Solar Photocatalytic Process for Treatment of Textile Industrial Wastewater

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Abstract — The worst impact of rapid development in dyes and textile industries in the recent decades has resulted in the accumulation of large quantities of recalcitrant pollutants into our water cycle. Traditionally physicochemical and biological methods used for wastewater treatment have inherent limitations in their applicability, effectiveness and cost. The combination of photo catalytic process using both homogeneous and heterogeneous catalysts like Fenton’s process and TiO2 and its modified forms respectively, with biological treatment for the degradation of organic pollutants can provide a viable alternative for the detoxification and recycling of industrial wastewater. In this study, treated the textile effluent using catalyst namely TiO2 under the sunlight. It reduces the COD and color of the effluent very sharply. The reaction conditions were optimized such as the catalyst concentration at 0.8 gm/l, pH of the effluent at 5.5 and the rate of degradation at 1ml oxidant per 200ml effluent sample.

Keywords — Photocatalytic, Watewater, Textile effluent, TiO2, COD

I. INTRODUCTION

Textile mills are major consumers of water and consequently one of the largest groups of industries causing intense water pollution. Around 10 kg and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used extensively in dyeing and printing industries. Textile processing employs a variety of chemicals, depending on the nature of the raw material and products. It estimates that about 10 % of the chemicals are lost in industrial wastewater [1]. The wastewater generated by the different production steps (i.e. Sizing of fibers, scouring, desizing, bleaching, washing, mercerization, dyeing and finishing) has a high pH and temperature. It also contains a high concentration of organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulfide, soda, and alkalinity. In addition, the high salt conditions of the reactive dye baths result in high-salt wastewater, which further exacerbates both their treatment and disposal. The fate of these chemicals varies, ranging from 100% retention on the fabric to 100% discharge with the effluent. As a result, textile industry is confronted with the challenge of both color removal (for aesthetic reasons) and effluent salt content reduction. In addition, reactive dyes are highly water-soluble and non-degradable under the typical aerobic conditions found in the conventional biological treatment system.

More worrying is the fact that current legislation only governs the amount of biochemical oxides, and the level of alkalinity and acidity of industrial effluents, but not the dye concentration. If polluted fluids are discharged directly into the aquatic environment, their toxicity will be absorbed by aquatic creatures and will eventually find its way through the food chain into human beings.

In general, the current practice in textile mills is to discharge the wastewater into the local environment without any treatment. This wastewater causes serious impacts on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, and oil and grease in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. Effluent from mills also contains chemicals; effluents are dark in color, which increases the turbidity of the water body. This in turn hampers the photosynthesis process, causing alteration in the habitat. Besides, the improper handling of hazardous chemical content in textile water has some serious impacts on the health and safety of workers. Contact with chemical puts them the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and even leads to respiratory problems [2].

Several studies focused on the decolonization of industrial wastewater using different methods of treatments; however, most of these methods have difficulty in practical uses. In recent studies, different systems were used, such as, ozonation [3,4], H2O2/UV [5-7], photocatalysis [8,9], photo-Fenton [10,11], electrocoagulation [12], sonolysis [13], gamma-radiolysis [14], biological [15,16] and combined anaerobic–photocatalytic treatment [17].

To overcome the shortcomings in the existing treatment techniques, research and development in innovative technologies during the last decade have
shown that advanced oxidation processes (AOP’s) that are combination of powerful oxidizing agents like UV light, UV/TiO$_2$, O$_3$/UV, H$_2$O$_2$ to mention a few are highly promising for the remediation of complex organic compounds which are present in contaminated water /effluent systems without generating any sludge or solid material of hazardous character [18].

Among heterogeneous AOP’s, Titanium dioxide (TiO$_2$) – mediated photocatalytic oxidation appears to be a promising alternative, since the optical absorption of TiO$_2$ is in the near UV –A region and is the major advantage of the photocatalytic method over the UV-C has driven AOP’s that require light of shorter wavelengths and hence cannot make use of solar irradiation. The photocatalytic detoxification has been discussed as an alternative method for cleanup of polluted water in the scientific literature since 1976 [19].

The photocatalysis implies the combination of photochemistry with a catalyst. Both radiation and catalyst are necessary to achieve or to accelerate a chemical reaction. Heterogeneous photocatalysis employs semiconductors as catalysts. Besides catalyst and a proper radiation no additional chemicals or expensive processes are necessary. The biggest problem of the photocatalysis nowadays is the low quantum efficiency of generation of reactive species, capable of oxidation or reduction of organic molecules. New development in the research field of photocatalysis might improve this to the degree that photocatalysis will be soon economically acceptable for specific applications.

