a semiconductor sensitive to light rays of appropriate intensity as a catalyst. In this situation we are taking heterogeneous photo catalysis because photoreaction occurs on the catalyst's surface. The heterogeneous photo catalysis allows the transformation and mineralization, of large groups of organic compounds as global chemical reaction.



The principle of the photo catalytic transformation is simple. When a substance is illuminated by light of energy larger than the band gap of it, separating the filled valence band and vacant conduction band, exciting electron from valence band energy level to conduction band and thereby resulting in formation of the positive holes (h^+) and excited electrons (e^-)⁶.

These holes and electrons oxidize and reduce chemical species on the surface of catalyst, unless they recombine to give no net chemical reaction but heat. Along the surface, the photo degenerated electrons reduces to an electron

acceptor A, the photo degenerated holes oxidizes to electron donor D. The electrons-holes recombination occurs inside the particle or at the outer surface. Therefore, the capture of an electron by part of a species A generates a radical A^\cdot . Meanwhile the capture of a hole by part of a species D generates a cation radical D^+ . These radical ions are very reactive and can react among them and with other absorbents, and inclusive they can be made from the semiconductor surface into the interior of the solution and participates in a chemical reaction in the sine of the aqueous phase.

The composition of photo catalyst remains unchanged if equal number of holes and electrons consumed for chemical reaction. It is evident from the apparent rate of photo chemical reaction depends on the photocatalyst, because efficiency of the photocatalyst of utilization of incident light energy is generally smaller than unity. This efficiency as called quantum yield may vary from zero to unity by changing photocatalyst.

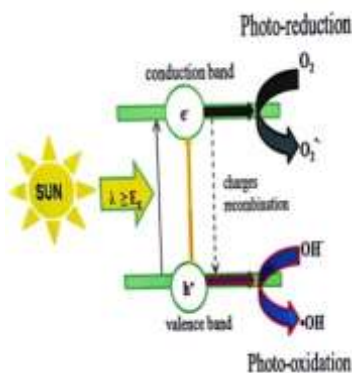


Fig. 1:- Principle of photocatalytic process

In the present work we try to design a laboratory scale batch photo reactor that uses the artificially generated photons for the purpose of detoxification of azo dyes, it's considered as the most costly material used during the operation of photocatalytic treatment plants of waste water. This emphasizes the use of sunlight as an economically viable and ecologically sensible light source, here simple agitation of the dye solutions was done by mechanical means (using magnetic stirrer). Here we try to combine the existing knowledge about the organic waste transformation ability of Resin Dowex-11 by immobilizing it with photosensitized methylene blue dye, later we use immobilized resin dowex-11 as photocatalyst and reactor engineering and to develop a simple, efficient photoreactor, which utilizes solar as well as artificial light sources⁷⁻⁸.

Literature Review:-

Wastewater when generated from different industries poses a great threat not only to mankind but also to the natural flora and fauna as well as landmass fertility. In order to meet the hard and fast international standards, treatment of industrial wastewater is obligatory. Heterogeneous photo catalysis having the great potential for removal of pollutants and waste water treatment. A lot many survey of literature has been carried out to know the latest advancements regarding the heterogeneous photo catalysis process for the treatment of textile waste water and dyes. Nasr C., et al., (1996)⁹ works on de-coloration of textile dye, Naphthol Blue Black by using TiO_2 as a catalyst which has been come into view as potentially powerful and it is a multifaceted method for dealing with the problem of textile wastewater which is containing different colorful dyes. A lot of research groups have dealt with photocatalytic degradation of this class of dye in the presence of UV-A or visible light with very supportive results. Joshi P et al. (2001)¹⁰ works on the photocatalytic decolorization of two simulated textile dye bath wastewaters. As dye bath wastewaters was subjected to photo-catalytic degradation in a batch annular immersion and photo reactor that has been equipped with a 400W Medium Pressure Mercury Lamp (MPML). When the UV illuminated with TiO_2 which is containing aqueous suspensions found to remove chemical oxygen demand (COD) and color. The photocatalytic activity was examined by measuring the COD removal and rate of de-colorization. The first order rate constant k (app) for de-colorization was 3-9 times higher than the k (app) for COD removal.

