

Reductive Photocatalysis for Degradation of Toxic Pollutants in water: A Short Review

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Abstract

The levels of toxic pollutants in the water supply sources are increasing beyond the acceptable limits due to human activity. Heterogeneous photocatalysis has been studied as a method of air cleaning and water purification. Most of the studies are based on the oxidative mechanism of photocatalysis. Limited work is done for exploring the use of reductive photocatalytic as an effective method for removal of toxic pollutants in water. This review illustrates the mechanism of reductive photocatalysis in brief along with the factors affecting the efficiency of the process. Role of the hole scavenger and importance of proper selection of hole scavenger is also highlighted. Photocatalytic reduction of some of the toxic pollutants is explained in brief.

1. Introduction

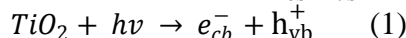
Increasing levels of many organic and inorganic pollutants in water poses a serious risk not only to the human beings but ecosystem as a whole. In recent years the concentration of these pollutants in water supply sources is increasing. Most of these excess pollutants come from the human activities like industries, mining and agricultural activities. These pollutants have been extensively studied and their effects on human health are regularly reviewed by international bodies such as the WHO. Among them pollutants which are of major concern are heavy metals (like Chromium, cadmium, selenium, mercury, lead, copper) pentachlorophenol, nitrate etc. Many of these pollutants are potential carcinogens and/or endocrine disrupting substances. They are also responsible for other types of disorder, for example excess nitrate can cause blue baby syndrome. So the removal of these pollutants is imperative to make water safe for human consumption.

Traditional methods use for removal of these toxic pollutants includes ion exchange, precipitation, membrane processes, liquid-liquid extraction, biological treatment, chemical treatment and activated carbon adsorption. However most of these techniques have their own limitations. For example membrane processes produce concentrated waste stream, which further requires treatment. Precipitation creates a significant amount of hazardous sludge, requiring further treatment. Adsorption only transforms the pollutants from one phase to another. Chemical treatment often utilizes potentially hazardous or polluting substances.

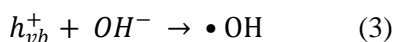
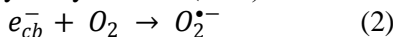
In recent years the application of heterogeneous photocatalysis, which uses a light source with semiconductor material to initiate the photoreaction is increasing. The initial interest in the heterogeneous photocatalysis was started when Fujishima and Honda (1972) discovered the photocatalytic splitting of water into hydrogen and oxygen with TiO_2 [1]. After that the interest of scientists in heterogeneous photocatalysis has grown very much especially in the area of environmental remediation. The advantages of photocatalytic technology are (i) oxidation and reductions occurs simultaneously, (ii) complete mineralization of toxic pollutants without addition of additional reagents, resulting in low cost, (iii) process can continue at very low concentration and (iv) freely available solar light can be used resulting in greater economy.

Semi-conductors allow flow of electrons when some kind of external energy is given. Semiconductors like TiO_2 , ZnO , CdS , Bi_2O_3 , ZrO_2 , iron oxides can be used as catalyst directly or with some modifications for photocatalysis. But the majority of research on the application of photocatalysis for air and water

purification involves the use of the TiO₂ due to its exceptional optical, electronic properties, chemical stability, non-toxicity and low cost [2]. Irradiation of TiO₂ particles with photon energies equal to or larger than the band gap (3.2 eV) generates electron-hole (e_{cb}^-/h_{vb}^+) pairs.



The negative electron reacts with oxygen molecule to form superoxide anions ($O_2^{\bullet-}$) while the positive hole reacts with hydroxyls to form hydroxyl radical ($\bullet OH$)



The hydroxyl radical oxidizes the organic pollutant to mineralized products.



Hence following irradiation the TiO₂ particles act as either electron or hole donors, which then take part in photoreduction and photooxidation reactions, respectively.

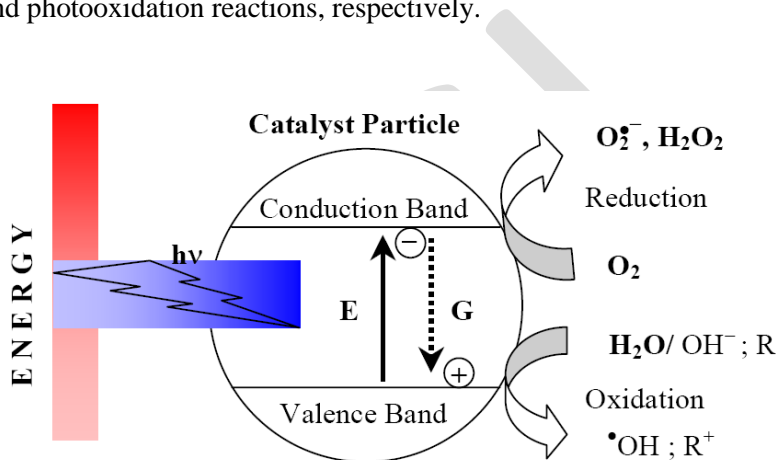


Figure 1. Mechanism of photocatalysis [3]

