A Review on TiO₂ Photocatalytic Disinfection of Water with Pathogenic Micro-organisms

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Abstract—During disinfection, the formation of byproducts such as trihalomethanes and other chlorinated byproducts are a major concern. The best alternative to avoid the byproducts formation is photocatalysis. In the past two decades, the studies on photocatalysis have been done using a semiconductor for the treatment of air and water. Among the various semiconductors, TiO₂ is used in various industries as it gives the highest efficiency with the highest stability at a lower cost. This is a powerful process used for disinfecting environment contaminated with pathogenic microorganisms. In this study, a review of previous developments made in the TiO_2 photocatalysis for the disinfection of water contaminated with pathogenic microorganisms is carried out. This paper concludes that TiO_2 photocatalysis can be used in different ways either in suspension or in the form of thin films to disinfect water contaminated with pathogenic micro-organisms presenting a potential hazard to animals and human beings. If properly designed and optimized TiO_2 photocatalytic disinfection can be used by a small community very efficiently.

Keywords: Photocatalytic disinfection, TiO_2 catalyst, microorganisms, TiO_2 coatings

1. INTRODUCTION

Water disinfection is the process of removing, killing or deactivating the pathogenic micro-organisms which result in termination of their growth and reproduction. Among various used disinfection process chlorination is mostly used worldwide about 62%, including chloramination (20%), chlorine dioxide (2%), ozonation (8%) and UV (8%). During water disinfection, Disinfection by-products (DBPs) are formed on which studies are being carried out since last 30 years. These DBPs are formed during reactions between organic and inorganic matter in water, with chemical treatment agents added during the water disinfection process [1]. Even though chlorination reduces the microbial risk, it results in the formation of DBPs that are dangerous to the consumers. The most common DBPs are trihalomethanes (THMs), halo acetonitriles (HANs), halo ketones, which are carcinogenic in nature. In a 3 year case-control study conducted in Spain on causes for Bladder cancer linked with THM levels and geographic study areas, it is found out that a long-term THMs exposure was associated with a twofold bladder cancer risk.

Experimental evidence suggests that exposure occurs through inhalation and dermal absorption[2]. In a study conducted on spontaneous abortion relation to amount and source of drinking water consumed in early pregnancy in 1992 in California country, it is observed that women with high bottled water consumption and no tap water had a reduced rate of spontaneous abortion compared to those drinking tap water and no bottled water[3]. Therefore to eliminate the intake of carcinogenic DBPs we need to shift from conventional processes. Use of solar energy for disinfection process is increasing day by day and to enhance the process we use photocatalysis. Photocatalysis is a promising technology based on the interaction of light with solid semiconductor particles and is able to produce highly oxidative species that not only deactivate bacteria but also destroys a large variety of chemical contaminants in water [4].

2. PHOTOCATALYSIS

Photo-Catalysis can be defined as "acceleration of a photoreaction in the presence of a catalyst". Photo-catalyst when gets activated by UV lights can oxidize organic pollutants into non-toxic materials, such as carbon dioxide, water and also disinfect certain bacteria. There is no change in catalyst it doesn't get consumed in the chemical reaction. In photocatalysis, light is absorbed by an adsorbed substrate like a Semiconductor photocatalyst, the photocatalytic activity (PCA) of the Semiconductor depends on the ability of the catalyst to create electron-hole pairs, that generates free radicals (hydroxyl radicals: OH) which are able to undergo secondary reactions. In photocatalytic oxidation (PCO) process, semiconductor photocatalysts can act as sensitizers for light-induced redox processes, due to the electronic structures of these photocatalysts that are characterized by a filled valence band and an empty conduction band [5]. The formation of electron/photo hole pair is done when a photon of energy greater than band gap energy is absorbed. The stored energy is dissipated within few nanoseconds by recombination, during the absence of suitable scavengers. The conduction band electrons are good reductant (+0.5 to -1.5 V), whereas the valence band holes act as powerful oxidants (+1.0)

to +3.5V). Various factors may intervene in the PCA such as particle size, crystalline form or active site density etc., but among them, the influence of the surface area appeared is of prime importance [6].

Among all semiconductors, photocatalysts studied including TiO_2 , ZnO, Fe_2O_3 CdS and ZnS most researchers has most focused on TiO_2 because of its relatively high photocatalytic activity, as well as its chemical stability in aqueous systems and its low cost. [7]. The light that with a short wavelength within the UV range (<380nm) are powerful enough in activating the photocatalytic reaction, as the band gap energy of TiO_2 is about 3.0-3.2 eV. The high cost associated with the generation and supply of UV light from electricity has constituted one of the major drawbacks hindering the commercialization of this process in actual water and wastewater treatment. A solution to this problem may resort to the utilization of the solar energy that is naturally available (Fujishima, 2000). However, the UV light only accounts for about 3-4% of the sunlight.

3. TIO₂ (METAL OXIDE PHOTOCATALYST)

The comprehension of photocatalysis by means of TiO₂ has been made by many[1], [4], [6], [8]–[12]. A number of parameters have been found to be of crucial importance in optimizing the process of disinfection using TiO₂ photocatalysis. These include TiO₂ concentration, UV light intensity, microbial starting concentration, temperature, pH, and aeration. Destruction of wide range species, with the TiO2/UV process being shown to successfully inactivate many microorganisms including bacteria such as E. coli , L. acidophilus, Serratia domonas stutzeri, Bacillus pumilus, Streptococcus mutans, yeasts such as S. cerevisiae, algae such as Chlorella vulgaris, and viruses such as phage MS2, B. fragilis bacteriophage, Poliovirus I, Cryptosporidium parvum , and Giardia intestinalis[13].

