SOLAR DETOXIFICATION OF DYEING EFFLUENTS

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Abstract : Textile and dyeing industries are responsible for contaminating water due to discharge of colored effluents. So water pollution due to color from textile and dyestuff industries is a topic of major concern of scientist today. The textile dyeing industries has been condemned as being one of the world's most offenders in terms of pollution. The use of conventional textile wastewater treatment processes becomes drastically challenged to environmental engineers with increasing more and more restrictive effluent quality by water authorities. Conventional treatment such as biological treatment discharges will no longer be tolerated as 53% of 87 colors are identified as non-biodegradable. The removals of dyes present in these industrial effluents have been received great potential in last few years. It is due to increasing environment awareness and implementation of ever strict environmental rules. These textile effluents are highly toxic as they contain a large number of metal complex dyes. These high concentrations of dyes may cause water borne diseases and increase the BOD level of receiving water. In the present work, we design an apparatus for treating these effluents and analyse them for an efficient design. Solar detoxification process is used in this application for which TiO_2 is used. This process holds great promise to provide alternative for better treatment and protection of environment.

Keywords : Titanium dioxide, dyeing effluents, solar energy, solar detoxification, water purification.

Introduction : Textile industry uses large quantity of water in its production processes and highly polluted and toxic waste waters are discharged into sewers and drains without any kind of treatment. Textile wastewater includes a large variety of dyes and chemicals additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. In textile production, opportunities exist for the release into the ecosystem of potentially hazardous compounds at various stages of the operation. In India, 690 textile units are discharging their wastes into water bodies without any effective waste water treatment. Physical and chemical methods for treatments of dyes are discouraged due to high cost, inefficiency and chemical pollution. Biological treatment is safe and cost effective way for control of pollution. Colored waste water from textile industry is rated as the most polluted in almost all industrial sectors. It has been estimated that over 10,000 different textile dyes and pigments are in common use and the total world organic colorant productions are more than 100,000 tons/year [9][11]. Huge amount of dyes in textile sectors are continuously being exhausted in wastewater streams due to their poor absorbability to the fiber. Dyes have environmental implications, because up to 50% of the initial dye mass up to or exceeding 800 mg/L used in the dyeing process remains in the spent dye bath in its hydrolyzed form which no longer has an affinity for the fabric [9]. The treatment of textile waste water is still a major environmental concern, because of synthetic dyes, which are difficult to be removed by conventional treatment systems.

The majority of physical, chemical and biological color removal techniques work either by concentrating the color into sludge, solid supports, or by the complete destruction of the dye molecule [10]. Traditional methods for the cleanup of pollutants usually involve the removal of unwanted materials through sedimentation and filtration, and subsequent chemical treatments such as flocculation, neutralization and electro-dialysis before disposal. These processes may not guarantee adequate treatment of the effluent [10]. Moreover, they are often laborious and expensive, considering the volume of wastes released during the industrial production process. Thus we propose to apply solar detoxification process using titanium dioxide to treat these textile effluents. We have designed apparatuses and conducted experiments and selected the efficient apparatus.

Dyeing Effluents

Sources of Dyeing Effluents

- Soap and detergent Industry
- Paper mill industry
- Textile mill effluent
- Brewery industry
- Tannery industrial effluent
- Soft drink effluent
- Chemical industry

Table I: Examples of waste effluents generated by industries[11]

Type of waste	Type of Plant
Oxygen-consuming	Breweries, dairies, distillers, packaging houses, pulp and paper, tanneries, textiles
High Suspended Solids	Breweries, coal washers, iron and steel industries, Distillers, pulp and paper mills, palm oil mills
High Dissolved Solids	Chemical plants, tanneries, water softening
Oily and Grease	Laundries, metal finishing, oil fields, petroleum refineries, tanneries, palm oil mills
Coloured	Pulp and paper mills, tanneries, textile dye houses, palm oil mills
High Acid	Chemical plants, coal mines, iron and steel
High Alkaline	Chemical plants, laundries, tanneries, texitile finishing mills
High Temperature	Bottle washing plants, laundries, power plant , textiles

