

Factors Influencing The Rate Of Photocatalytic Degradation Of Hazardous Organic Pollutants From Industrial Effluents: A review

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Abstract: This Review states that synthesis and characterisation of photocatalyst, photocatalytic degradation of dyes and also discuss about what are the factors effecting rate of degaradation i.e change of pH, amount of catalyst, dye concentration and amount of oxidant etc. Various types of dyes are being used in the leather, ink, food, paper and textile industries. The waste water from these industries contains remnant dyes, which are disposed in to aquatic source causes serious environmental problems because they are less biodegradable and carcinogenic in nature. Hence, remediation of organic dyes from disposed water is very essential. Photocatalytic degradation is the advanced oxidation process for removal of dyes under visible light irradiation.

Key words: Photocatalyst, Photocatalytic degradation, pH effect, visible light.

I. Introduction

Wastewaters from various industries, factories, laboratories, etc. are serious problems to the environment as shown in Fig 1. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [1]. Though several methods such as adsorption, ultrafiltration, reverse osmosis, ion exchange, biosorption, chlorination and ozonation were proposed for remediation of industrial waste waters, these processes have their own advantages and disadvantages. For instance, adsorption, filtration, ion-exchange and biosorption result in transfer of pollutant from one phase to another and lead to more serious secondary pollution, where as chlorination and ozonation are not cost effective. So, in addition to conventional primary and secondary treatment processes, scientific community has been in the search for complete degradation methods of toxic pollutants into environmentally benign and non-hazardous products [2]. To overcome these problems an alternate method heterogeneous photocatalytic degradation processed under visible light irradiation with the help of metal oxides such as TiO₂ [3], ZnO [4], SnO₂ [5], CeO₂ [6], Bi₂O₃ [7], Cu₂O [8] etc. and mixed metal oxides such as ZnWO₄ [9], Fe₂Mo₃O₁₂ [10], Bi₂Mo₃O₁₂ [11], BiVO₄ [12], LaVO₄ [13], CuBi₂O₄ [14], Bi₂WO₆ and Bi₂MoO₆ [15].

II. Research Methodology

The present study was performed by an objective of to knowthe methods/processes of redegradation or recycling the contaminated water from discharging from Industries or laboratories or other agencies. The main source of the data and information taken from various articles, various web sources like pollution, purification of water, Magzines and other books.



The present work is slated to review the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO₂-based as well as non-TiO₂ based photocatalysts. A brief review of the methods of preparation of the photocatalysts will also be presented.

Photocatalysis may be termed as a photoinduced reaction which is accelerated by the presence of a catalyst [16]. Every semiconducting material either TiO₂ –based or non-TiO₂ based having corresponding band gap energy i.e energy gap between valance band and conduction band. Hence, photocatalysts in this process were activated by absorption of energy from sun light or visible light produced through other sources such as metal halide lamp, xenon lamp or mercury lamp. The absorption leads to a charge separation due to promotion of an electron (e⁻) from the valence band to the conduction band, thus generating a hole (h⁺) in the valence band and electron (e⁻) in the conduction band. Fig 2 depicts schematic representation of heterogeneous photocatalytic degradation process.