Wang, C., et al., (2004)¹¹ works on the photo degradation of methyl orange dye as a probe reaction by using the photo catalyst ZnO/SnO_2 , and also found to be related to the calcinations temperatures and the Sn contents. The photo-stability of the ZnO/SnO_2 photo catalyst was also studied.

Comparelli R., et al., (2005)¹² works on the azo dyes Methyl Orange and Methyl Red that has been carried aqueous medium in the presence of and tri-n-octylphosphine oxide (TOPO)-capped anatase TiO_2 nano crystal powders having the mean particle size 6 nm and oleic acid by the process of UV-induced photo catalytic degradation dyes. Significantly, although all titania catalysts were very effective in removing their related derivatives and both parent dyes, and the rate of degradation by using OLEA-capped TiO_2 nano crystals was doubled which are obtained with TiO_2 P25 Degussa and TOPO-capped analogous.

Pekakis, P., et al., (2006)¹³ has found the oxidative degradation of an actual textile dye house wastewater by using photocatalysis. By using the process of UV induces photocatalytic oxidation over TiO_2 suspensions was capable of reducing chemical oxygen demand about 40% and 90% after 4 hours treatment depending upon the operating conditions and also decolorize the effluent present in waste water. Anatase and rutile are crystalline forms of TiO_2 , when their photocatalytic activity was tested it was found that anatase is more active than rutile. The experiments were performed where catalyst was reused and recovered to assess the catalytic activity. Finally, after the photocatalytic treatment luminescent marine bacteria *Vibrio fischeri* was used to assess the acute ecotoxicity of samples prior.

Habibi, M. and Talebian, N. (2007)¹⁴ the decolorization of commonly used as textile dye X6G (C.I. Reactive Yellow 2), by using the photo catalyzed ITO and TiO_2 thin films. The degradation can be completed in the order of minutes at optimal operational parameters. Using advanced oxidation processes (AOP,s) and comparison between photo activities of both films reveal that, indium tin oxide can be used as a suitable alternative to TiO_2 thin films for water treatment. ITO and TiO_2 thin films prepared by e-beam evaporation technique and UV light. The thin films were characterized by XRD, AFM, and UV-vis. The photocatalytic activity of ITO thin films at 500.C is obviously higher than those of TiO_2 thin films.

Material Used And Experimental Set-Up:-

the materials and methods which are used during the experiment including the chemical, UV photoreactor, UV-Vis Spectrophotometer and pH adjustment, procedures which are used to treat dye and effluent solutions, Dowex-11, Methylene Blue, magnetic stirrer, yellow 6 dyes with varying concentrations.

Set-Up of Photoreactor System:-

The photo transformation was performed in a batch reactor placed in dark chamber containing 50 ml of dye solution and defined amount of photocatalyst. A magnetic stirrer was fixed for continuous stirring of the reaction mixture. After 15min in dark, the reactor solution was illuminated with a 200W mercury lamp. The lamp was positioned just above the reactor.

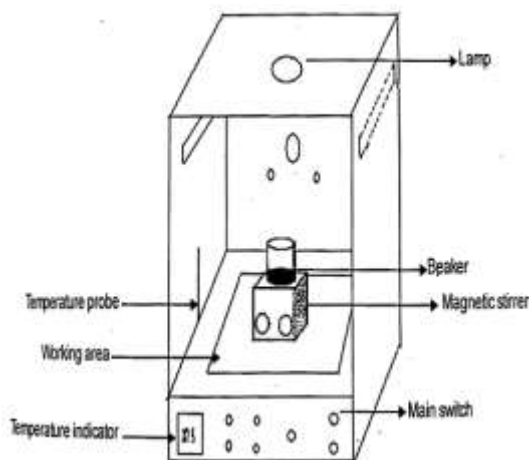


Fig. 2:- Experimental Setup of Photochemical Reaction Chamber

Observation of optical density: To remove the catalyst particle the sample of 10 ml were taken and filtered at regular time interval through a .45 μm Millipore filter membrane. The optical density of dye solution was monitored spectrophotometrically with an UV/Vis spectrophotometer (shimadzo UV 2101 PC) at optimal analytical wavelength.