Impact of Organic Wastes : Contributing to the menace of indiscriminate discharges of industrial effluents in receiving water bodies is the improper disposal of domestic wastes, particularly in urban centers of most developing countries. Open and indiscriminate dumping of solid wastes in drainages and riverbanks is one of the most critical problems. Sewage effluents rich in decomposable organic matter, is the primary cause of organic pollution. Domestic wastes in the country like in many other developing countries may now contain modern environmental health hazardous substances thus posing additional risk to public health Due to population and industrial growth, inland waters (rivers, lakes, etc.) become often the recipient of organic matter in amounts exceeding their natural purification capacity, while in the past, natural purification and dilution were usually sufficient. Secondary organic pollution is defined as the surplus of organic matter, which is the sum of undecomposed organic material introduced into the water body with primary pollution and of the material resulting from an extremely increased bio productivity within the polluted ecosystem itself. Organic wastes mineralize in the receiving water bodies and the resulting nutritive elements stimulate plant production, leading to eutrophication. In this situation, the biomass increases considerably and goes beyond the assimilation limit by herbivores. This secondary organic pollution is considerably greater than the primary organic load. The excessive production of organic matter leads to the buildup of "sludge" and the mineralization process consumes all dissolved oxygen from the water column, which causes fish kills. Consequently, organic pollutants are called oxygen demanding wastes. The relatively high temperatures in tropical countries accelerate this process.

Composition Of Chemicals In Effluents: The chemical composition plays a important role in detoxification. The chemical content is directly proportional to the time taken for detoxification. The below table give the average value of various chemicals in effluents. In this present work we are concerned about the dye content alone.

Table II chemical composition in Textile effluents[9]

No.	Parameter	Concentration
1	Dye	120
2	pH	8.0
3	Total solids	7500
4	Total suspended solids	320
5	Total dissolved solids	7180
6	BOD at 20°C	560
7	COD	3200
8	Chlorides	3800
9	Sodium	7900

All the values except pH are in mg/L

Methodology Methods of Textile Effluent Treatment : The effluent treatment method is broadly classified into three main categories: physical, chemical, and biological treatments. There are four stages, preliminary, primary, secondary, and tertiary treatments to treat the textile effluents [10][11]. The preliminary treatment processes are equalization and neutralization. The primary stages involve screening, sedimentation, floatation, chemical coagulation and flocculation. Secondary stages are used to reduce the organic load, facilitate physical / chemical separation and biological oxidation. Tertiary stages are important because they serve as polishing of effluent treatment.

Preliminary treatment : The conventional treatment systems like physico-chemical treatment followed by biological treatment are installed in majority of textile industries. The first step in the wastewater treatment is to mix and equalize the wastewater streams that are discharged at different time, and different intervals from different stages in processes. The efficiency depends on amount of COD

Primary Treatment : The primary treatment involves screening, sedimentation, floatation, but after the treatment of effluents by above processes some fine or suspended and colloidal particles cannot be efficiently removed. In such cases mechanical flocculation or chemical coagulation is employed. In chemical coagulation the effluent is then subject to flash mixing for the addition of coagulants such as lime[$Ca(OH)_2$], alum, ferrous sulphate ($FeSO_4$), ferric chloride($FeCl_3$), electrolyte and processed through clariflocculator or flocculator and settling tank.

Secondary treatment : In secondary treatment, the dissolved and colloidal organic compounds and colour present in wastewater is removed or reused and to stabilize the organic matter. This is achieved biologically using bacteria and other microorganisms. These processes may be aerobic or anaerobic. In aerobic processes, bacteria and other microorganisms consume organic matter as food. They bring about the following sequential changes:

1. Coagulation and flocculation of colloidal matter
2. Oxidation of dissolved organic matter to carbon dioxide.
3. Degradation of nitrogenous organic matter to ammonia, which is then converted into nitrite and eventually to nitrate.

The efficiency of this process depends upon pH, temperature, waste loading, absence of oxygen and toxic material.

Tertiary Treatment: The above mentioned types are used at present and this project gives out a new idea of using solar detoxification to treat the effluents replacing the present tertiary treatment processes as this is expected to be more efficient and energy concerned than other methods. This method uses photo catalytic degradation and photo chemical reaction as its principle.

Principle And Mechanism : A wide range of semiconductors may be used for photo catalysis, such as TiO_2, ZnO, MgO, WO_3, Fe_2O_3, CdS. The ideal photo catalyst should process the following properties (i) photo activity, (ii) biological and chemical inertness, (iii) stability toward photo corrosion, (v) suitability towards visible or near UV light, (vi) low cost, and (vi)lack of toxicity

TiO_2 is known to have and excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications, such as electro ceramics, glass and in the photo catalytic degradation of chemicals in water and air. It has been used in the form of a suspension, or a thin film in water treatment Titanium dioxide has different crystalline forms. The most common forms are anatase and rutile. The third crystalline form is brookite, which is uncommon and unstable. Anatase is the most stable form by 8-12 KJ mol,-1 and can be converted to rutile by heating to temperatures ~ 700 ºC [1]. The density of rutile is greater at 4.26 g/ml, while anatase has a density of 3.9 g/ml. In the photo catalysis applications, it is known that, anatase is more efficient than rutile, having an open structure compared with rutile.

