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# An overview to photo-catalytic degradation of dyes in waste water

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## ABSTRACT

Organic dyes used in textile and food industries are the important sources of environmental contaminations due to their non-bio degradability and high toxicity to aquatic creatures and carcinogenic effects on humans. This demands environmental remediation by the use of techniques which are environmentally benign. For this purpose, a general overview of dye degradation by light in the presence of materials as photo-catalysts has been given. The mechanism of action has also been described. Importantly, the materials involved in dye degradation usually involve nano-composites of either conducting polymers or metal-oxidesor graphene based systems which are insoluble in aqueous solutions, hence will be environmentally benign and can therefore be recovered after use.

***Keywords:*** Nano-materials; Organic dyes; Photo-catalysis

## 1. Introduction and criteria for materials to be best photo-catalysts for dye degradation

The use of dyes in textile industries has become a serious environmental issue because of the unacceptable color of dye effluents, high chemical oxygen demand and resistance to bio-degradation on account of having complex aromatic structures. For this purpose, dyes in waste water are either removed by adsorption or degraded by photo-catalysis. In this area, semiconductor materials have attracted much attention. Among semiconductors, $TiO_2$ is considered a bench mark photo-catalyst for dye degradation. This is because of having high efficiency, low cost, chemical corrosion inertness, and long-term stability against photo-corrosion and chemical corrosion. Moreover, it is a photosensitive material, possesses high photo-catalytic activity, is stable in aqueous systems and has low environmental toxicity[1].But the major shortcoming to the use of $TiO_2$ photo-catalysts lies in having low quantum efficiency and the confined utilization of sunlight. For a material to exhibit high photo-catalytic activity, it must be porous and possess high surface to volume ratio so as to lead increased adsorption of dye. The high surface to volume ratio (surface area) can be attained provided the material to be either highly porous or nano-sized. This is the reason that benchmark $TiO_2$photo-catalyst has been found to be less efficient than nano-sized $TiO_2$.The material must exhibit slower recombination rate of photo-generated electron-hole pairs. This will help to cause facile degradation of dyes. ZnO was found to have almost same band gap energy as that of $TiO_2$, hence it was anticipated to be a better an alternative for $TiO_2$ photo-catalysts, but the fast recombination rate of photo-generated charge carriers limits its applicability. Reduction in the recombination rate can be attained by forming hetero-junctions between different components. This is indicative of making a composite material. However, this would demand the proximal interface contact. Moreover, materials with wider absorption range lead to enhanced efficiency in the degradation of dyes. For such a factor, $TiO_2$ again has limited applicability as it absorbs only a small portion of UV light. Thus to widen its absorption band spectrum, doping, composite science and the formation of hetero-junctions is essential. All the factors discussed above are complementary to one another. This we mean to say that a material with high surface to volume ratio does not suffice to be a good photo-catalyst unless other factors are more or less favoring. This demands the balance in the properties of materials desirable for photo-catalysis[2-5].

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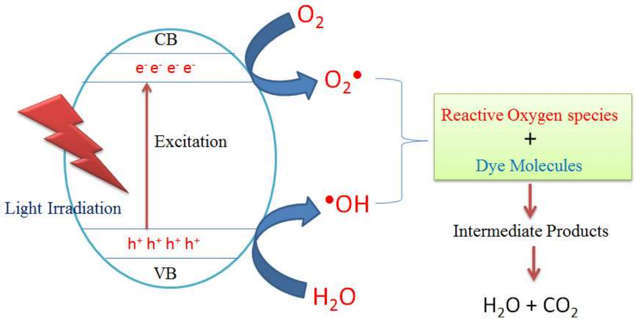
## 2. Mechanism of Action and the development of systems

The mechanism of dye degradation involves the excitation of electrons from valence band (VB) to conduction band (CB) of the material by light irradiation. Due to this excitation, a vacancy is created in valence band called as hole. As the dye solutions are aqueous, holes produced in valence band trap water ($H_2O$) molecules to generate $^{\bullet}OH$ radicals while the electron in conduction band get trapped by the preadsorbed $O_2$ molecules thereby leading to superoxide ($O_2^{\bullet -}$) radicals which would react with protons to generate $^{\bullet}OH$ radicals. These radicals, since having strong oxidizing activity, then interact with dye molecules for causing their degradation into $CO_2$ and $H_2O$ molecules which are environmentally benign[6].



The presence of reactive oxygen species (ROS) for the degradation of dyes and hence the mechanism of degradation is normally proved by adding radical scavengers such as disodium salt of EDTA (EDTA-$Na_2$) and t-butyl alcohol. Their addition to the reaction mixture leads to the scavenging of such ROS thereby causinga reduced efficiency of dye degradation.