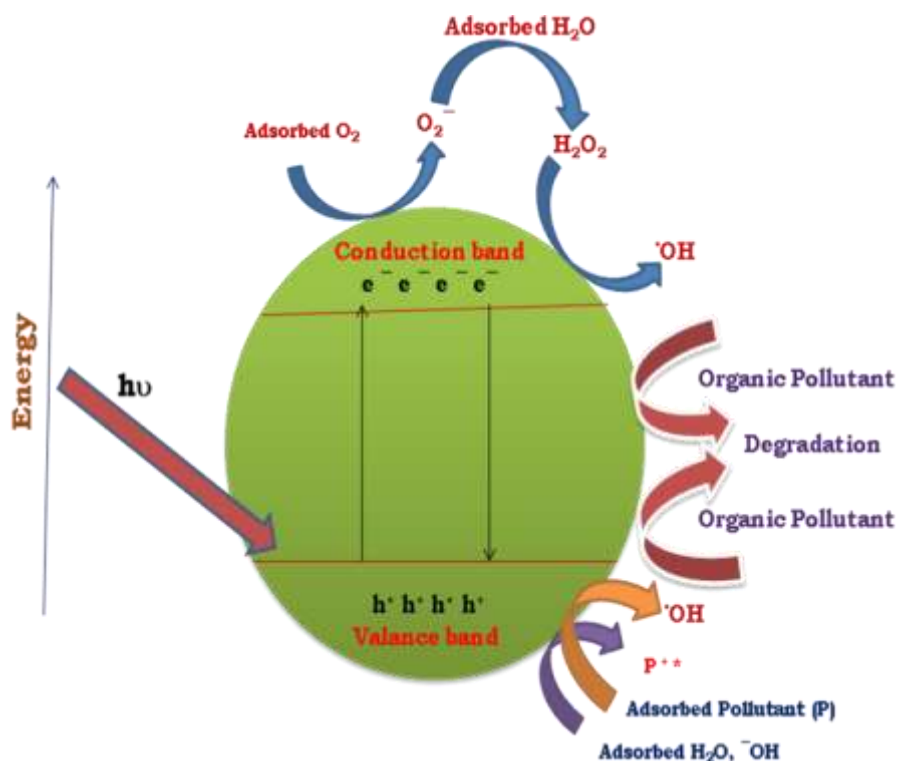


Fig 2 Schematic representation of redox reactions of a dye in presence of a photocatalyst (either TiO₂ based or non-TiO₂ based)under UV/visible light irradiation.

Factors affecting the rate of photocatalytic degradation of dyes

The oxidation rates and efficiency of the photocatalytic system are highly dependent on a number of operational parameters that govern the photodegradation of the organic molecule [17-21]. Several study have been reported the significance of operational parameter.

Effect of dye concentration

The initial concentration of dye in a given photocatalytic reaction is an important factor which needs to be taken into account. Generally speaking the percentage degradation decreases with increasing amount of dye concentration, while keeping a fixed amount of catalyst [22]. This can be rationalized on the basis that as dye concentration increases, more organic substances are adsorbed on the surface of Photocatalyst, whereas less number of photons are available to reach the catalyst surface and therefore less •OH are formed, thus resulting in less degradation percentage. Figure 1 is showing the photodegradation of methyl orange with different photocatalyst. The photodegradation of dyes are increase with decreasing the concentration of dyes with the photocatalyst [23].

Fig 3 depicts UV-visible absorption spectra of Rhodamine –B with change initial concentration of dye. The reaction is conducted in different concentrations such as 5 ppm, 10 ppm and 15 ppm with suprastoichiometric Ferric molybdate under visible light irradiation.

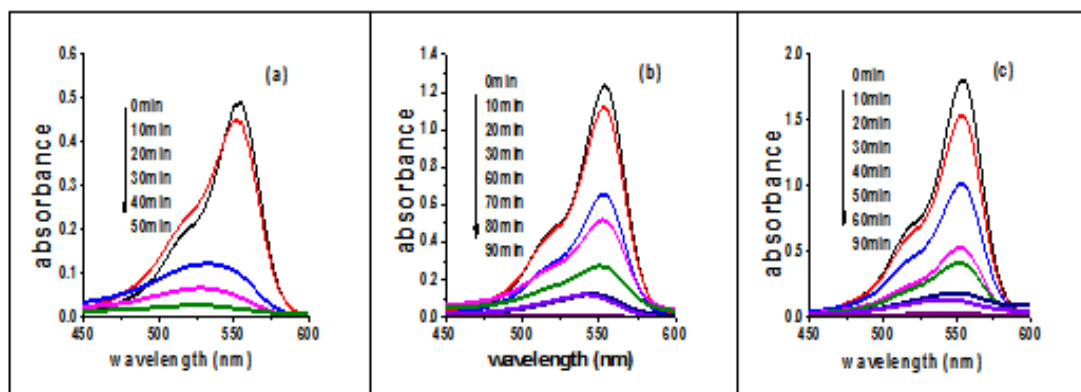


Fig. 3 Spectra relating to photocatalytic degradation of Rh-B with different initial concentrations of pollutant of (a) 5 ppm (b) 10 ppm and (c) 15 ppm, as a function of irradiation time.

