International Journal of Scientific Research and Management Studies (IJSRMS)
ISSN: 2349-3771 **Volume 1 Issue 6, pg: 242-247**

A REVIEW: NANO SCIENCE FOR ENVIRONMENTAL REMEDIATION

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ABSTRACT

Polluted waste water plays significant role in environmental pollution. Industrial effluents contain different chemicals especially synthetic dyes which are carcinogenic in nature. Some dyes decompose aerobically and anaerobically resulting in the formation of carcinogenic compounds. Classical techniques which are still in use to decontaminate polluted water include adsorption, chlorination, coagulation, ion flotation, membrane process, sedimentation and solvent extraction. The end products of these techniques need to be processed further for complete purification. There are newer advanced oxidation processes which can be used to degrade harmless products and into carbon dioxide and water. These include biodegradation fenton, photofenton, photocatalytic radiation, sonolysis, ozonation, and UV photocatalytic processes. These advanced oxidation processes are better than chemical ones however these are much costly. Evolution of a new branch of science known as nano science has completely replaced the previous technologies due to the following reasons (Nanomaterials completely mineralize most of organics and are inexpensive. Semiconductors remove completely organic matter from polluted water. Nanophotocatalyst are non-toxic, non-corrosive and stable chemically and thermally Photocatalyst are easily available, inexpensive and stable to corrosion in the presence of water and chemicals.). A number of nanosized advanced materials have been synthesized for photocatalysis using different techniques. These catalysts find applications in environmental remediation, sterilization, hydrogen production and renewable energy. Nanophotocatalyst has been used successfully for the treatment of hazardous materials such as industrial effluents containing dyes. The study of composition, surface area, shape, size and nanostructure of these photocatalyst may help in current and further development of photocatalysts for environmental remediation.

KEY WORDS: *Nano materials, Remediation, Nano-photocatalyst, Nanoscience.*

I. INTRODUCTION

Photocatalytic research is basically related to the development of solar energy use. The use of solar energy technology can be divided into solar batteries [1], solar heat [2] and photo-catalysis .The core technology among them is to convert solar energy into chemical energy. This conversion refers to the synthesis of chemical energy to induce a chemical reaction. In the early 1970s, Fujishima and Honda [9] revealed the possibility of hydrogen production through water decomposition by photocatalysis and solar energy, and explosive research began. Afterwards, the interest in TiO_2 photocatalysis has been growing in the academic and industrial fields, and has been applied actively to hydrogen production ,air cleaning, metal anti-corrosion [3] and hydrophilic ,self-purifi-cation and antibacterial activity [4]. Some of these technologies have been released on the market. Fig. 1 shows the various applications of TiO_2 catalysis in a recent. Photocatalysis may be termed as a photoinduced reaction which is accelerated by the presence of a catalyst. These type of reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy of the catalyst). The absorption leads to a charge separation due to promotion of an electron (e-) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole in the valence band, the

schematic diagram of the process is presented in Fig1. The recombination of the electron and the hole must be prevented as much as possible if a photocatalyzed reaction must be favored (Fig. 1). Semiconductor molecules contain a valence band (VB) occupied with stable energy electrons and empty higher energy conduction bands (CB), the band gap of the semiconductor energy with higher energy is used to emit light inside the semiconductor to induce a reaction with the absorbent material on its surface via a redox reaction. This is called the photocatalytic reaction. Photocatalytic reactions are based on solar energy absorption in the bad gap of the semiconductor and the following photo-generated electron transfer. Therefore, all semiconductor materials can be used in photocatalysis. On the other hand, there are few effective semiconductors as photocatalysts, and TiO_2 is the most widely used among them.

II. FUNDAMENTALS AND MECHANISM OF TIO2 PHOTOCATALYSIS

The fundamentals of photophysics and photochemistry underlying the heterogeneous photocatalysis employing the semiconductor TiO_2 catalyst have been intensively reported in many literatures. The semiconductor TiO_2 has been widely utilised as a photocatalyst for inducing a series of reductive and oxidative reactions on its surface. This is solely contributed