Type of catalyst: An anion exchange resin dowex-11 has been taken as a catalyst. This resin has capability to exchange their one anion with dye solution anions and activated oxygen of solution in presence of visible light. This activated oxygen and photo catalytic action of this dye degrade azo bond of dyes and degrade complex organic molecule in to simpler molecules. Some of the commercially available anion exchange resin are Amberlite 400 and Dowex-3, 11, 22 etc.

Variation in catalyst loading: The amount of the photo catalyst also effects the photo catalytic transformation of dyes. The experiment is carried out at varying amount of photo catalyst at constant dye concentration and pH and light intensity.

Variation in initial dye concentration: The influence of initial concentration of the dye solution on the photo catalytic transformation is an important aspect of the study. The effect was investigated by varying the initial concentration at constant catalyst loading and at optimum pH.

Variation in initial pH: To investigate the influence of pH on rate of de-colorization experiment carried out at different pH. Adding .01 N NaOH or .01 N H₂SO₄ adjusted the pH initially. Oxalic acid was used to standardize the alkali solution. pH of solution was measured by digital pH meter of Agronic.

Variation in light intensity: The influence of light on the transformation efficiency has been examined at constant dye concentration, pH and catalyst loading. The light intensity is simply altered by varying power of mercury lamp (5.4 mWcm⁻²).

Variation in radical quencher (propanol): The effect of variation in radical quencher (propanol) on the transformation rate was investigated by varying the concentration of the propanol in the ratio 5:45 and 15:45 by keeping initial concentration of the dye, pH, light intensity and catalyst loading constant.

Results and Discussion:-

An effort is aimed primarily on the development of a photocatalytic process that aims to remove conventional, less efficient and more costly treatment technologies. Underlying objectives for the present investigation involve proper selection of photocatalyst and optimal operational parameters, all of them are necessary for complete oxidation process and thus preventing the formation of colorful by products.

The main objective of the work presented is to seek attention of researchers towards the efficiently better and easy implementing photo catalyst. Since Dowex-11 is an ion exchange resin. Dowex-11 has been especially engineered with unique porosity to optimize organic removal. In present experiments immobilization technique is applied just to fill the porosity of the resin with photosensitized dye methylene blue so that the photocatalyst can be developed. The important observations of different systems are discussed under different parameters, which are reflecting the overall outcome of the presence studies and justifying the significance of this process.

Variation of optical density with time: The photo catalytic transformation of the azo dye (yellow 6) is observed by measuring the rate of decreasing optical density of the solution. At a fixed time interval, optical density of the solution is measured and it is found that optical density of the solution is decreased with time.