Effect of amount of catalyst

Rate of photocatalytic degradation effected also by the amount of catalyst. As increasing amount of catalyst in the photocatalytic process rate of photodegradation also enhanced. This can be explained on the basis that as increase in amount of catalyst commonly enhance the number of active sites on the surface of the photocatalyst thus causing an increase in the formation of number of $\bullet\text{OH}$ radicals which can take part in actual discoloration of dye solution. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing [24].

Fig 4 depicts UV-visible absorption spectra of Rhodamine –B by changing the amount of suprastoichiometric Ferric molybdate ($\text{Fe}_2\text{Mo}_3\text{O}_{12} \cdot x\text{MoO}_3$) i.e 100 mg, 200 mg and 300 mg used as photocatalyst under visible light irradiation. Metal halide lamp is used as source for visible radiation.

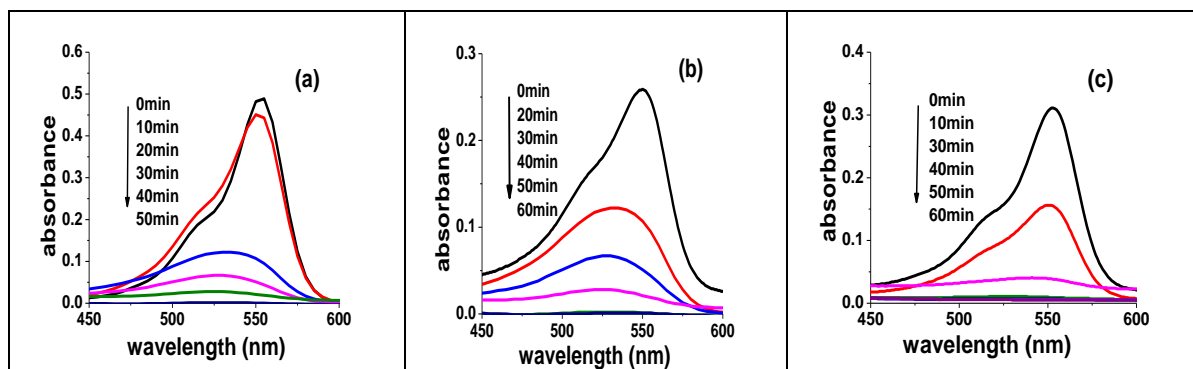
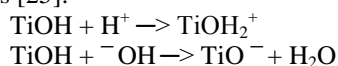


Fig. 4 Spectra relating to photocatalytic degradation of Rh-B with (a) 100 mg, (b) 200 mg and (c) 300 mg photocatalyst, as a function of irradiation time.

Effect of pH of the dye solution

The Photodegradation of dyes are affected by the pH of the solution. The variation of solution pH changes the surface charge of TiO_2 particles and shifts the potentials of catalytic reactions. As a result, the adsorption of dye on the surface is altered thereby causing a change in the reaction rate. Under acidic or alkaline condition the surface of Titania can be protonated or deprotonated respectively according to the following reactions [25].



In acidic conditions the surface of the titania will remain positively charged while in alkaline medium it will becomes negatively charged. At lower pH titanium dioxide exhibit higher oxidizing activity where as in higher pH level reaction rate will be decreased. TiO_2 behaves as a strong Lewis acid due to the surface positive charge. In other words, the anionic dye acts as a strong Lewis base and can easily adsorb on the positively charged catalyst surface. This favours the adsorption of the dye under acidic conditions, while in the alkaline conditions this complexation process is not favoured presumably because of competitive adsorption by hydroxyl groups and the dye molecule in addition to the Columbic repulsion due to the negatively charged catalyst with the dye molecule [26]. The extent of dye adsorption depends on the initial dye concentration, nature of the dye,

surface area of photocatalyst and pH of the solution. The pH determines the surface charge of the photocatalyst. Adsorption of the dye is minimum when the pH of the solution is at the isoelectric point (point of zero charge) [27]. The surface of the photocatalyst is positively charged below isoelectric point and carries a negative charge above it.

