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Review: Photocatalytic Degradation of Textile Azo Dyes

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ABSTRACT-*The textile dyeing and finishing industry is one of the major polluters among industrial sectors, in the scope of volume and the chemical composition of the discharged effluent. Textile industry effluents can be classified as dangerous for receiving waters, which commonly contains high concentrations of recalcitrant organic and inorganic chemicals and are characterized by high chemical oxygen demand (COD) and total organic carbon (TOC), high amounts of surfactants, dissolved solids, fluctuating temperature and pH, possibly heavy metals and strong colour. Advanced oxidation processes (AOPs) based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been used with an increasing interest due to their high oxidant power. Photo-catalysis is found to be one of the most effective ways to degrade dyes from wastewater.This paper presents the review of the effect of various parameters on the photo-catalytic degradation of textile dyes by using photo-catalysis process. The findings revealed that various parameters, such as the initial pH of the solution, oxidising agents and catalyst loading exerts their individual effect on photo-catalytic degradation of dyes in wastewater*.

Keywords: *Azo dyes, Photocatalytic degradation process, textile dyes, COD, TOC, Advanced oxidation Process, Photocatalysis etc*.

I. INTRODUCTION

Effluents produced by industries are harmful to human health. When unenviable particles present in the effluents, it can be disastrous or their presence pose severe threat to the immediate recipients. Wastewater produced from various industries and factories are the serious issues to the environment. The waste containing dyes are carcinogenic and toxic to aquatic life and human life[1].This destructive effects of chemicals on the environment are cause the reasons for serious concern [2,3].

About 1-20% of total world production of dyes is lost during dyeing process and is release in textile effluents [5]. The discharged of these coloured wastewaters in the eco-system is a considerable source of non-aesthetic pollution and can produced the harmful by products through oxidation, hydrolysis or other chemical reactions. It is noticed that dyes can produce toxic effects and reduce light penetration in wastewater [6]. Degradation of dyes in industrial wastewater has received more attention and some methods of industrial wastewater have been proposed. Some traditional and physical techniques such as adsorption on activated carbon, ultrafiltration, reverse osmosis, ion exchange on synthetic adsorbent resin etc. have been used for dye removal [4-7]. Thesemethods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. Thesewill have required a further treatment of secondary pollution. Which will add more cost to the process. Bio-degradation [9], Ozonation[10] and advanced oxidation processes [4,11] have also been use for dyes removal.

Traditional wastewater treatment technologies have been proven to be ineffective for handling waste water of synthetic textile dye,because of chemical stability of these pollutants most textile dyes are photo-catalytically stable and refractory towards chemical oxidation [12] and these characteristic provide them resistance toward decolourization by bio-chemical and physio-chemical methods.

The present paper gives general idea on effect of parameter like different dye concentration, catalyst loading and pH of the solution on photo-catalytic degradation of textile dye using photo-catalysis. It also emphasis on the ability of the process to completely mineralise the targeted pollutants.

1.1. PHOTOCATALYSIS

It is the acceleration of a photoreaction in the presence of a catalyst [15]. This type of reaction is activated by absorption of light with sufficient energy [16]. The absorption leads to excitation of electron from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole in the valance band. The recombination of the electron and the hole must be prevented as much as possible if a photocatalyzed must be favoured. The aim of a process is to have a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reluctant to produce an oxidising product. The photo-generated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the catalyst surface or dissolved in water, reducing it to superoxide, radical anion O_2^{-}[4]. The photo-generated holes can oxidised the organic molecule to form R^+, or react with OH^- or H_2O oxidising then into $OH^{\cdot}$Radicals.The resulting $OH^{\cdot}$ Radical, being an oxidised most azo-dyes to the mineral end product.

1.2. SEMICONDUCTOR

Semiconductor (such as TiO_2, ZnO, Fe_2SO_3, CdS, and ZnS) is sensitive to light. As light incidence, the redox-process occurs due to the electronic structure of metal atoms in chemical combination. Semiconductors are characterised by a filled valance band, and empty conduction band [17]. Upon irradiation, valence band electron is promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or carrying interacts separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidising species like hydroxyl or superoxide radicals.