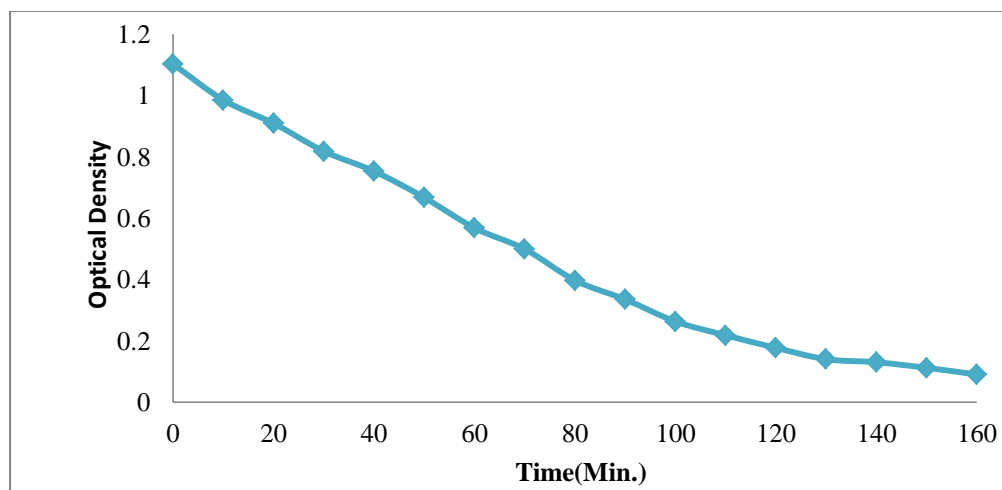


Fig. 3:- Change in Optical Density with Time

Effect of variation in dye concentration: The effect of initial concentration of the dyes in solution on the photocatalytic transformation rate is a significant parameter of the study. The effect was observed and systematically studied by varying the initial concentration of Yellow 6 dye respectively at constant catalyst loading 2.2g optimum pH 7.3 and at 10.4 mWcm^{-2} light intensity. As seen in the figures, transformation efficiency is governed by the dye concentration that is photocatalytic transformation decreases with enhancing initial concentration of the dye solution.

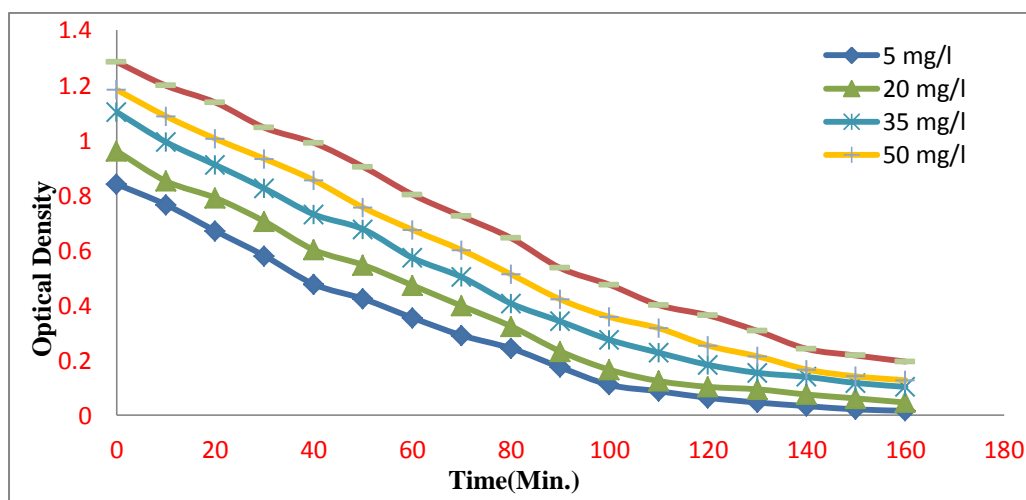


Fig. 4:- Effect of variation in dye concentration for Yellow 6- Photocatalytic system (catalyst loading: 2.2 g, pH: 7.3, solution volume: 50 ml and light intensity 10.4 mWcm^{-2})

We observed the effect of varying dye concentration on photocatalytic transformation and found that as concentration level of dye is increased the rate of transformation decreased¹⁵⁻¹⁶.

Effect of variation in catalyst loading: The volume of catalyst is one of the main parameter for the transformation studies from the view point of economical aspect. In this work Methylene Blue immobilized Dowex-11 was used as photo catalysts. The extent of photo catalytic transformation observed after 2.5 hours determine by the reduction in absorbance of visible light by dye solution shows successful decolorization of dye molecules and colored water convert into transparent water.

The volume of photo catalyst also affects the photo catalytic activity. Experiments were conducted by varying the amount of photo catalyst. The rate of decolorization was evaluated at pH 7.3 with different concentrations of photo

catalyst. As the amount of photo catalyst increased the rate of transformation of the dye solution also increased up to a limit.