II. SELECTION OF TiO$_2$ CATALYST
Titanium dioxide (TiO$_2$) is a biologically and chemically inert, photostable, largely available and inexpensive, what are its additional advantages in comparison to the other photocatalysts. Some advantages of TiO$_2$ photocatalysis over the other AOP’s could be summarized like (i) Low cost and high chemical stability of TiO$_2$. (ii) It needs only O$_2$ and UV photons for the activation. Also the solar energy could be used as a source of UV photons. (iii) It can be applied to the systems with very low concentrations of highly toxic pollutants. (iv) Ions, generally present in water, do not decrease its activity considerably. (v) Total mineralization for many organic compounds could be achieved. (vi) Other decontamination methods could be efficiently combined with TiO$_2$ photocatalysis thus increasing its efficiency. (vii) TiO$_2$ photocatalysis works at room temperature, therefore no additional input of thermal energy is necessary.

III. MATERIALS AND METHOD
A. Materials
The actual wastewater sample was collected from the equalization tank of Raymond textile industry located at the Jalgaon city of the Maharashtra (India).

The photocatalyst used in all the experiments was anatase form of titanium dioxide powder (the BET surface area is 50 ± 15 m$^2$/g with an average particle size is 30 nm). Hydrogen peroxide was used as an oxidant. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) was used to adjust the pH. All chemicals are purchased from the Jalgon city.

B. Methods
The wastewater characterization was done in environmental laboratory of the Jalgon city. The wastewater sample was highly concentrated. Hence, the sample was diluted in the ratio of 1:1 by using distilled water. The initial pH of the sample was adjusted by using HCl and NaOH solution. The sample was treated in a natural sunlight, as shown in Fig.1. The outside temperature was measured by using a thermometer. Samples were withdrawn after every one hour and filtered. COD of the samples were measured in the environmental laboratory. The results were then optimized variation of oxidant addition, pH adjustments, catalyst loading. The tests were repeated for getting the reproducibility of results.

![Fig. 1. Photocatalytic treatment of wastewater in sunlight](Image)

IV. RESULT AND DISCUSSIONS
A. Wastewater characteristics
Raw wastewater was collected directly from the equalization tank of the Raymond textile Industry. The analyses were done in the environmental laboratory and those shown in Table 1. The sample was found with highly concentrated on the TS, TSS and TDS. So some pre-treatment is required, so as to safely discharge the water.

B. Effect of Catalyst (TiO$_2$) concentration on the reduction of COD
Catalyst (TiO$_2$) concentration was varied from 2.0 g/l to 10 g/l (i.e. 0.2% to 1.0%) during reactions in sunlight. It was observed that the rate increases with an increase in catalyst concentration and becomes constant above a certain level. The reasons for this decrease in degradation rate are as: (i) Aggregation of TiO$_2$ particles at high concentrations causing a decrease in the number of surface active sites, and (ii) Increase in opacity and light scattering of TiO$_2$ particles at high concentration leading to decrease in the passage of irradiation through the sample.

As the concentration of the catalyst is increased, the number of photons absorbed and the number of pollutant molecules absorbed are increased owing to an increase in the number of TiO$_2$ particles. The density of particles in the area illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules available are not sufficient for adsorption by the increased number of TiO$_2$ particles. Hence the additional catalyst amount is not involved in the catalytic activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit. Surface active sites also decrease due to aggregations of TiO$_2$ particles at high concentrations. This observation is in agreement with the observations reported in literature and an amount of 3.0 mg/l has been taken for the subsequent experiments for studying the effect of oxidant addition and pH of the solution.

![Fig. 2. Effect of catalyst concentration on the COD reduction](image)

**Table 1. Characteristics of the raw wastewater sample of Raymond textile mill**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Parameter</th>
<th>Prevailing Range( mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>COD</td>
<td>240 – 250</td>
</tr>
<tr>
<td>2.</td>
<td>TS</td>
<td>681600</td>
</tr>
<tr>
<td>3.</td>
<td>TDS</td>
<td>297600</td>
</tr>
<tr>
<td>4.</td>
<td>TSS</td>
<td>384000</td>
</tr>
<tr>
<td>5.</td>
<td>COLOUR</td>
<td>Light pink</td>
</tr>
<tr>
<td>6.</td>
<td>pH</td>
<td>9.54 – 10</td>
</tr>
<tr>
<td>7.</td>
<td>Temperature</td>
<td>34 °c</td>
</tr>
</tbody>
</table>

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Fig. 2 shows the effect of catalyst concentration on the COD reduction. It was observed that the COD continuously decreases from 240 to 20 mg/L on increasing the catalyst concentration from 0.2 g/l to 1.0 g/l. An optimum of catalyst concentration has to be taken when the decrease in COD level is to be within acceptable limits. Use of higher concentration of catalyst will increase the cost of the process and decrease the permeability of sunlight.

![Fig. 2. Effect of catalyst concentration on the COD reduction](image)

**C. Effect of operating pH**

The wastewater from textile industries usually has a high pH value (nearly 10). Further, the generation of hydroxyl radicals (AOP’s) is also a function of pH. Thus pH plays an important role both in the characteristics of textile wastes and the generation of hydroxyl radicals. Hence, attempts have been made to study the influence of pH in the degradation of dye in the range 3 - 10.