Semiconductors are material whose valance band and conduction band are separated by energy gap, also known as band-gap. When semiconductors absorb light energy with energy equal to or greater than its band-gap, electrons in the valance band can be exited and moves to conduction band, in order to have photocatalyzed reaction [18]. Among all this semiconductors titanium dioxide is widely used.

1.2.1 HYDROGEN PEROXIDE PHOTO-CATALYST

Hydrogen peroxide is used in certain wastewater treatment processes to remove organic impurities. This is achieved by advance oxidation processes, such as photo-catalysis, which use it to generate highly reactive hydroxyl radicals (·OH). These are able to destroy organic contaminates which are ordinarily difficult to remove, such as aromatic or halogenated compounds. Hydrogen peroxide can be photolyzed by UV radiations absorbed at wavelengths ranging from 200 to 300 nm, yielding the homolytic scission of the O-O bond of the H_2O_2 molecule and leading to the formation of ·OH radicals which can also contribute to the decomposition of $H_2O_2$by secondary reactions. In these conditions, several successive and competitive reaction steps can take place:

$$H_2O_2 + h\upsilon \rightarrow 2\,{}^{\bullet}OH \tag{1}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{2}$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \tag{3}$$

$${}^{\bullet}OH + HO_2^{-} \rightarrow HO_2^{\bullet} + OH^{-} \tag{4}$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{5}$$

$${}^{\bullet}OH + HO_2^{\bullet} \rightarrow H2O + O_2 \tag{6}$$

$$2\,{}^{\bullet}OH \rightarrow H_2O_2 \tag{7}$$

Equation (1) corresponds to the initiation step, equations (2) - (4) to the propagation steps, and equations (5) - (6) to the termination steps. [33]

II. OPERATING PARAMETERS IN PHOTOCATALYTIC PROCESS

In Photocatalytic degradation of dyes, the following operating parameter which affects the process are, pH of the solution, oxidizing agents, and catalyst loading.

2.1. EFFECT OF PH ON PHOTOCATALYTIC DEGRADATION OF DYE

The effect of pH on the efficiency of degradation of dye by photo-catalysis process is very difficult task because of its multiple roles [4]. First, it is related to the ionization state of surface according to the following reaction.

$$TiOH + H^+ = TiOH_2^+$$

$$TiOH + OH^- = TiO^- + H_2O$$

As well as that of reaction dye and products such as acidic and amines. The change in the pH can effect on the adsorption of dye on the catalyst surface which is an important step in photo-catalysis [22]. Second, the reaction between hydroxide ions and positive holes for the formation of hydroxyl radical. The positive holes are considered as major oxidation process at low pH, whereas hydroxyl radical considered as the predominant species at neutral or high pH level[23]. Hydroxyl radicals are easily generated by oxidising more hydroxyl ions available on catalyst surface in the alkaline solution, thus the efficiency of process is enhanced [52]. Third, it is also noted that catalyst particle tends to jumble under acidic condition and surface area available for dye adsorption would be reduced[22].The mechanism of photo-catalytic reaction in the presence of catalyst consist of free radical reaction initiated by UV light [25]. The mechanism may depend on the ability of the degraded compound to be adsorbedon the surface of the catalyst.

The degradation rate of azo-dyes increases with decreasing pH [4]. At pH<6, a strong adsorption of the dye on the catalyst particle is observed as a result of the electrostatic attraction of the positively charge catalyst with the dye at pH>6.8 as dye molecule are negatively charged in alkaline media [25,26]. The effects of pH on photo-catalytic degradation of dyes have been studied by many researchers. In studying the effects of Ph on the photo-catalytic degradation of dyes, two things must be borne in mind; one, industrial effluents may not be neutral, and two; pH of the reaction mixture influences the surface-charge -properties of the photo-catalysts [13].**Sleiman et al.** [11] reported that influence of pH on the photo-catalytic degradation of Metanil Yellow, an anionic dye with a sulphonate group, over TiO_2photo-catalyst under UV illumination. The result shows that the process efficiency is not over a wide range of pH (4-8). The author resulted that, the nature of the substance to be degraded affects the operating pH of the system. **Zhiyonget. al.** [46]

reported on the effect of pH on the Photocatalytic degradation of Orange II, an anionic dye with -SO_3group. Their result indicates that the Photocatalytic activity was most favour at low pH (3.0) and more effective at neutral pH.