Degussa P25, is commercially available, consists of two forms of TiO_2 (closely approximating to 25% rutile, 75% anatase) and has been used in many studies of photocatalytic degradation. Studies employing P25, have been widely reported because of its chemical stability, ready availability, reproducibility, and activity as a catalyst for oxidation processes

Principles : Photo catalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor producing electron-hole (e^-/h^+) pairs, as written in the equation

$$TiO2 \longrightarrow e^-_{cb}(TiO_2) + h^+_{vb}(TiO_2) \quad (1)$$

Where cb is conduction band and vb is the valence band. Consequently, following irradiation, the TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding medium. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical effect.

Mechanism of Generation Of Oxidation Species

Heterogeneous photocatalysis is a complex sequence of reactions which follows five steps. These are: "(i) diffusion of reactants to the surface, (ii) adsorption of reactants onto the surface, (iii) reaction on the surface, (iv) desorption of products from the surface, and (v) diffusion of products from the surface".

$$TiO_2(h_{vb}^+) + H_2O_{ads} \longrightarrow TiO_2 + HO_{ads} + H^+ \quad (2)$$

$$TiO_2(h_{vb}^+) + HO^-_{ads} \longrightarrow TiO_2 + HO_{ads} \quad (3)$$

In general, donor (D) molecules such as H_2O will adsorb and react with a hole in the valence-band and an acceptor (A) such as dioxygen will also be adsorbed and react with the electron in the conduction band (ecb–),

$$TiO_2(h_{vb}^+) + D_{ads} \longrightarrow TiO_2 + D^+_{ads} \quad (4)$$

$$TiO_2(e_{cb}^-) + A_{ads} \longrightarrow TiO_2 + A^-_{ads} \quad (5)$$

It is generally accepted that oxygen plays an important role. Oxygen can trap conduction-band electrons to form superoxide ion (O_2^-) equation These superoxide ions can react with hydrogen ions (formed by splitting water), forming HO_2

$$TiO_2(e_{cb}^-) + O_{2ads} + H^+ \longrightarrow TiO_2 + HO_2 \quad O_2^- + H^+ \quad (6)$$

H_2O_2 could be formed from $HO_2^{\bullet}$ via reactions

$$TiO_2(e_{cb}^-) + HO_2 + H^+ \longrightarrow H_2O_2 \quad (7)$$

Cleavage of H_2O_2 by one of the reactions may yield an OH radical

$$H_2O_2 + hv \longrightarrow 2HO \quad (8)$$

$$H_2O_2 + O_2^- \longrightarrow HO + O_2 + HO^- \quad (9)$$

$$H_2O_2 + TiO_2(e_{cb}^-) \longrightarrow HO + HO^- + TiO_2 \quad (10)$$

Apparatus Design : In our project we designed two apparatus of same surface area to carry out solar detoxification and found out the efficient one to be used. The planar and tubular design has their own advantages and disadvantages and so we are to compare them and find the efficient one.

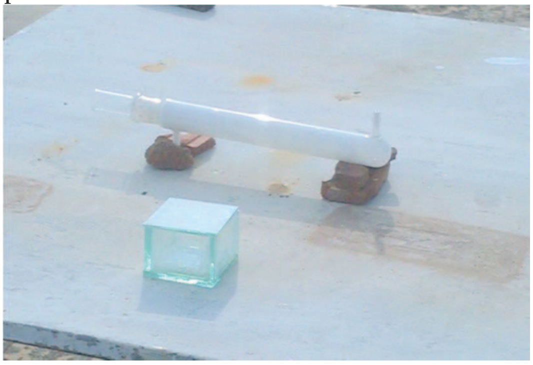

Fig 1: planar and tubular design

Planar Design

In a planar design, the photovoltaic system is placed external to the main sub-module, which is transparent to UV and the visible component of solar light. The second cover is also transparent to visible light. The internal surfaces of the photo-catalytic module, corresponding to the transparent covers, can support the photo-catalyst or it can be carried suspended in the water

Fig 2 : planar design with TiO_2 coating

Fig 3: experimental planar set-up

Tubular Design: A tubular design introduces advantages for photo-catalytic systems in terms of improved water flow, reduced system cost, maintained pressure, and reduction of land area; along with the previously discussed system advantages. A further key feature of the tubular receiver designs is that it can be integrated in a wide range of system designs including non-concentrating systems, low concentration systems such as CPC´s, and medium concentration systems [2][3].