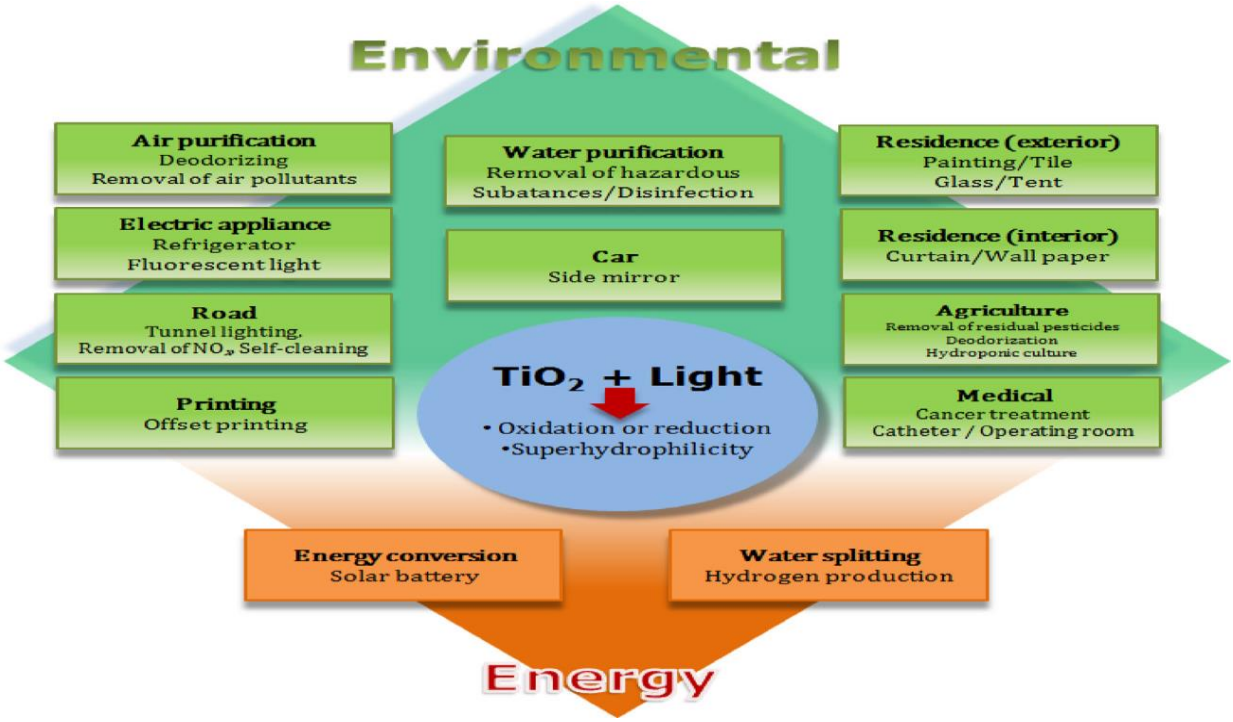
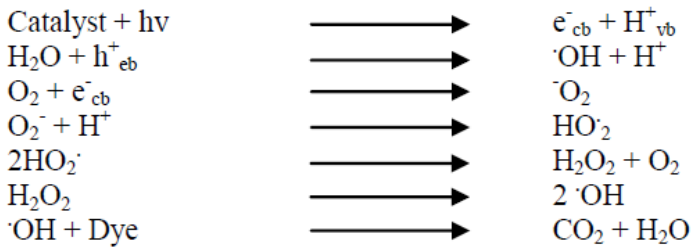


Fig-1 various applications of TiO_2 photocatalysis in environment and energy fields.

by the distinct lone electron characteristic in its outer orbital. When photon energy of greater than or equal to the band gap energy of TiO_2 is illuminated onto its surface, usually 3.2 eV (anatase) or 3.0 eV (rutile), the lone electron will be photo excited to the empty conduction band in femtoseconds depicts the mechanism of the electron hole pair formation when the TiO_2 particle is irradiated with adequate hv. The light wavelength for such photon energy usually corresponds to $l < 400$ nm. The photonic excitation leaves behind an empty unfilled valence band, and thus creating the electron-hole pair. The series of chain oxidative reductive reactions that occur at the photon activated surface was widely postulated.

The mechanism of the photocatalytic degradation is as under.



III. SYNTHESIS TECHNIQUES

There are several techniques to synthesize nanophotocatalysts

3.1. Ball-milling or High Energy Ball-milling

Transition metal oxides, borides, carbides and silicides can be synthesized by ball milling which is also known as mechano chemical method. Different alloy composite can also be obtained by mechanical activation in ball mills e.g. metal alumina composites [5]. We can prepare nanosized particles by alloying mechanically in ball mills. High energy ball mills are indispensable in material science and engineering. Nano crystalline powders with new and unusual properties can be prepared by ball milling which is a good state processing method [6]. Powdered particles are broken and welded repeatedly forming nano structured alloys in ball mills.

3.2. Hydrothermal technique

Nanoparticles can also be synthesized by this technique which is also known as solvo-thermal technique [7]. The reactions are carried out in an autoclave at a pressure of 2000 pounds per square inch and a temperature of 200˚C or higher. Nanoparticles prepared by this method show better crystallinity and grain size. Nanophotocatalyst with specific sizes and morphology can be synthesized by continuous hydrothermal technique. Reaction kinetics can be increased by microwave heating during hydrothermal technique. Microwave hydrothermal technique needs lower temperature as 150˚C and shorter time as 25 min as compare to conventional hydrothermal technique.

3.3. Sole-gel technique

This method is one of the most popular processes for producing nanophotocatalyst mentioned in several books [8]. Over the years, solution precipitation and sol–gel processing have come to be used interchangeably, mostly by people on the fringes of the technical community. There are distinct differences between the two methods, as will be made clear below. Transition metal precursor is hydrolyzed with water and product is allowed to react to form precipitates, which are washed, dried and calcined at elevated temperatures to form nanocrystals of metal oxides. Smaller particles can be produced by slow and controlled hydrolysis and base catalyzed condensation reaction form denser particles.