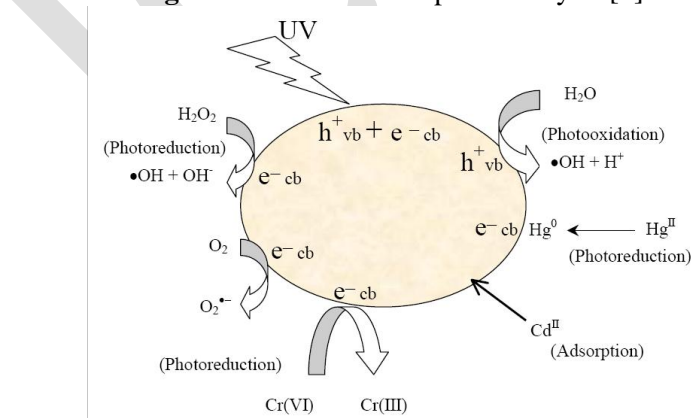


Figure 2. Examples of some reactions that can occur on illumination of TiO₂ [3]

2. Photocatalytic reduction

Photocatalytic oxidation and photocatalytic reduction are two sides of a coin [4]. Irradiation of TiO₂ with UV light result in formation of electron and hole pair. The hole thus generated reacts with adsorbed water or hydroxyl ions to form hydroxyl radical $\bullet OH$ which is responsible for oxidation of organic pollutants. The electron generated, takes part in reductive decomposition. The photogenerated electron had a strong reducing potential (0.5 to -1.5V) [5]. Lot of research has been done on oxidation pathway but

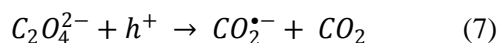
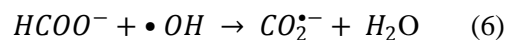
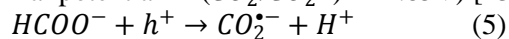
limited research has been done for use of reductive photocatalysis for degradation of toxic pollutants. In recent years photocatalytic reduction has gained importance in water/wastewater treatment, especially in removal of toxic metal ions (Pb, Cd, Hg, Cu, Cr, Se). The photoreduction reaction involves metal ions being reduced to form metal deposits on the surface of the catalyst. The deposited metal can subsequently be recovered by mechanical and/or chemical methods. Photoreduction has also been studied for removal of nitrate ions and some organic compounds. The rate of recombination of the hole and electron significantly affects the efficiency of the process. Some techniques used to overcome the rate of recombination rate includes metal doping and used of electron and hole scavenger. Selection of suitable hole scavenger is very important for desired efficiency of the process. Oxygen is generally not desired in photoreduction process as it competes with the substrate for the photogenerated electrons. If oxygen is present, its reaction with the electron results in formation of super oxidized anions ($O_2^{\bullet-}$). Photocatalytic reduction experiments are generally done with either nitrogen or argon purging to remove the oxygen.

On the basis of thermodynamic analysis, the possibility of photoreduction of any chemical species can be predicted. In order to photoreduce a chemical species, the conduction band of the semiconductor photocatalyst must be more negative than the reduction potential of the chemical species. Therefore, the energy level of the bottom of the conduction band is a measure of the reduction strength of the photogenerated electrons [14]. At 25°C and pH=0 the energy of the conduction band of TiO₂ (P25) is -0.3V [15]. Energy level of conduction band changes with pH, at pH 7 the energy of conduction band of TiO₂ is -0.5V [16]. So pH is also an important factor for photoreduction.

Some other factors affecting the rate of photoreduction are surface area of the catalyst, concentration of hole scavenger, adsorption of the substrate on the surface of photocatalyst, catalyst dosage and irradiation time.

2.1 Role of hole scavenger

Photogenerated electrons are responsible for the reduction of the pollutants. To obtain greater number of electrons for reduction process, holes must be filled with an electron through the oxidation of other compounds to maintain electroneutrality. This is done by a hole scavenger (electron donor)[6] As the reduction by photogenerated electrons takes place simultaneously with oxidation by the photogenerated holes, organic compounds are often added as the hole scavenger to allow for the photocatalytic reduction [7]. Hole scavenger is good electron donor, the function of the hole scavenger is to scavenge valance band holes. It can irreversibly combine with either photo-induced hole or surface hydroxyl group, decrease the recombination rate of photogenerated electron and hole, free more reductive equivalents and enhance the effect of photocatalytic reduction [8]. So selection of proper hole scavenger is very important for photocatalytic reduction. Photoreduction using different organic compound like formic acid, oxalic acid Methanol, ethanol, EDTA, Citric acid, Succinic acid has been investigated. Prairie et al. [9] suggested that conduction band reduction reactions were faster for organics that were easily oxidized. To be an effective hole scavenger, the organic compound has to be able to adsorb on the catalyst surface [10]. Efficiency of photoreduction also increases due to formation of reducing radicals. It has been well recorded that when formic acid [11] and oxalic acid [12] is used as hole scavenger, carboxyl anion radical $CO_2^{\bullet-}$ is formed which is a strong reductant (normal potential $E^0(CO_2/CO_2^{\bullet-}) = -1.85V$) [13]