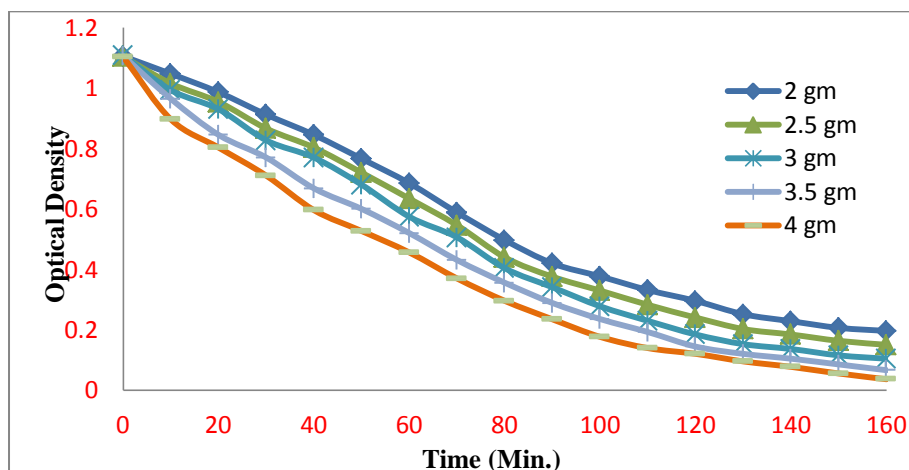


Fig. 5:- Effect of variation in dye catalyst loading for Yellow 6- Photocatalytic system (catalyst loading: 2.2 g, pH: 7.3, solution volume: 50 ml and light intensity 10.4 mWcm^{-2})

The experiments were conducted by varying catalyst loading from 2.0 – 4.0g for dye solution of 50mg/L at pH 7.3. We found that with the concentration of the photo catalyst (immobilized Dowex-11) increased the rate of photocatalytic decolorization was also increased. Increased rate of transformation with the increase in volume of catalyst, due to more availability of catalyst surface areas for absorption of photons and interaction of molecules in the reaction mixture with catalyst, results is that number of holes, super oxide radicals and hydroxyl radicals were increased. These were the main oxidizing intermediate in advanced oxidation process and increased the rate of decolorization. Thus it can be concluded that in order to avoid the use of high dose of catalyst may not prove beneficial both in terms of aggregation along with reduced irradiation field due to light scattering by catalyst it is imperative to find out the optimal loading for efficient removal of dye¹⁷⁻¹⁹.

Effect of variation in pH: pH value is one of an important factor governing the rate of transformation, in the photocatalytic processes. It is also a significant operational variable in actual waste water treatment. pH plays important role in process of transformation of the dye molecules. The decrease in photocatalytic transformation at low pH was investigated in acidic media, no appreciable change was found. Therefore, photocatalytic decolorization could not occur well at low pH range.

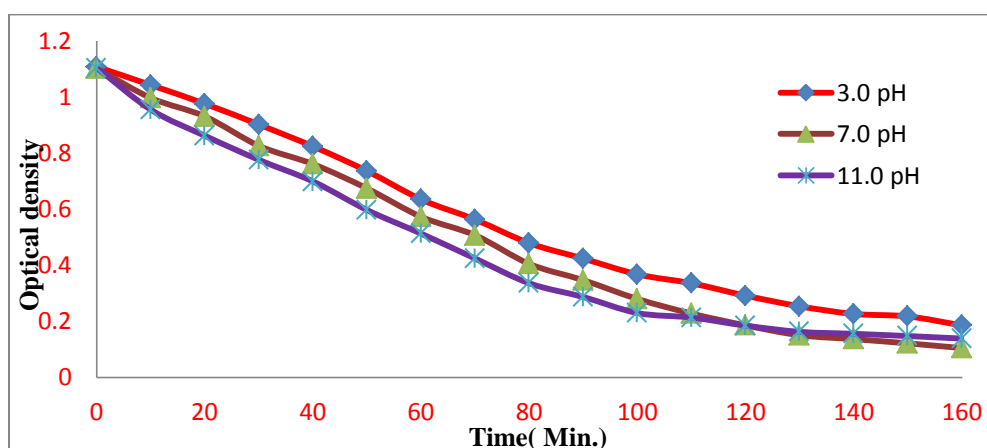


Fig. 6:- Effect of variation in pH for Yellow 6- Photocatalytic system (catalyst loading: 2.2 g, solution volume: 50 ml and light intensity 10.4 mWcm^{-2}).

