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Heterogeneous photocatalytic treatment of organic dyes: A review

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Abstract

This review focuses on the Heterogeneous Photocatalytic treatment of the polluted water mainly due to dyes. The semiconductors such as TiO2, CdS, ZnO are used as photocatalyst along with some other ternary compounds also. The topic concerned includes various types of dyes, the history and importance of Heterogeneous Photocatalysis. The characteristics of TiO2 which makes it suitable for photocatalysis and some other catalyst are also discussed. The mechanism for the dye degradation and the various parameters which affect the rate of dye degradation are also stated. The various applications of heterogeneous photocatalysis such as Self-cleaning, Air purification, Anti-fogging are also stated. The recent advancement in the topic such as coupled photocatalyst for enhanced dye degradation, solar photocatalysis, the Z-scheme and Heterojunction mechanism are also discussed. The challenges in the field like efficient charge separation, carrying out photocatalysis using solar light, problems associated with the reactor design are also covered.

Keywords: Heterogeneous, Dyes, Solar Photocatalysis, Z-Scheme, Heterojunction

Introduction

Industrial effluents are one of the major sources of the waste water produced across the globe. The major portion of the industrial effluent is released from the dyes and textile industries. Due to recent increase in industrialization and urbanization the environmental pollution has become agigantic issue. The waste water emitted from the dye industries is highly toxic, colored, carcinogenic and non-biodegradable. Removing color from waste water is often more important than removing other organic compounds as even a small amount of color is clearly visible and influences quality of water considerably. This directly affects the aesthetic merit of the streams and other water resources. They decrease the light penetration capacity of water which indirectly affect the aquatic life.[1]The conventional methods presently being used cause other kind of secondary pollution.[2] The sludge formed after the water treatment is also difficult to dispose. These methods induces high electricity costs, requirement of hazardous chemicals and are incapable of treating large volumes.[1]Advanced oxidation process is one of the modern techniques used for degradation which is based on the generation of highly reactive radical species.

Heterogeneous photocatalysis is one of the AOPs.[1]

The photocatalyst and substrate both are in different phases. This method brings about complete mineralization toCO_2 and H_2O which are simpler in nature and also less polluting. The photocatalysts used are generally a semiconductor. When it is irradiated with a light of suitable radiation, the charge separation occurs and the degradation take place.[2]

Background

A. Types of dyes

Different types of dyes, their characteristics and their application are as given in Table 1.

B. Different methods for treatment [4],[5]

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

1. Physical or Physico-chemical techniques

Precipitation, flocculation, coagulation, ionexchange, adsorption and membrane separation. This remove or separate color physically and result inneed for solid waste disposal along with expensive regeneration of adsorbent.

2. Chemical techniques

Ozonolysis, Chemical oxidation-reduction, Advanced Oxidation process etc. This technologies remove the color from breaking down the dye into simpler fragments and destroy the chromophore responsible for color. 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. It is a very slow process.

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 physiochemical precipitation of sludge.

C. Evolution of the field of heterogeneous photocatalytic treatment of organic dyes

The first instance of dye instability was seen in the presence of an inorganic semiconductor and illumination appears to be in 1969 when the photocatalytic reduction of Methylene blue took place. Intentional attempts to photochemically destroy the dye have been investigated only almost a decade later when electron transfer from TiO_2 to Methyl Orange was seen which resulted in bleaching of dye absorption and later it converted to hydrazine. Ultimately it was concluded that bleaching required TiO_2 and source of illumination and thus it was proved that photcatalytic process involved initial light absorption and the generation of electron and hole pair.[3]

Different photocatalysts

A. TiO_2

TiO_2 is a very widely used photocatalyst for the dye degradation. The property which makes TiO_2 suitable or dye degradation is its band gap. Based on optical absorption spectra, the band-gap energies were estimated to be 3.0 eV for Rutile and 3.2 eV for Anatase. When irradiated with UV light, the charge separation takes place and the degradation occurs. It is one of the best catalyst which works very efficiently in UV region.