3. Photocatalytic procedure

Photocatalytic experiments are generally carried out in glass tubular/cylinder reactor with a cooling water jacket. Depending upon the catalyst used and the pollutant to be removed either a UV light source like mercury lamp or a visible light source is used. Desired concentration of the pollutant to be removed is prepared using stock solution of the respective reagents. Photocatalyst and hole scavenger is added and the mixture is kept in dark with slow stirring and nitrogen/argon purging to establish an

adsorption/desorption equilibrium. The mixture is then irradiated with UV/Visible light for a suitable duration with continuous purging of inert gas. The samples are collected at regular interval for analysis. Different set of experiments with different hole scavengers, different concentration of hole scavengers, different pH and different irradiation time is done to find out the optimum combination. The collected samples can be analysed by UV-Vis-spectrophotometer, LC-MS or GC-MS depending upon the pollutant to be detected.

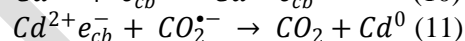
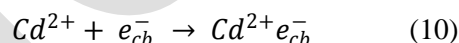
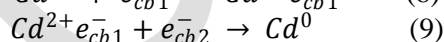
4. Application of photocatalytic reduction of toxic pollutant

Photocatalytic reduction can be used to remove variety of toxic pollutant like heavy metals, nitrate, pentachlorophenol etc. from water. This paper gives brief insight of removal of some of the toxic pollutants

4.1 Cadmium

Cadmium contamination originates from industries like mining, metallurgy, chemical, food and leather and from agricultural activities. Cadmium compounds are also used in re-chargeable nickel-cadmium batteries and if these batteries are not disposed properly cadmium can enter in to water supply sources. If the levels of cadmium exceed the limits (0.01 mg/lit IS 10500.1999) it can affect primarily the kidney and also the bones.

Many researchers (Prairie et al., 1993; Rajh et al. 1996b; Thurnauer et al 1997; Davis et al. 1999; chenthamarakshan et al. 2000) have investigated photocatalytic reduction of cadmium. Photocatalytic reduction of cadmium ion by using TiO₂ as catalyst was studied by V.N.H.Nguyen et al [7] using formic acid and methanol as hole scavenger. They found that cadmium, with a negative redox potential (-0.403V), can be photocatalytically reduced in a UV illuminated TiO₂ suspension in the presence of formate at neutral pH. On the other hand when methanol was used as a hole scavenger, no reduction was observed. The positive effect of formate on the photo reduction of cadmium was attributed to the fact that formate can be adsorbed onto the TiO₂ surface and can be significantly mineralized to CO₂. It may also due to the ability of formate to form strong reducing radicals. Following reactions shows two possible ways of reduction of cadmium ions:



Equation 8 and 9 shows reduction by conduction band electrons (Henglein 1988) while equation 10 and 11 shows reduction involving carboxyl radicals (Nedoluzhko et al 1996)

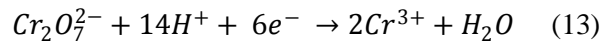
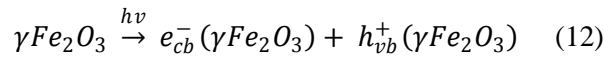
4.2 Chromium

Chromium is commonly found as a contaminant in water and soil as a result of extensive use in the industry. Chromium exists in two major oxidation states: Cr (III) and Cr (VI). Cr (III) occurs naturally and is a dietary supplement. Chromium (VI) needs attention because of its high toxicity to plants and animals as well as its carcinogenicity to humans.

Photocatalytic reduction of Chromium has been investigated by P.Mohapatra et al. 2006; L.B.Khalil et al. (1998); C.R chenthamarakshan et al 2000; L.Wang et al 2008.

