

TiO₂ and ZnO as Heterogeneous Photocatalysts for Wastewater Treatment

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Abstract:

Industrial effluents always cause a major environmental issue. Dyes are extensively used in textile and printing industry. Ever increasing growth of industrialization and urbanization causes gigantic problem of environmental pollution. An industry consumes large quantity of water for their processes. The effluents from dye industry are highly colored, toxic and carcinogenic. The textile industries are responsible for pollution; large amount of waste water is released through cloth dyeing and washing processes. The effluents from these industries are highly organic and toxic in nature with non bio degradable properties. Removing color from wastes is often more important than other colorless and organic substances, because the presence of small amount of dyes (below 1 ppm) is clearly visible and influences the water environment considerably. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove color from textile effluents.[1]

Keywords: photocatalysis, solar light, photoreactor, TiO₂, composites

1. Introduction

Wastewater produced by industries is required be treated before it is discharged into the water bodies. Governments of all countries have laid down rules and regulations for the same. The Gujarat Pollution Control Board (GPCB) in Gujarat have also prescribed some standards and norms for wastewater discharge. This invariably corresponds to a release of about 615 tons per day into the environment and ecological system. Due to their toxicity and recalcitrance, these dyes are hazardous to the environment and even when they are present in very low concentrations, can present serious carcinogenic effects.[1]

1.1 Textile dyes and environmental concerns[2]

Although dyes constitute a small portion of the total volume of waste discharged in textile processing, color removal from effluent is a major problem for textile industry because of several reasons:

1. The presence of even a small fraction of dyes in water is highly visible due to high tinctorial value of dyes and affects the aesthetic merit of streams and other water resources.
2. Most dyes have complex aromatic structure resistant to light, biological activity, ozone and other degradative environments and hence not readily removed by typical waste treatment processes.
3. Possible long term effects of a few dyes and dye degradation products are becoming of increasing concern. The possible mutagenic, carcinogenic and allergenic effects of dyes have been established.
4. Unless and otherwise properly treated dyes can significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to certain forms of aquatic life due to presence of metals and chlorides in them. There is a little evidence that dyes found in water courses are toxic to fish and other wild life at the concentrations likely to be present. Most of the

studies on toxicity of dyes and pigments are concerned with the hazards due to occupational exposure of employees to dyes in the user industry.

5. Dyes have also been known to interfere with certain municipal waste water treatment operations i.e UV disinfection etc.

2. Different techniques for color removal[2],[3]

Owing to their high chemical stability, dyes form highly toxic complexes by combining with various heavy metal oxides and should be treated before discharge

Most current practices for waste water decolorization treatment fall into following main four classes.

1. Physical or Physico-chemical techniques

Precipitation, flocculation, coagulation, ion-exchange, adsorption and membrane separation. This remove or separate color physically and result in need for solid waste disposal. The main disadvantage of this process is high sludge formation, handling and disposal problems, expensive regeneration of adsorbent, incapable of treating large volumes.

2. Chemical techniques

Ozonolysis, Chemical oxidation-reduction, Advanced Oxidation process etc. This technologies remove the colour from breaking down the dye into simpler fragments and destroy the chromophore responsible for colour. The major disadvantages are high electricity cost and the requirement of various hazardous chemicals.

3. Biological techniques

Aerobic and anaerobic digestion, whereby decolourization takes place either by adsorption of dye on activated sludge or by biological degradation of dye molecules. The disadvantages include Slow process, performance depends on some external factors (pH and salts), large area required.

4. Electrochemical techniques

Electrodialysis or ion oxidation. It combines the oxidation of the dye and other polluting contaminants by means of the electrolytic process with the physico-chemical precipitation of sludge. The disadvantages include high sludge formation, high electricity costs, works well only with selected dyes.

2.1 Advantage of Advanced Oxidation Process over other conventional Process[3],[1]

This a modern process used for the water treatment and colour removal. Advanced oxidation processes (AOPs) are therefore mostly based on the generation of highly reactive radical species (especially the hydroxyl radical HO.) that can react with a wide range of compounds, including compounds that are otherwise difficult to degrade, e.g. dye molecules.

Photocatalysis, which is one of the Advanced Oxidation Processes, is a new method used to mineralize dye compounds . The utilization of photocatalysis has been attracting increasing attention. It may be developed to a useful process for the reduction of water pollution caused by dyeing compounds because of their mild conditions required and their efficiency in the mineralization. It also has the potential ability to oxidize most of the organic contaminants to CO₂ and H₂O

3. Photocatalysis[4]

The problem with the photocatalytic process is that when the natural sunlight is being used it consists of a large variety of wavelengths but most of the catalysts which are used have a large band gap which requires high energies and thus small wavelengths are needed. But the UV radiation from the sun's radiation is only about 5 %. Due to this the rate of degradation of the dye molecules is slow. But if the band gap of the catalyst is small then it can work well with the radiation of low energy. According to the equation

$$E = \frac{hc}{\lambda}$$

If the energy required is low it means that the wavelength of that radiation is large. So we can efficiently use the visible region of the solar radiation. So there is a need to develop an efficient catalyst with a small band gap and which can be used in the visible region.[8]