3.4. Chemical co-precipitation

A facile and convenient method to prepare nanoparticles is chemical co-precipitation technique. Two or more soluble salts solutions are mixed in a definite ratio and co-precipitated with a base solution under inert atmosphere [9]. Solutions of two or more water soluble salts of metals are dissolved in water, mixed and co-precipitated with alkali very slowly (in approximately 2 hours). Afterwards the resulting solution was stirred for 6 hours. The precipitate thus formed were filtered, washed, dried and sintered at about 400-600○C for 4-6 hours

3.5. Reverse Micelle technique

Micro emulsion of oil in water is used to prepare uniform sized nanoparticles. This emulsion contains three components oil, water and surfactant which form thermodynamically stable, single phase, isotropic transparent solution. The reacting reagents are present in nano water droplets surrounded by surfactant molecule. These water droplets containing reagents coalesce rapidly allowing mixing and

precipitating the nanoparticles. Nano droplets of water solution are spherical and surrounded by surfactant molecular wall which act as a cage of growing particles. The size of precipitated molecule changes with size of water pool in micelle. Mono dispersed nanoparticles of different morphologies and sizes can be synthesized by this technique. This method is costly and have low yield.

IV. OPERATING PARAMETERS IN PHOTOCATALYTIC PROCESSES

In photocatalytic degradation of toxic organic compounds or dyes in wastewaters, the followings are operating parameters which affect the process: pH of the solution to be degraded, and the pH of the precursor solution (catalyst's solution during preparation of catalyst); oxidizing agent, calcination temperature, dopant content, and catalyst loading. These parameters will be considered one after the other as they influenced the photocatalytic processes of the degradation of dyes or toxic organic compounds in wastewaters.

4.1. Photocatalyst concentration

Heterogeneous photocatalysis is influenced by the concentration of photocatalyst [10]. $OH\cdot$ radicals are increased with the increase in concentration of photocatalyst resulting decolorization of the dye. After a certain limit of time concentration of catalyst solution become opaque and light radiation cannot enter in to activate the catalyst particles. Hence the rate of dye degradation decreased.

4.2. PH of the Solution

PH of the solution also affect the rate of photo degradation of the dye by changing the surface charges of the nanophotocatalyst particles. Hence adsorption of charged particle at the surface of catalyst is altered which changes the rate of degradation reaction [11]. Photocatalyst surface may protonate or deprotonate with the change of pH value. Anionic dyes will be degraded more at lower PH. Reductive cleavage may take place in azo dyes at low pH favoring the degradation of azo dyes.

4.3. Free Oxygen in solution

O_2 molecule in solution accept the e- from conduction band and form stabilize $O_2\bullet$ radicals decreasing the e^-/h^+ recombination rate. $O_2\bullet$ radicals oxidize the dye molecule and degrades. O_2 does not adsorb on the surface of catalyst. Free O_2 present in solution stabilize intermediate radicals which are responsible for the mineralization of the dye molecule. It also induces the cleavage mechanism of aromatic bonds in organics which pollute water

4.4. Intensity of light and time of irradiation

Intensity of light and irradiation time both have affect on the rate of photo degradation of pollutants [12]. The degradation reaction rate changes linearly if the intensity of light increases at low intensity values (0-20mW/Cm^2) but the rate of reaction changes with the square root at intermediate intensity (25 mW/cm^2) [13-16]. At higher light intensity the rate of degradation become independent of light intensity. Rate of degradation initially increase if the intensity is increased .Time of irradiation also affect the degradation rate at longer irradiation time byproducts are accumulated on the active sites of nanoparticles resulting in the deactivation of photocatalyst

V. SOLAR COLLECTOR TECHNOLOGY GENERALITIES

Traditionally, different solar collector systems have been classified depending on the level of concentration attained by them. The *concentration ratio* (CR) can be defined as the ratio of the collector aperture area to the absorber or reactor area. The *aperture area* is the area intercepting radiation and the absorber area is the area of the component (either fully illuminated or not) receiving concentrated solar radiation. This CR is directly related to the working system temperature and, according to this criterion, there are three types of collectors [17-18]:

- Non concentrating or low-temperature, up to 150º C
- Medium concentrating or medium temperature, from 150º C to 400º C
- High concentrating or high temperature, over 400º C.

Fig-2 solar collector

VI. CONCLUSION

Scientists around the world have performed very extensive and promising work in this field. But still there is room to work in this field due to the following grounds. Synthesis of visible light induced nanophotocatalyst with enhanced activity in a controlled and large production manner to meet the commercial requirements. There is evidence of eco-toxicity of nanoparticles and free radical formation in troposphere. There should be a method for efficient and complete removal of these nanoparticles from treated waste water on commercial scale.

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