The pH of the solution significantly affects TiO$_2$ activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valence bands. In our experiments, maximum degradation was observed at pH nearly 6. As shown in Fig.3. Other pH values also responded to good degradation rates, but the final pH after photocatalytic treatment which was the deciding factor for determining the optimum pH, which was found to be in the range of 6.0-7.0. So it is clear that an optimum pH should be at 6.0, because maximum degradation was achieved at this pH and final pH gets to be 7.0, which was suitable for the biological process.
Fig. 3. Effect of pH on the % degradation of the effluent (0.4% catalyst loading)

D. Effects of Oxidant addition

One possible way to increase the reaction rate would be to increase the concentration of OH radicals because these species are widely considered to be promoters of photocatalytic degradation. The addition of hydrogen peroxide to the heterogeneous system increases the concentration of OH radical, since it inhibits the electron-hole recombination, according to the following equation:

$$\text{TiO}_2 (\text{e}^-) + \text{H}_2\text{O}_2 \rightarrow \text{TiO}_2 + \text{OH}^- + \text{OH}^- \quad (1)$$

Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation. It accepts a photo generated electron from a conduction band and thus promotes the charge separation, and it also forms OH radical, according to Eq. (1). However, at high concentration of H$_2$O$_2$, it also acts as a scavenger as shown in the following equations.

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (2)$$

$$\text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (3)$$

In the experiments, the hydrogen peroxide concentrations were varied from 1.0 to 5.0 ml per 1000ml of the effluent. The best results were found, when oxidant addition came out to 1ml/200ml of effluent and has been taken as the optimum amount required for maximum effective degradation of pollutants.

E. Color Removal

Color is usually the first contaminant to be recognized in wastewater. Many azo dyes, constituting the largest dye group, may be decomposed into potential carcinogenic amines under anaerobic conditions in the environment. Color removal from wastewater is often more important than the removal of soluble colorless organic substances, a major fraction of which contribute to the COD and BOD besides disturbing the ecological system of the receiving waters. The traditional techniques used for color removal are activated carbon (charcoal), filtration and coagulation. Each method has a few advantages and disadvantages. For example, the use of charcoal is technically easy, but has high waste disposal cost. Although filtration potentially provides pure water as the final product, it is possible for low molar mass dyes to pass through the filter system. Coagulation using alums, ferric salts or limes is a low cost process, but all these methods have a major disadvantage of simply transferring the pollutants to another phase rather than destroying them. Biological treatment is a proven technology and cost effective, however, it has been reported that the majority of dyes is only adsorbed on the sludge and not degraded.

F. Reuse of TiO$_2$

The catalyst’s lifetime is an important parameter of the photocatalytic process, due to the fact that its use for a longer period of time leads to a significant cost reduction of the treatment. For this reason, the photocatalytic experiment was repeated 3 times with the same amount of TiO$_2$ P-25 as catalyst. The quantity of the catalyst was reduced day by day, but only in a very small percentage (1% of the initial quantity was lost). No more catalyst was added. Catalyst recycling depends upon the following factors: 1. Fouling of catalyst, 2. Nature of pollutants, 3. Reaction conditions, 4. Activation, etc.

V. CONCLUSIONS

In this study, we treated the textile effluent using catalyst namely Titanium dioxide under the sunlight. The Titanium Dioxide reduces the COD of the wastewater to a very approachable and also it retains the properties of water and the color reduction was also very sharp. During photocatalytic pretreatment, reaction conditions were optimized for getting the economical benefits of the process. Catalyst concentration was optimized at 0.8 gm/l, pH of the effluent was optimized in 5.5 and the rate of degradation was enhanced by optimizing 1ml oxidant per 200ml effluent sample.

The chemical process could be used as pretreatment in order to increase the biodegradability of the wastewater or as a post-treatment to remove the non-biodegradable compounds. The solution resulting from the photo treatment stage is considered to be biologically compatible after the elimination of: the initial biorecalcitrant and/or toxic compounds, the inhibitory and/or non-biodegradable intermediates, and any chemical reagent (H$_2$O$_2$, O$_3$,…).

These requirements, together with information concerning the evolution of toxicity and biodegradability of the pretreated solution, allow the determination of optimal operational conditions, which corresponds to the best cost-efficiency compromise. Finally, this strategy could be used as a useful guide, as it proposes an easy way to determine the most feasible methods for any industrial wastewater treatment. This photocatalytic method is quite easy and cheap for the treatment of wastewater as the main energy for the treatment is available free of the cost. It is easy to setup in the industry as the cost of setup is much lower than the other methods.

The only disadvantage of this process was found that the total solids, total dissolved solids and total suspended solids increases by a considerable amount.

REFERENCES