For this arrangement, two concentric structures are required; a main outer tube containing the photo-catalyst, and an optimized internal structure containing the encapsulated solar cells. This second structure is placed inside the main tube and must be optimized according to the particular system requirements including optimisation for the optics of the collector; the fluid flow characteristics; and system cost structure [7][8].

Fig 4: Inner and outer tubes displayed

Fig 5 : Describing picture of the setup

Fig 6: experimental setup of tubular design with TiO_2 coating

Design Calculation

Diameter of the inner tube = 20 mm

Diameter of the outer tube = 40 mm

Length of the pipes = 300 mm

Volume of the tubular section = $3.14*((d_1^2-d_2^2)/4)*h$

$=3.14*((40^2-20^2)/4)*300$

$=282600\ mm^3$

Length of the flat plate = 75 mm

Breadth of the flat plate = 75 mm

Height of the flat plate = 50 mm

Volume of the flat plate = l*b*h
=75*75*50
= 282600 mm^3

Experimental Study : The set-up for both, planar and tubular design was fabricated with the same surface area and the readings are taken in the same time of the day with varying the proportions of the dye with water. With these different proportions of dye and water, different solutions were prepared. Then the time taken for decolourization was found out for each solution.

Table III: observation of time taken for decolourisation with varying the dye concentration

Date of Experiment DD/MM/YYYY	Amount of Dye (ml)	Amount of water (ml)	Time taken for decolourisation (mins)	
			Tubular	Planar
19/09/2012	2	282.6	6.6	7.9
20/09/2012	5	282.6	9.7	11.8
21/09/2012	8	282.6	11.4	13
22/09/2012	10	282.6	13.7	16.9
24/09/2012	15	282.6	18.2	22.5
27/09/2012	20	282.6	24.6	30.2
28/09/2012	30	282.6	36.1	41.3

Dye: Prussian blue pigment
Starting time: 12:00 p.m.
Place: Thiruparankundram, Madurai, India

Results And Discussion : The observed results through recording the time taken for decolourization by varying the amount of dye were tabulated. With this graph is drawn for tubular and planar design (fig.7 and 8). Then a comparison between the amount of dye and time taken for decolourization for tubular and planar is shown in fig. 9. From this comparison we could see that as the concentration of dye increases the time taken to decolourize also increases exponentially

From the comparison between tubular and planar design, we could see that the time taken for decolourization increases exponentially with the increase in the amount of dye. Thus with these results, we could come to a conclusion that the tubular design is more efficient than that of the planar design. More over the tubular has certain advantages such as portability, leak proof, etc.

Conclusion: In India due to textile dyeing industries, the main negative impact afflicting the local environment severely is the hazards caused by dye effluents, which contain both chemical and organic pollutants. These can be highly toxic. Research has found that the volume of such effluents often exceeds acceptable standards. Though the volume of effluents from individual small-scale dyers might be small, the concentration of pollutants is generally high. The impact is significant where several producers are located at one place and discharge effluents into the same body of water. Large-scale dyers on the other hand generate greater volumes of effluent but show lower pollutant content per cubic meter of water. The concentration of these pollutants is increasing in an alarming rate with the increasing number of textile dyeing industries. So the above mitigation measure can be effective to minimize the pollution to a significant extent. By adopting this detoxification process the effluent waste's concentration, impurities, pH, etc. can be highly reduced which directly decreases the water pollution and its respective diseases. Last of all, for the greater benefits of our country, all people involved in textile dyeing should be environmentally conscious to preserve our environment and should install such new technological methods and thus maintaining the environment clean and green.

This present work gives a solution to detoxify the effluents using green solar energy at a low cost in a simple method using titanium dioxide in an apparatus. Two apparatus was designed of same surface area and the experiment was carried out for finding the time taken for decolourization of the dyes present in the effluents. Further work may done to prove that the procedure does reduce the pH, COD, TDS, etc. From the results we could conclude that the tubular design looks more advantageous that planar design by efficiency, portability, leak proof and many more.