1. Oxidizing species at TiO_2 surface

To understand the photocatalytic mechanism it very important to know the oxidizing species which are responsible for the dye degradation. Many efforts have been devoted for clarifying the oxidizing species generated at the irradiatedTiO_2 surface. It is found that the oxidizing species include holes, either free or trapped, •OH radicals, $O_2^{\bullet -}$, and O_2.[6]

Dyes	Characteristics	Application
Direct dyes	(i) simplest and cheapest dyes (ii) Water soluble anionic dyes (iii) High affinity for cellulose fibers	Cotton, cellulosic, regenerated cellulose, paper, leather, nylon, and blends
Acid dyes	(i) Water soluble anionic dyes (ii) Typical pollutants: color, organic acid, unfixed dyes (iii) Dyeing methods: exhaust, beck, and continuous	Silk, wool, synthetic fibers, leather, nylon, modified acrylics, paper, ink-jet printing, food, cosmetics
Basic dyes	(i) Water soluble cationic dyes (ii) Yield colored cations in solutions (iii) Salt-forming counter ion	Silk, wool, cotton, polyacrylonitrile, modified nylons, modified polyester, tannin-mordanted
Azoic dyes	(i) Consist of electron accepting substituents and electron donating substituents (ii) Named as carbocyclic azo dyes if include only aromatic groups	Printing inks, pigments

2. Limitations of TiO2

Though TiO2 is one of the most versatile photocatalyst used across the world but the major limitation is there combination of the photogenerated charge carriers which decreases the quantum efficiency of the overall reaction. Trapping of the photo-generated electrons by the reduction of surface Ti4+ ions to Ti3+ species happens in ~30 ps, while there combination occurs within 10 ns. Many methods including heterojunction formation, doping with ions, and nano sized crystals have been demonstrated to reduce photo-excited charge carrier recombination. Another serious drawback of theTiO2 photocatalyst is the wide band gap of anatase TiO2 (Ebg~3.2 eV), which restrains its use to UV light ($\lambda \leq 390$ nm).Because of this, TiO2 displays a high photocatalytic activity only when it is irradiated by UV light. This means that only ~5% of the solar radiations can be utilized by the conventionalTiO2 photocatalyst, which adversely affect the commercialization of TiO2 based photocatalysts.[7]

3. Visible light induced photocatalysis

Both the Rutile and the Anatase structure of the TiO2 havewide gaps due to which they only work in UV region but itcauses a problem when it is used under the solar light as only5% of the total radiation is in UV region. So some methods are proposed which can make TiO2 work even in the visible region. For this efforts are made by doping with some impurity, coupling with other semi-conductor with small band gap, preparing oxygen deficient TiO2, and doping TiO2 with non-metal atoms such as C, N, P, S and F.[8]

B. Other photocatalyst

B.1 Binary compound [9]

(1) ZnO: ZnO has been often considered a valid alternative toTiO2 because of its good optoelectronic, catalytic and photochemical properties along with its low cost. ZnO has a band gap of 3.0 eV. Due to the position of the valence band of ZnO, the photogenerated holes have strong enough oxidizing power to decompose most organic compounds. Several studies have shown that ZnO was quite active under visible lighti llumination for the photodegradation of some organic compounds in aqueous solution.

(2) WO3: WO3 is a visible light-responsive photocatalyst that absorbs light up to ca. 480 nm. Anyway, WO3 has generally showed a low photoactivity to degrade pollutants that has been attributed to the high recombination rate of the photo produced

electron/hole pairs and/or to the low rate of electron transfer toO_2.

(3) Bi_2O_3: Bi_2O_3, with a direct band gap of 2.8 eV, can be excited by visible light.

(4) CdS: CdS, with a direct band-gap energy of 2.42 eV. CdSis not suitable for the photocatalytic removal of organic pollutants because it is unstable under irradiation and suffers photo corrosion that not only destroys the photocatalyst but, more importantly, releases toxic cadmium ions in solution.

B.2 Ternary photocatalyst [9]

The Ternary photocatalyst have been proved to be more efficient than the binary compounds. It helps to overcome the intrinsic limitations and new materials have also been developed which are suitable to exploit the visible component of sunlight. The photocatlyst are $BiVO_4$, Ag_3VO_4, $BiWO_6$.

Mechanism for degradation of dye

The steps involved in photocatalytic reactions are explained below. [10],[11]

1. Separation of charge carriers by photons absorption of photocatalyst: When any photocatalyst is subjected to a radiation of suitable frequency, it absorbs the radiation and the electron hole pairs are created due to energy gain and excitation.