It has been observed that single walled titania ($TiO_2$) nanotubes are less efficient to cause dye (Methylene Blue) degradation under UV-light than double walled titania. This has been attributed to the greater surface area of later[7]. To enhance the separation of photo-induced charges and to reduce the rate of recombination, $Bi_2O_3$ has been coupled with $BaTiO_3$. The resulting hetero-junction was found to have an efficient interfacial contact, owing to which the photo-catalytic degradation of Rhodamine-B (RhB) has been enhanced to around 60% than pristine samples[8]. ZnO microspheres have been coupled with $CuInS_2$ and $CuInSe_2$. It has been observed that ZnO/$CuInS_2$ is having more photo-catalytic efficiency to degrade RhB dye as compared to ZnO/$CuInSe_2$ hetero-junction. This has been ascribed to the large surface area of former owing to small size. Moreover a high value of degradation efficiency has been achieved with ZnO/$CuInS_2$/$CuInSe_2$ system as shown in **Figure 1**. This is because of the formation of double hetero-junctions which lead to greater absorption of light and prevents effectively the recombination of electron-hole pairs[9].

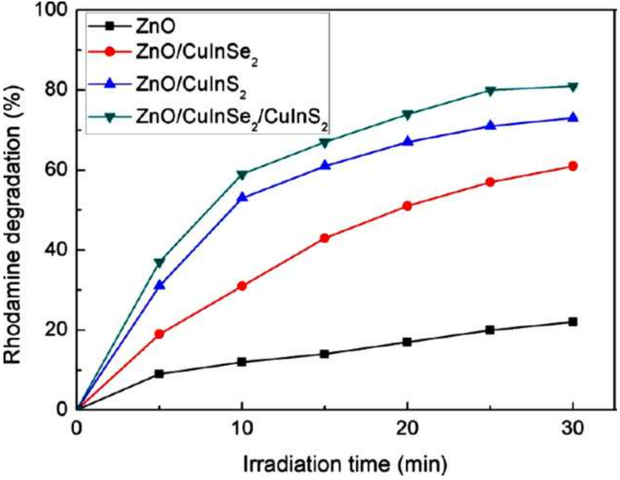


**Figure 1.** Photo-catalytic degradation kinetics of RB aqueous solution with an addition of ZnO microspheres, ZnO/$CuInSe_2$ (with mass ratio of 5:1) hetero-junction photo-catalyst, ZnO/$CuInSe_2$ (with mass ratio of 5:1) hetero-junction photo-catalyst, and ZnO/$CuInSe_2$/$CuInS_2$ (with mass ratio of 10:1:1) double hetero-junctions photo-catalyst.

In addition to the development of above hetero-junctions,conducting polymer based nanocomposite photo-catalysts have attracted much attention. For instance, many metal complexes form nano-composites with conducting polymers like polythiophene (PTh), Polyaniline (PANI) etc. PTh/[Fe$(CN)_3$(NO)(bpy)]4$H_2O$ nanocomposite fibers have been found to exhibit enhanced photo-catalytic activity. The main contributing factor for enhanced activity has been ascribed to the proximal interface contact as the surface area of such a sample has not impressed much. The proximal interface contact between [Fe$(CN)_3$(NO)(bpy)]4$H_2O$ and PTh has been justified by photoluminescence (PL) measurements. For the identification of ROS, scavangers like EDTA-$Na_2$ and t-butyl alcohol have been used that lead to reduced methyl orange (MO) dye degradation as shown in **Figure 2**[10].

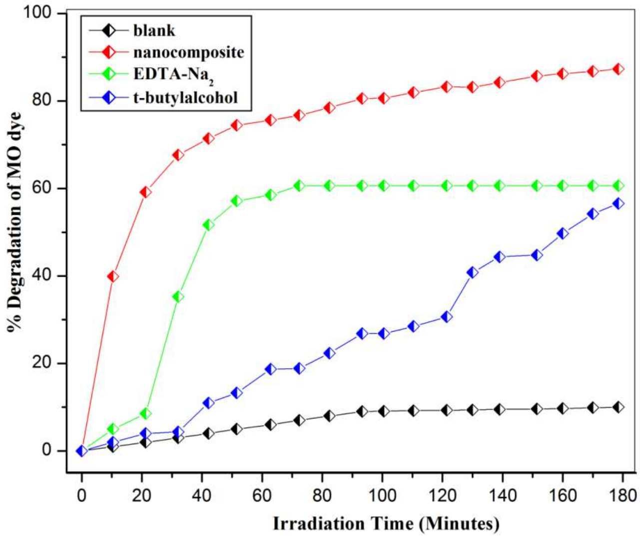


**Figure 2.** Dye degradation of nanocomposite and nanocomposite in the presence of scavengers

## 3. Conclusion

Water treatment is a necessity inorder to minimize the scarcity of water and to avoid environmental contamination from the textile industries. The understanding of eco-friendly materials as photo-catalysts by which environmental remediation can occur has been assessed. The factors responsible for the enhancement or reduction in the degradation of dyes have been taken into consideration.

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