We observed that the rate of transformation was extremely low in high acidic pH range, when pH was reduced than 3.0 rate of decolorization was very minimal, as pH increased rate of transformation also increased, when pH switched to basic range the rate of decolorization increased rapidly, in pH range 7.0 to 9.0 decolorization rate was

appreciable. On further elevating pH the rate of decolorization started to decrease, nearby pH range 10 or above rate of decolorization was less than before and decreased as pH further shooted. Therefore, we concluded that rate of transformation in basic medium was more than the acidic medium. The increased rate of photo catalytic decolorization may be due to the more abundance of -OH ions in pH range 7.0 to 9.0 which may generate more $\bullet\text{OH}$ radicals by combination with the holes formed due to electronic excitation in catalyst. Formations of hydroxyl radicals resulted in more photocatalytic transformation than super oxide radicals. At higher pH value the decolorization rate decreased. This effect was observed due to competition arising between -OH groups to attach to the active site of catalyst, resulting in rate of attachment of -OH groups getting decreased. Result is formation of hydroxyl radical ($\bullet\text{OH}$) decreased and due to factor rate of transformation also decreased²⁰⁻²¹.

Effect of variation in light intensity: In any photo catalytic activity light plays a very important role because irradiation produces the photons utilized for the electron transfer from the valence band to conduction band of a photo catalyst that are responsible for decolorization. The light sources of different intensities (different watts) were used to observe the influence of light intensity on the photo catalytic decolorization.

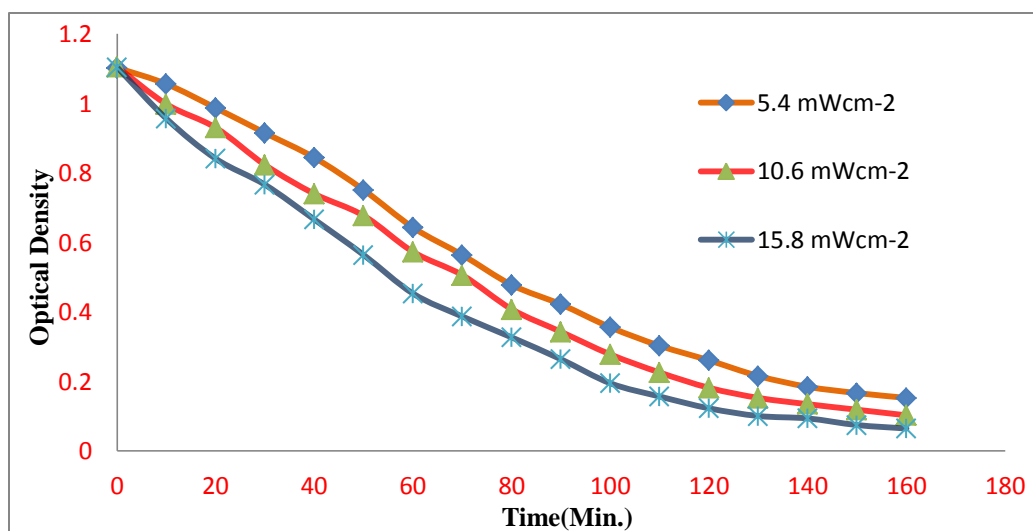


Fig. 7:- Effect of variation in light intensity for Yellow 6- Photocatalytic system (catalyst loading: 2.2 g, pH: 7.3, solution volume: 50 ml)

It was observed from experimental analysis that transformation increased in linear fashion with the gradual increase in light intensity and the effect was examined at fixed dye concentration and loading of catalysts. The altering of light intensity was accomplished by varying power of mercury lamp (5.4 - 10.6 - 15.8 mWcm⁻²).