The potential required for the oxidation of hydroxide radical to hydroxyl radical is 2.4V. So the potential of the conduction band of the catalyst should be more than 2.4V. Similarly the potential required for the reduction of oxygen to superoxide anion is -0.33V so the valence band of the catalyst should have a potential less negative than this. To fulfill this condition if we select a single photocatalyst, the band gap required to achieve this is too high and the required energy cannot be provided by the visible region radiation. To overcome this problem we select a combination of 2 catalyst such that one catalyst which can easily reduce and the other which can easily oxidize and the two have small band gap overlapping each other.[8]

3.1 Z-Scheme

In this mechanism the photogenerated electron in the valence band of the semiconductor are transferred into the conduction band and annihilate the holes of the catalyst with lower valence band potential. Here again the charge separation takes place and the electrons are transferred to the conduction band of that catalyst. Finally the holes are present in the catalyst whose valence band potential is relatively higher than the other and the electrons are present in the conduction band of the catalyst with more negative potential. Here the reactive radicals are generated and the dye molecule gets converted into simpler form.

An example of this catalyst is SnO_{2-x}/g-C₃N₄

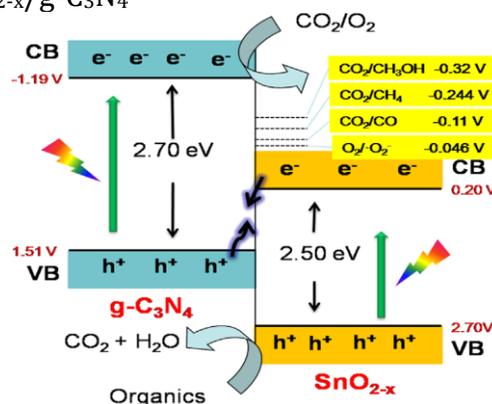


Figure 1 Z-Scheme combination of SnO_{2-x}/g-C₃N₄ [9]

3.2 Heterojunction

Upon irradiation, the electrons gets excited conduction bands of individual photocatalyst. When it loses its energy, they get transferred from photocatalyst whose conduction band is at relatively higher potential to the other at the lower potential.

Similarly, the electrons in the valence band which is relatively at higher potential gets transferred to the photocatalyst whose valence band is at relatively lower potential. It is equivalent to the movement of holes from the lower potential valence band to relatively higher one. Thus the charge separation takes place and the chances of the recombination are reduced which increases the activity of the composite photocatalyst.

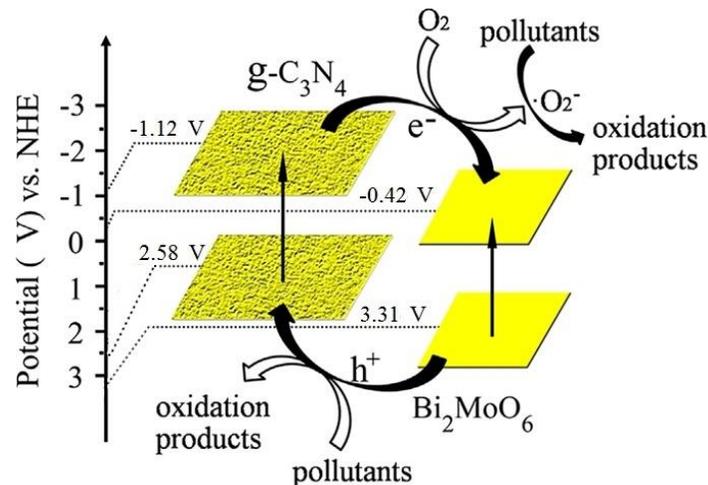


Figure 2 Heterojunction scheme for g-C₃N₄/Bi₂MoO₆ [10]

3.3 Advantages of Solar Photocatalysis

1. Cost effective
2. No sludge formation like other methods such as adsorption, coagulation, flocculation.
3. This method does not generate any other secondary pollutant like other methods as the dye is converted to CO₂ and H₂O.
4. Very small quantity of photocatalyst is required for the treatment
5. The selected catalyst poses no toxicity to human health.
6. Wide application especially to molecular structured complex contaminants
7. Low capital investment.
8. Environmentally appealing.
9. Energy self-sufficient process as it can work under solar radiation.

4. Experiments

4.1 ZnO vs TiO₂

To study the phenomena of photocatalysis, the catalysts selected for experiment were ZnO and TiO₂ and the organic dye selected for the degradation was methylene Blue.

For carrying out the experiment, a dark solution of methylene blue in water was prepared with constant stirring. Equal dye solution was taken in 2 conical flasks and equal dye amount of ZnO and TiO₂ was added to the solution. A small sample of initial dye solution was pipette out as first observation sample.