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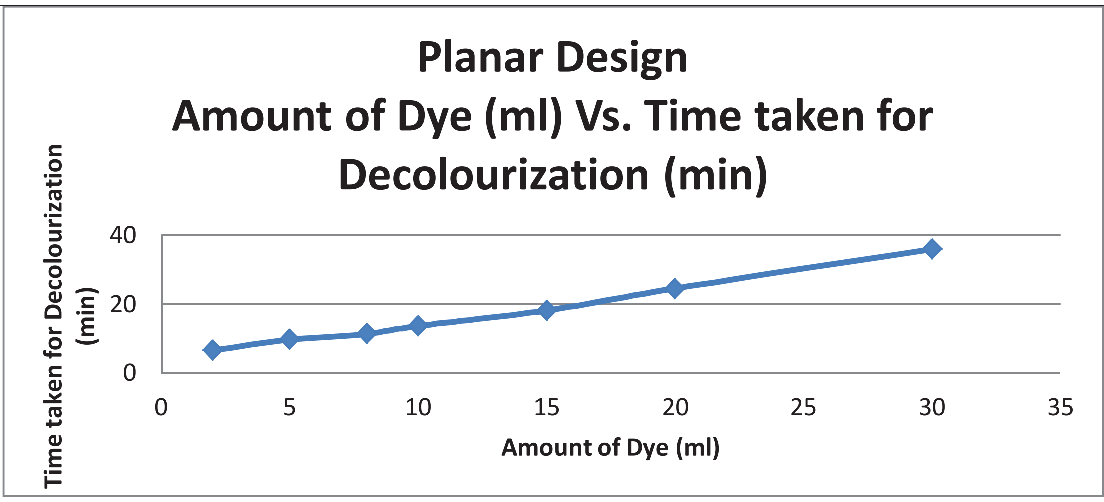

Fig 7: planar design graph

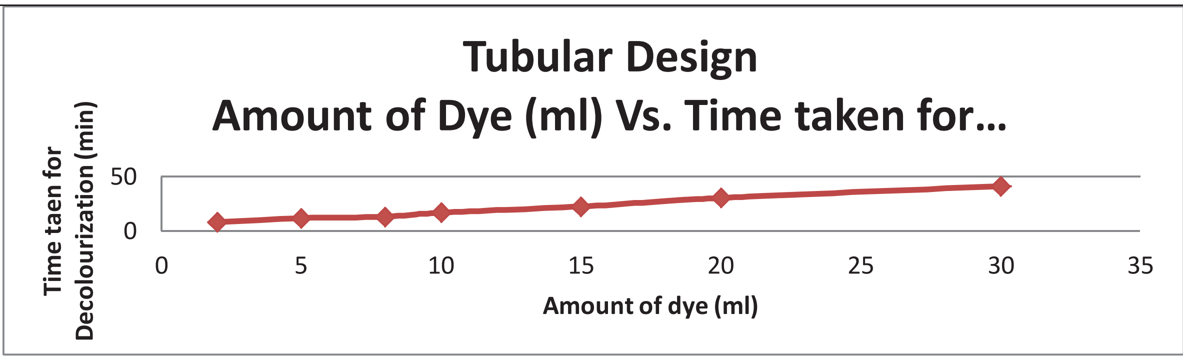

Fig 8: tubular design graph

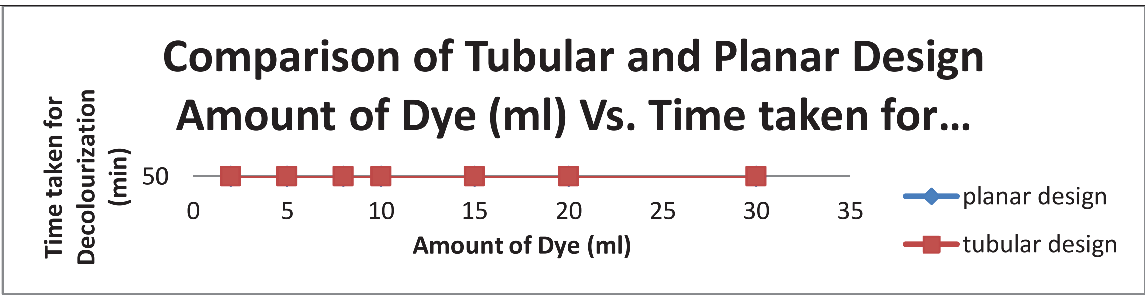

Fig 9: Comparison graph of Planar and Tubular

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