Effect of pH

pH can be observed as a sensitive parameter for photocatalysis. The photocatalytic destruction of coliform bacteria and poliovirus in secondary wastewater effluent was unaffected by pH changes in the range of 5-8. Disinfection of E. coli the bacteria were more sensitive towards photocatalysis when pH is in the range < 4.0 or >9.0, than at an optimal pH 7.0 [14]. Photocatalytic reactions performed in the pH range 5-8 does not affect the experimental outcome [15]. The pH of the solution during photocatalysis has an effect on the electrostatic charge of the TiO₂ surface; this determines the density of $TiOH_2^+$ groups. The adsorption on TiO_2 , of bacteria and the activity towards the destruction of bacteria by TiO₂ photocatalysis, is pH dependent. Microbial growth is also pH dependent; a decrease in the growth rate is observed when the pH is changed in either direction away from the optimum pH. The vast majority of human pathogens are neutrophils, i.e., they prefer a neutral pH[16].

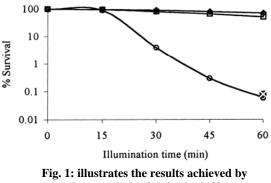
4. METHODS OF USE OF TIO₂

In the process of using TiO_2 as a photocatalyst, we can use it in different ways of exposure. TiO_2 can be used in suspension (where it adds TiO_2 to water directly in a powder form) or in the form of a coating (for this TiO_2 powder can be coated onto various materials and this will be introduced into water for photocatalytic disinfection).

TiO₂ in suspension

Many studies have been carried out to show the disinfecting effect of TiO_2 used in suspension as a photocatalyst. A field experiment was carried out in Switzerland using compound parabolic collector under direct solar irradiation to show the inactivation of E. coli in the absence and presence of TiO_2 . This study concluded that in the absence of TiO_2 the complete disinfection was not reached every time and bacterial recovery was also observed. While using TiO_2 complete disinfection was achieved and no bacterial recovery was observed after 24 hours of exposure[12].

A study on two groups of microorganisms was carried out i.e. bacteria and fungi using solar photocatalytic disinfection. The pathogenic organisms were: Escherichia coli, Pseudomonas Aeruginosa, Staphylococcus Aureus, Saccharomyces Cerevisiae, Candida Albicans, and Aspergillus Niger. Aqueous suspensions containing all these microorganisms $(1.10^5 \text{ cfu}/\text{ml})$ were prepared and irradiated with a 400 W UV lamp in the presence of TiO₂. The results showed that bacteria were destroyed in 40 min and fungi in 120 min[17].



photocatalytic disinfection[18]. For a study in (Sigma, St. Louis, USA) E. coli (ATCC 27325) were grown aerobically. The viability of TiO₂-treated cells was determined by colony counting after 24 h of incubation. The survival curves in Fig. 1 shows that when E. coli cells (approximately 10^6 cfu /ml) underwent illumination for 15 min in the presence of 1mg/ml TiO₂, almost all of the cells were still viable. After 20 min of treatment, however, only 12% of the cells retained their viability. At the end of 30 min of illumination, more than 96% of the cells lost their viability

[18].

Disinfecting effects of TiO2 thin films

The use of TiO_2 films has been investigated by several authors and found that it is as effective as the suspended form [6], [9], [19]. This method overcomes the disadvantage of having to separate catalyst from the liquid at the end of the experimental period. Therefore, there is no need to filter out catalyst after disinfection process is complete.

The technical feasibility and performance of photocatalytic TiO_2 coatings in batch-process solar disinfection (SODIS) reactors to improve potability of drinking water in developing countries have been studied at Plataforma Solar de Almeria (PSA) solar research facility in Almeria, Spain. Borosilicate glass and PET plastic reactors were fitted with flexible plastic sheets coated with TiO_2 powder. After the experiment, the results showed 20% and 25% more effective than using only solar disinfection for the inactivation of E.coli respectively [9].

Titanium dioxide (TiO_2) is also used as a photocatalytic disinfecting material in the food and environmental industry. In a study carried out in Japan workability of TiO₂ in different conditions and different exposures was tested. They developed a TiO₂ powder coated packaging film and tested its ability to inactivate Escherichia coli both in vitro and in actual tests, using two different particle sizes and two types of illumination at different intensities. No inhibition effect of the testing method on the growth of E. coli was observed. The cells of E. coli were found to have decreased 3 log cfu/ml after 180 min of illumination by two 20 W black-light bulbs (wavelength of 300–400 nm) on TiO₂-coated oriented polypropylene (OPP) film, while E. coli decreased 1 log cfu/ml with black-light illumination of uncoated OPP film[19].

5. CONCLUSION

From the above discussion, we can conclude that TiO₂ photocatalysis is an effective for process degradation/deactivation of various microorganisms that generally exist in drinking water. This technology will help us minimize the exposure of people to THMs in a metropolitan city as well as for the uneducated people in a remote area, as usage is also very easy and safe. The TiO₂ thin film coating technology is more efficient than in suspension as there will be a reduction in cost. The technique for producing the TiO₂coated plastic inserts is an appropriate and affordable technology for developing countries. There must be some research work done to describe the effect of TiO₂ photocatalysis on inorganic and organic additives.

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