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Visible/solar light active photocatalysts for organic effluent treatment: Fundamentals, mechanisms and parametric review

Leena V. Bora, Rajubhai K. Mewada*

Department of Chemical Engineering, Institute of Technology, Nirma University, Sarkhej-Gandhinagar Highway, Ahmedabad, Gujarat- 382481, India

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ABSTRACT

Intensive research work is being undertaken globally to effectively use the process of photocatalysis for the degradation of organic pollutants from industrial effluents. For the same, TiO_2 has been extensively explored, which however, has a limitation of being able to utilise the UV spectrum only, due to its high band gap property. Since a substantial percentage of the solar spectrum is visible light, it is imperative that for an effective and versatile utilisation of the incident solar energy, visible light active photocatalysts, having a relatively smaller band gap are developed. Smaller band gap, however, often results in rapid recombination and conversion of photonic energy into non-usable heat. This article is a review of the science behind the performance of visible/solar light active photocatalysts. The first part includes the fundamentals of photocatalysis, including thermodynamics, reaction kinetics and recombination. The second part reviews the visible/solar light active photocatalytic materials as well as the significant research efforts made so far in the exploration of possible mechanisms of photoexcitation and remedies for minimization of recombination. Finally, an operational overview is provided which is helpful in assessing the influence of key parameters on the photocatalytic activity. This review presents a single point reference for a comparative study and ready assimilation of the basics and new directions in photocatalysis, thus making it more conducive to further research and active commercialisation.

1. Introduction

1.1. Industrial effluent and water pollution

Water is a fundamental prerequisite of all life forms on earth but obtaining a decent quality of water is a huge challenge for developing countries like India. This situation is further severed by industrial effluent mixing with natural resources and reservoirs of water. Several life forms across the globe have faced health issues due to consumption of impure water. The organic, inorganic and microbial contaminants present in these effluents pose a threat to human, aquatic and biotic life. A major fraction of these effluents consists of colour-imparting dyes coming from industries related to textile, cosmetics, food, paints, etc. These dyes can be toxic and carcinogenic in nature. Hence, removal of these dyes and other organic contaminants from the effluents is of utmost importance. The ubiquitous problem faced globally is the plausible discharge of the industrial effluent. Several stringent norms have been laid down by governments of various countries to combat the issue.

Generally, the conventional methods only convert one type of pollution into another, e.g., adsorption of pollutant from liquid effluent onto a solid adsorbent treats the liquid, but transfers the contaminant onto the solid. The adsorbent then becomes the new pollutant requiring treatment, in order to comply with the discharge norms. Hence, the issue of effluent treatment still remains unaddressed unless the pollutant is satisfactorily degraded. Moreover, the conventional treatment methods need extensive design and incur considerable inventory and energy. Hence, industrialists and researchers are constantly in search of eco-friendly treatment methods capable of degrading the pollutants instead of just converting them from one form to another.

1.2. Solar energy utilisation

Another issue in the treatment of dyes and organic pollutants is that these methods are generally a costly proposition. Hence, researchers are focussing attention on utilisation of cost effective sources of energy and/or tools for the same. Owing to its huge availability, sustainability and cleanliness, the concept of harvesting solar energy for various

* Corresponding author.
E-mail addresses: leena.bora@nirmauni.ac.in (L.V. Bora), rkmewada@nirmauni.ac.in (R.K. Mewada).

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Nomenclature

Dye/Pollutant

2,4-DCP	2,4-dichlorophenol
4-CNP	4-chloro-2-nitrophenol
4-CP	4-chlorophenol
AB14	Acid Brown 14
AO7	Acid Orange 7
AR-B	Acid Red B
BA	Benzoic Acid
BF	Basic Fuchsin
BPA	Bisphenol
BR9	Basic Red 9
C343	Coumarin 343
CG-R	Congo Red
DBS	Dodecylbenzenesulfonate
IP	Isopropanol
MB	Methylene Blue
MO	Methyl Orange
MV	Methyl Violet
P	Phenol
PCP	Pentachlorophenol
RhB, RM-B	Rhodamine B
RhG	Rhodamine 6G

Standard units

g	Gram, mass
g/L	Gram per Litre, concentration
hr(s)	Hour(s), time
L	Litre, volume
mg	Milligram, mass
mg/L	Milligram per Litre, concentration
min	Minute, time
mL	Millilitre, volume
μM	Micromolar, concentration
M	Molar, concentration
μmol/g	Micromole per gram, concentration
nm	Nanometer, length
ppm	Parts per million, concentration
TW	Terawatt, energy
V	Volt, potential
W	Watt, energy
$Wm^{-2}\ \mu m^{-1}$	Watt per sq. meter per micrometer, irradiance

Constants

k'	Used in Eq. (13).
$K_{apparent}$	Used in Eq. (14).
β_1, β_2, β_3	Used in Eqs. (15) and (16).

Subscripts

0	Initial (time =0)
i	Species
inc	incident
max	maximum
Ox	Oxidant
R	Recombination
Red	Reductant

Technical terms

C	Concentration
C_0	Initial concentration
C_A, C_B, C_i	Concentration of species A, B and i, resp.
E	Activation energy
ΔG	Gibb's free energy change
h	Planck's constant
ΔH	Enthalpy change
I	Intensity of light
k	Rate constant
k_0	Frequency factor
K_i	Adsorption equilibrium constant
r	Reaction rate
R	Universal gas constant
ΔS	Entropy change
t	Time
T	Temperature
θ_{Red}	Fraction of electron-donating reductant adsorbed
θ_{Ox}	Fraction of electron-accepting oxidant adsorbed
λ	Wavelength
ν	Frequency
Φ	Intrinsic quantum efficiency
χ	Formal quantum efficiency
ξ	Photonic efficiency
ϵ	Energy conversion efficiency

Acronyms

A, B	Reactants
AOP(s)	Advanced Oxidation Process(es)
BG	Band Gap
CB	Conduction Band
C, D	Products
COD	Chemical Oxygen Demand
CPC	Compound Parabolic Concentrator
e^-	Electron
e_{CB}^-	Electron in Conduction Band
E	Energy
h^+	Hole
h_{VB}^+	Hole in Valence Band
IR	Infrared
L-H	Langmuir Hinshelwood
LDH	Layered Double Hydroxides
MWCNT	Multi-Walled Carbon Nanotubes
NB	Nanobelt
NHE	Normal Hydrogen Electrode
NP	Nanoparticle
PZC	Point of Zero Charge
(R)GO	(Reduced) Graphene Oxide
SPR	Surface Plasmon Resonance
SWCNT	Single-Walled Carbon Nanotubes
TOC	Total Organic Carbon
UV	Ultraviolet
VB	Valence Band

applications is booming all over the world. On the basis of energy, the solar spectrum constitutes about 3–5% UV ($\lambda < 400$ nm) and about 47% visible light ($400 > \lambda < 700$ nm) as depicted in Fig. 1. Theoretically, the earth receives about 89,300 TW of solar insolation [1,2]. However, there is a huge gap between its availability and its employment in various applications, which must be addressed intelligently. Environmentalists are finding out ways and means to harvest and utilise it for the purpose of effluent treatment.