We observed that the intensity of light that increased the rate of decolorization of molecules of dyes also increased up to certain limit and after that no changes were observed in rate of transformation. The increase in the rate of decolorization of dye molecules by increasing intensity of light was because of the increase in number of photons generated, sufficient for electron transfer from valence band to conduction band of photo catalyst. As a result of which number of holes, super oxide radicals and hydroxyl radicals increased and rate of transformation for the dye molecules also increased.

On further increased in light intensity there was zero effect on transformation, this was because maximum number of photons which were required for excitation were available in fix range irradiating light intensity and after it further increased light intensity no considerable changes were observed in rate of decolorization because there was no requirement of more photons for excitation. The cause was that all molecules became active (excited) in fix light intensity range. When further increase, the rate of transformation remains unchanged²²⁻²⁴.

Effect of variation in radical quencher: From the observation we see that transformation rate of dye solution decreases as the ratio of the concentration of propanol increases from 5:45 to 15:45 in comparison to dye solution in absence of propanol. Alcohols such as propanol and ethanol are generally used to quench hydroxyl radicals and superoxide. So, the rate of transformation decreased as ratio of propanol is increased in dye solution. This enables us

to draw the conclusion that small amount of propanol inhibits the photocatalytic decolorization and hence oxidative species like superoxide ions and hydroxyl radicals plays a major role in photocatalytic activity²⁵.

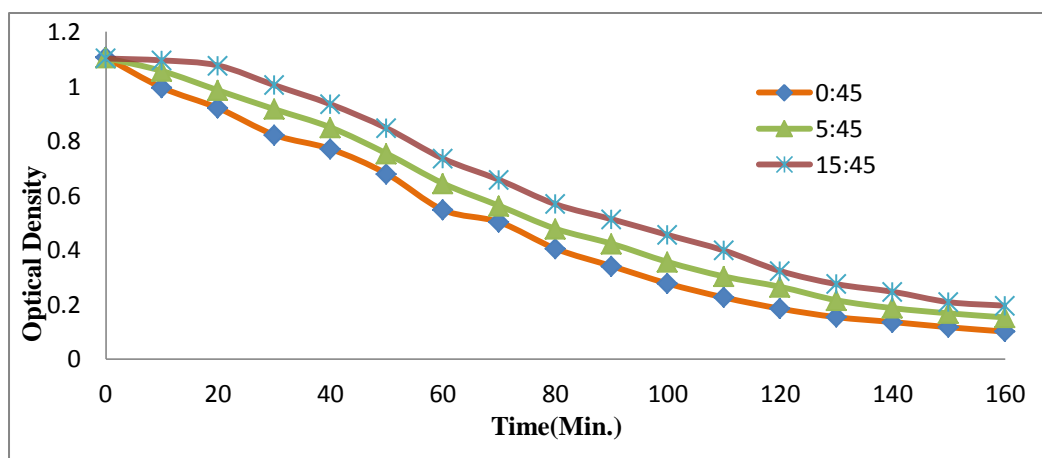


Fig. 8:- Effect of variation in radical quencher (Propanol) for Yellow 6- Photocatalytic system (catalyst loading: 2.2 g, pH: 7.3, solution volume: 50 ml and light intensity 10.4 mWcm⁻²)

Conclusion:-

So, it is concluded that for treatment of industrial waste water that contains organic compounds and dyes from textile industries can be used as efficient and environmental friendly technique. In Indian context the development of this technology is importance as sunlight is in abundance. And presently the existing technology in textile industry is inefficient or we can say that treating waste water resulting in discharge of colored water into public sewage system and rivers is health hazard.

Therefore, this technology has very good potential of converting complex organic molecule into simpler ones. Azo dyes lost in industrial waste water can be degrade into colorless and non-toxic compounds so this catalyst may applicable for industrial purpose for improvement in quality of the waste water of textile industries and many others.

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