$A + h\upsilon \rightarrow A(e^-_{CB} + h^+_{VB})$

2. Migration of photo-excited electrons and holes through surface of the photocatalyst. Due to instability the electron from the conduction band gets transferred to the valence band which generated the electron hole pairs.

3. Generation of intermediate species such as hydroxyl radical ($OH\bullet$), superoxide anion radical ($O_2\bullet^-$) andhydrogen peroxide (H_2O_2). As the band gap energy oflies in the visible region, the catalyst can harvest photon energy efficiently from the naturally available solar source and can then react with the dye molecule to degrade it.

$h^+_{VB} + H_2O \rightarrow OH\bullet + H^+$

$e^-_{CB} + O_2 \rightarrow O_2\bullet^-$

$O_2\bullet^- + H_2O \rightarrow H_2O_2$

$H_2O_2 \rightarrow 2OH\bullet$

$OH\bullet + Dye \rightarrow CO_2 + H_2O$

$h^+_{VB} + Dye \rightarrow$ Degradation Products

Factors affecting photocatalysis

A. Catalyst loading

The amount of catalyst used is directly propotional to the dye degradation rate. With increase in the amount of the photocatalyst, the rate of dye degradation should increase due the availability of more free sites. However when the amount of the photocatalyst is above certain level, the ability of the catalyst to absorb light decreases due the increase in turbidity of the solution and decrease in the surface area exposed to irradiation which decreases the light absorption coefficient. Hence the rate of degradation also gets affected. This stage is known as Saturation stage.[13],[14]

B. Effect of pH

If the nature of the dye is anionic, then lower pH is preferred and if the dye is cationic in nature then pH around 9is preffered.[14]

C. Effect of intensity of radiation

With the increase in the intensity of the radiation, more electron hole pairs are created and thus the rate of photocatalysis increases. But when the intensity is increased beyond certain limit, the electron-hole pairs generated are much more than dye molecules in the water and hence there combination of the electron-hole takes place. Such condition does not increase the rate and reaches at a saturation level.[15]

D. Effect of temperature

With increase in temperature the degradation rate increases as the mobility of the ions increase and also the rate of adsorption increases on the surface of the catalyst.[15]

E. Effect of dye concentration

The changes in dye concentration follows inverse relationship with the rate of dye degradation. When the concentration of the dye increases, the available hydroxyl radical and superoxide anion per unit amount of dye decreases and hence the rate of photocatalysis decreases. Similarly when the dye concentration is decreased, the rate of the reaction increases as more vacant sites are available for the dye molecules to get adsorbed.[13],[15]

F. Size and structure of photocatalyst

Surface morphology like particle size and agglomerate size, is an important factor to be considered in photocatalytic degradation process because there is a direct relationship between organic compounds and surface coverage of the photocatalyst. The number of photon striking the photocatalyst controls the rate of reaction which signifies that the reaction takes place only in the absorbed phase of the photocatalyst. The more the surface area higher is the rate of degradation.

Conclusion

Due to the limitations of the present conventional methods available for dye degradation like sludge formation, causing secondary pollution, large equipments required, Heterogeneous photocatalysis has proved to be a perfect alternative. It does not require much sophisticated equipments, does not form sludge and also does not cause any secondary pollution. TiO2 is one of the most popular photocatalyst used due to its small band gap and high efficiency in UV region. But the lack of visible light activity hinders its practical applications. To effectively utilize the solar radiation composite catalyst made by coupling of 2 or more catalyst is made. This is done to increase the promotion of the electrons to conduction band and also prevent the recombination of the electron-hole pair which increases its activity. The effects of different parameters on degradation are examined. The mechanism of the electron transfer which includes Z-scheme and heterojunction are also analysed using some examples. Due to this they find applications in manufacturing of self cleaning material, treatment of cancer, air purification etc. Recent advances like doping the photocatalyst with impurities and non-metals is done to reduce the recombination of charges. Though heterogeneous photocatalysis has an immense potential for dye degradation, it face various challenges like proper reactor design, making correct combination for coupled photocatalyst, preventing there combination of photogenerated charges need to overcome.

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