Effect of oxidising agent

Reports show that oxidizing agents have a great deal of influence on the photocatalytic degradation of dyes. It was demonstrated by Saquiba et al. [28] that hydrogen peroxide (H_2O_2), ammonium persulphate ($(NH_4)_2S_2O_8$) and potassium bromate ($KBrO_3$) have individual influence on the degradation of Fast Green FCF and Patent Blue VF using Hombikat UV 100 and Degussa P25 as respective photocatalysts. Their results revealed that potassium bromate and ammonium persulphate had a beneficial effect on the degradation rate for the decomposition of dye 1 in the presence of UV 100; whereas in the case of dye 2, all the electron acceptors were found to enhance the rate markedly in the presence of P25.

Suresh et al [2] reported that effect of amount of H_2O_2 on the degradation of Rhodamine-B. The rate of decolorisation was increased with increasing H_2O_2 concentration. The reaction was operated in different H_2O_2 concentrations i.e 8 mM, 10 mM and 12 mM. Fig 5 indicates % degradation of various dyes in presence and absence of H_2O_2 .

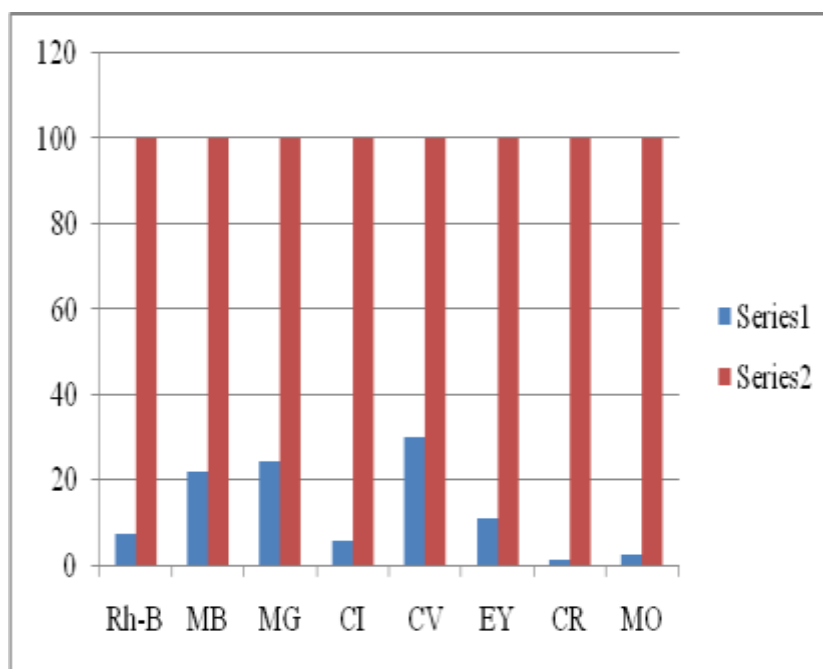


Fig 4. Variation of % degradation as a function of irradiation time for different dye solutions containing H_2O_2 in presence and in absence of (a) $Fe_2Mo_3O_{12}$ photocatalyst.

III. Conclusion

Discharge water from various industries like leather, ink, garment fabrication etc. contaminated with many hazardous chemicals like dyes, lead, tin, Hg etc. shows adverse effect on human beings, on aquatic life and causes other environmental problems. There are several methods such as adsorption, ultrafiltration, reverse osmosis, ion exchange, biosorption, chlorination and ozonation were proposed for remediation of industrial waste waters. Photocatalytic degradation is also one of the advanced oxidation processes for removal of dyes under visible light irradiation with the help of metal oxides such as TiO_2 , ZnO, SnO_2 , CeO_2 , Bi_2O_3 , Cu_2O etc. and mixed metal oxides such as $ZnWO_4$, $Fe_2Mo_3O_{12}$, $Bi_2Mo_3O_{12}$, $BiVO_4$, $LaVO_4$, $CuBi_2O_4$, Bi_2WO_6 and Bi_2MoO_6 . The present study used TiO_2 based and non-based photocatalyst. Photocatalyst degradation depends on effect of dye concentration, effect of amount of catalyst, effect of pH of the dye solution, effect of oxidising agent. Generally the percentage degradation decreases with increasing amount of dye concentration similarly with increasing amount of catalyst in the photocatalytic process rate of photodegradation also increased. The variation of solution pH changes the surface charge of TiO_2 particles and shifts the potentials of catalytic reactions thereby it is causing a change in the reaction rate. Further effect of oxidising agent shows a great deal of influence on the photocatalytic degradation of dyes.

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