A. Dris et al. used modified Polyvinyl Alcohol-alginate encapsulated ferro photo gels for Cr (VI) reduction [13]. Magnetic separable PVA-alginate beads were produced using PVA-alginate boric acid method [14] and were used with maghemite nanoparticles (γ -Fe₂O₃) for treatment of waste water containing Cr (VI). To make photocatalytic treatment commercially applicable, sunlight should be used as the light source, separation of catalyst after treatment must be easy and should be reusable. All these

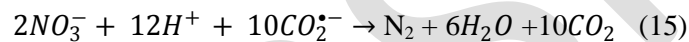
requirements were satisfied by using PVA-Alginate encapsulated ferro photo gels for chromium reduction. Cr (VI) was completely reduced to Cr (III) in 30 minutes. Beads could be reused for seven times without significant change in the efficiency of removal. Removal of chromium is explained by Equation 12 and 13.



4.3 Nitrate

The major sources of nitrates in drinking water are runoff from fertilizer use especially man made, leakage from septic tank, sewage treatment plants, industries and erosion of natural deposit. It is known to cause Methemoglobinemia or "blue baby" syndrome in the infants less than 6 months of age.

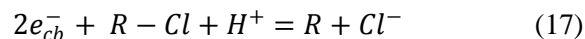
Many researchers have use different types of semiconductors and hole scavengers for nitrate reduction. Formic acid is found to be the best hole scavenger for nitrate reduction [6, 17-18]. Compare to TiO_2 , TiO_2 loaded with silver as co-catalyst gives higher reduction and better by product selectivity (nitrogen gas and ammonium ions) [17, 18]. Treatment can be done at ambient pH when silver is added as co-catalyst [18]. Using commercial TiO_2 optimum pH was 2.57[6]. The photocatalytic reduction of nitrate is done by the photogenerated hole and carboxyl radical produced due to use of formic acid as hole scavenger[17]. The nitrate reduction can be summarized by equation (14), (15) and (16)



4.4 Pentachlorophenol

Pentachlorophenol (PCP) is widely used in herbicides, pesticides and wood preservatives. It can damage the human immune system and reproductive system. When exposed in environment it can be transformed to more toxic polychlorinated compounds.

L.Yin et al used Ti-Doped β - Bi_2O_3 for reductive decomposition of Pentachlorophenol under visible light [4]. Formic acid was used as hole scavenger. To confirm that the reduction was mainly due to the reductive mechanism free radical measurement and electron scavenger like hydrogen peroxide was used. Optimum pH for the reaction was 11.2. The reduction reduced to half when pH was 2.3. PCP acts as electron acceptor. Electrons produced due to photocatalysis attack the C-Cl bond on the aromatic ring of chlorophenols, which resulted in the dechlorinated products



The results of product identification by LC-MS and GC-MS are shown in figure 3

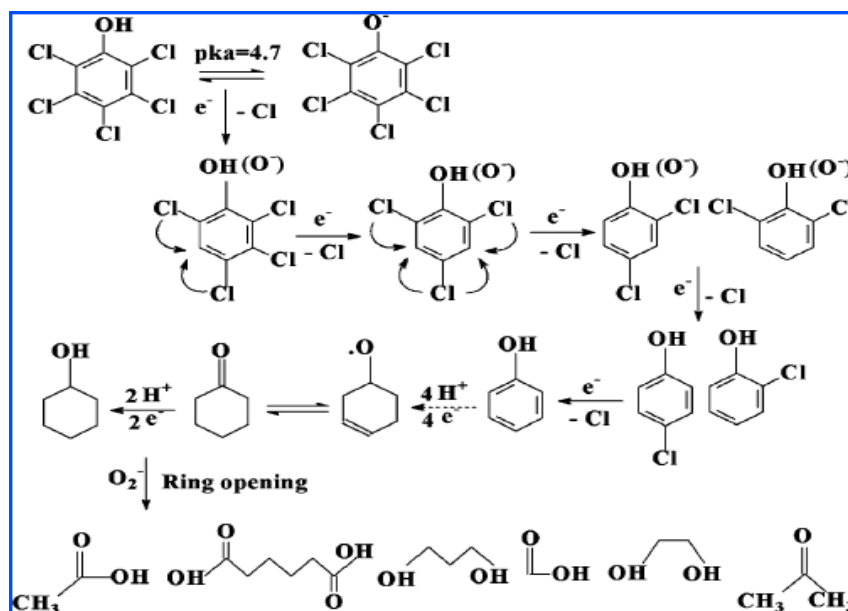


Figure 3. Identified products and reaction pathway for decomposition of PCP [4]

5. Conclusion

Photocatalytic reduction appears to be better method of removal of various toxic pollutants from water as pollutants are completely mineralized. The proper selection of hole scavenger is very important for efficient photocatalytic reduction. Other factors like dose of catalyst, pH, concentration of hole scavenger also affects the rate of photoreduction. To make photocatalytic reduction commercially applicable, catalyst immobilization and high activity of the catalyst under natural light is very important. Until then, photocatalytic reduction can be used on a smaller scale like treatment of ion-exchange brine.

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