The dye solution in the conical flasks were kept on two different hot plates. Both ZnO and TiO₂ being good adsorbent, the first two reading were taken in the dark. The observation sample were drawn every 10min. By keeping the solution in the dark, the maximum adsorption of dye would take place and after that the solution was exposed to solar radiation to carry out the photocatalysis which gave the correct idea how much photocatalysis took place.

Conclusion : From the experiment performed, we can say that for visible region the rate of methylene blue degradation was higher for ZnO than for TiO₂ and hence ZnO is more active in visible light than TiO₂. In order to study the effect of the catalyst loading, the degradation of methylene blue was studied with different amount of ZnO added.

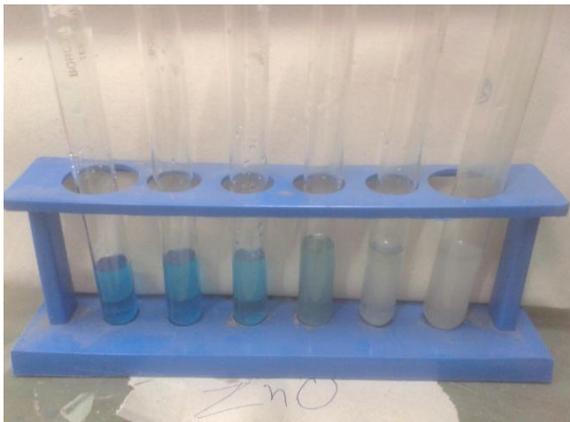
Refer figure 2-3.

4.2 Catalyst Loading

To study these 3 solutions of methylene blue of same concentrations were taken and ZnO added to solution was 1gm, 2gm and 3gm respectively. The three conical flasks were kept on a hot plate and the observations were initially recorded for dark and then were taken when kept in solar light. The observation samples were withdrawn at every 10min.

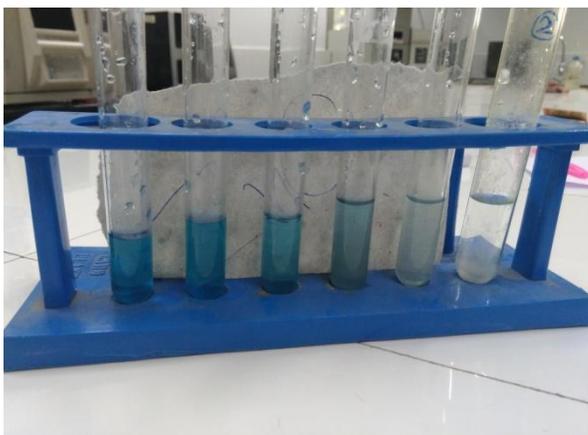
Conclusion: It was seen that the fastest color removal took place in the flask which had 3 gm of ZnO which was followed by the flask which contained 1 gm of ZnO. Thus it can be said that as the catalyst loading increases, the rate of color removal also increases as the free sites available for the dye to get adsorb on the surface increases which increases the rate.

Refer figure 4-5-6.

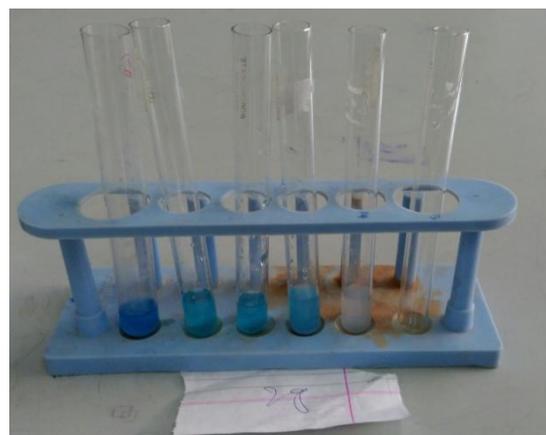


Vs

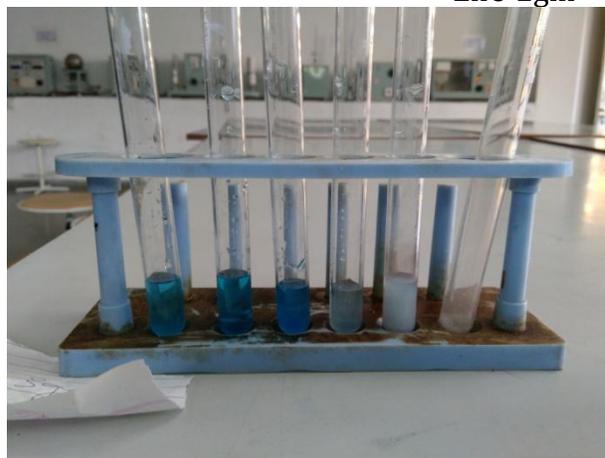
Figure 3-4 ZnO vs TiO₂



ZnO 1gm



ZnO 2gm



ZnO 3gm

Figure 5-6-7 Catalyst Loading ZnO 1gm,2gm,3gm

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