2.2. OXIDIZING AGENTS EFFECT ON PHOTOCATALYTIC DEGRADATION OF DYES

Saquiba et al.[19] the result indicates that oxidizing agents have great effect on Photocatalytic degradation of dye. It determines that hydrogen peroxide, ammonium persulphate and potassium bromate have individual effect on the degradation of Fast Green FCF (1) and Patent Blue VF (2) using Hombikat UV 100 and Degussa P25 as respective photo-catalysts.**Huang et al.** [39] also studied the effect of adding H_2O_2 on the decolorization of methyl orange. Their result shows that the decolorization rate was found to increase with increase in H_2O_2 concentration.**Zinyong et al.** [47] also reported that addition of H_2O_2 (1 mm) to methyl orange solution mediated TiO_2 Degussa P25 (0.5 g/l) under sunlight irradiated Photocatalyst brought about methyl orange degradation in 1h.**Konstantinou** and **Albanis** [6] their report shows that H_2O_2 and $S_2O_8^{2-}$ where beneficial for the photoxidation of the dyes including azo dyes.

Oxygen is required as electrons scavenger to keep the Photocatalytic reaction, and the amount of oxygen going into the system is an important parameter. The air flow in the system is well regulated, as poor flow can bring about and adverse effect on the Photocatalytic reaction [17].

2.3. EFFECT OF CATALYST LOADING ON PHOTOCATALYTIC DEGRADATION OF DYES

Konstantinou and **Albanis**[6], reported that whether in static, slurry or dynamic flow reactors the initial reaction rates were found to be directly proportional to catalyst concentration indicating the heterogeneous regime. However, it was observed that above a certain level of concentration the reaction rate even decreases and becomes independent of the catalyst concentration. The effect of catalyst loading on photo-catalytic degradation of dyes has been studied. In any reaction system, the initial rates were found to be directly proportional to catalyst concentration. They further observed that there is a limit of catalyst concentration that must be used for photo-degradation of particular pollutant in wastewater, above which the rate photo-catalysis will decrease. They also reported that an enhance degradation rate for optimum catalyst loading up to 0.4-0.5 g/l.

The reason generally advanced for this is that the increase in the amount of catalyst increases the number of active sites on the photo-catalyst surface, which in turn increase the number of hydroxyl and superoxide radicals. Again when the concentration of catalyst increases above the optimum value, the degradation rate decreases due to the interception of the light by the suspension [17].

2.4 NATURE AND CONCENTRATION OF THE SUBTRATE

Organic molecules which can adhere effectively to the surface of the photo-catalyst will be more susceptible to direct oxidation [26]. Thus the Photocatalytic degradation of the aromatics depends on the substituent group. It is reported that nitro phenol is much stronger an adsorbing substrate than phenol and therefore degrades faster[27]. In the degradation of chloro-aromatics pointed out that mono-chlorinated phenol degrades faster than di or tri-chlorinated member. In general, molecules with electron withdrawing group such as nitrobenzene and benzoic acid were found to adsorb significantly in the dark compared to those with electron donating groups [28].

During Photocatalytic oxidation the concentration of organic substrate over time is depend upon photonic efficiency [29]. At high substrate concentration however, the photonic efficiency diminishes and the titanium dioxide surface becomes saturated leading to catalyst deactivation [30].

III. CONCLUSION

The present paper gives general idea concerning the effect of parameters like pH, dye concentration and catalyst loading on dye effluents. The catalyst used with the photo-catalysis system enhances the decolorization and degradation rate. The pH has great influence on the treating solution. About 80% of the decolorization is influence due to acidic pH. The catalyst used for different dye effluents gives varied results depending upon the dye concentration in the solution. Here in this paper various dyes with various varying parameter are studied by researchers. The catalyst gives around 70% increase in the decolorization rate. The catalyst used gives synergetic effect in the photolysis system. This process has proved effective in treating various dye effluents.

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