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# Photodegradation of organic pollutants using N-titanium oxide catalyst

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ABSTRACT

Photoelectrocatalytic degradation of typical aromatic compounds with persistent reaction rate is studied using thin layers of N-titanium dioxide deposited on transparent and conducting glass substrates. Backside illuminated flow-through parallel plate photoelectrochemical reactors is used and electrical bias for suppressing charge carrier recombination is applied externally. The degradation experiments are performed under solar irradiation with the conditions aimed at reducing contaminant concentrations to maximal tolerated levels as specified under environmental regulations. From the observed COD–time relations, rate constants normalized to unit volume and photocurrent (kinetic parameters), characterizing the efficiency of the electrochemical oxidation process involving photogenerated valence band holes or their immediate reaction products, are calculated and compared to the decrease of optical extinction of the solutions. The parameters for salicylic acid, 4-chlorophenol, benzoic acid and oxalic acid are found to decrease as the main absorption peaks of these substances diminish in due course of degradation reaction. In order to realize a complete mineralization of such compounds, which should be an ultimate aim of water purification, COD and TOC is analyzed.

## 1. Introduction

Rapid growth in human population and industrialization on earth has led to the unprecedented demands for energy, food and clean water. Safe drinking water is the necessity of every human being and a nation for its sustainable economic growth [1]. However, out of available surface water from lakes and rivers, only 1% water is fresh, most of which is polluted [2]. To fulfil the demands of people with a focus on clean water and improved health, researchers have to come out with a robust technology incorporating large scale water purification and desalination systems. Upscaling to large water purification systems using novel materials with satisfactory performance should be the future approaches of researchers.

Over the years, a large number of semiconductors have been employed as photocatalysts for water purification. Among the most commonly studied photocatalysts such as $TiO_2$, ZnO and CdS [3,4], titanium dioxide ($TiO_2$) has turned out to be best photocatalyst and has been widely exploited for the detoxification of water from a number of organic pollutants [5]. In the near future, photocatalysis could emerge with new technologies for efficient removal of impurities from waste- and drinking water from biological and industrial origin. The state-of-the-art on water purification using photocatalysis is reported in the literature [6–10]. In a photocatalytic process, a semiconductor catalyst such as $TiO_2$ or any other transition metal oxide irradiated with near UV light generates strongly oxidizing species (valence band holes, $^{\cdot}OH$ radicals) that can destroy in principle any organic species in water adsorbed at the catalyst surface [11]. Such a powerful photocatalysis technique can be employed for removing organic materials (bacteria, hormones, endocrine disruptors, textile dyes, dioxines, etc.) that accumulate rapidly in the environment. Photocatalysis, however, necessitates photoactive nanoparticles to interact with the organic impurities. In this case, large reaction time is required since most of the photo-generated electron and holes get recombined rapidly, with little contribution from small fraction of electron and holes toward degradation reactions. Hence, longer duration time is required to have a reasonable degree of degradation under constant illumination. Moreover, difficulty in removal of nanoparticles from the purified water at the end of reaction is one of major disadvantages. The overall efficiency of this process is limited partly due to the semiconductor and in some cases, due to the chemical nature of the compound to be diminished.

Early work [12,13] showed that the major obstacle for efficient use of absorbed photons for water purification is the recombination of photogenerated charge carriers occurring at the bulk as well

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as semiconductor–liquid interface. The unavoidable recombination of $e^-$–$h^+$ occurs both at bulk of semiconductor and at the interface of semiconductor–liquid. In unbiased photocatalysis, the life time of photogenerated holes is very less (particularly in case of $TiO_2$) since they recombine to photogenerated electrons in their immediate vicinity. Hence, to increase the hole life time both at the bulk and interface, there should be some means to take the photogenerated electrons away from the vicinity of photogenerated holes so that holes will be readily available at the reaction site (at the surface to react with electrolyte). Application of external applied reverse bias executes this purpose. Applied bias drives the photogenerated electrons in single direction to reach at counter electrode, which increases the life time of photogenerated holes and thereby improves the degradation rate of organic species. Suppressing the recombination processes by application of bias necessitates the photocatalyst to be used in the form of electrode in which the semiconducting material is immobilized on an electrically conducting substrate. This has also the advantage of separating the photocatalyst from the reaction mixture, once the reaction is over. The application of bias to illuminated semiconductors for the decomposition of organic contaminants in water is successfully used for a wide variety of compounds [13–17]. Zan et al. [18] investigated the photocatalysis effect of nanometer $TiO_2$ particles and $TiO_2$-coated ceramic plate on Hepatitis B virus surface antigen (HBsAg). Dědková et al. [19] addresses laboratory preparation and antibacterial activity testing of kaolinite/nano$TiO_2$ composite in respect of the daylight irradiation time. Kaolinite/nano$TiO_2$ composites with 20 and 40 wt% of $TiO_2$ were laboratory prepared, dried at 105 °C and calcined at 600 °C. The calcination caused transformation of kaolinite to metakaolinite and origination of the metakaolinite/nano$TiO_2$ composite. Important organic compounds in industrial wastewater include dyes, phenols, chlorophenols, aliphatic alcohols, aromatics, polymers and carboxylic acids. Among these, the salicylic acid, benzoic acid, 4-chlorophenol and oxalic acid are identified as major water pollutants that are arising from a number of sources including paper milling, cosmetic industries and land fill leachate [20]. The destruction of these organic compounds is of considerable interest.

The aim of this work is to obtain and compare the photoelectrocatalytic degradation of aromatic compounds such as salicylic acid, benzoic acid, 4-chlorophenol and oxalic acid in water using scale-up 5at%N-$TiO_2$ electrodes with bias under sunlight. Experiments have been performed employing 5at%N-$TiO_2$ electrodes in a nine cell module reactor toward finding out a cost effective solution for removal of such organic contaminants from water. The correlation of total organic carbon (TOC) and chemical oxygen demand (COD) measurements for extent of the complete mineralization have been investigated.

## 2. Experimental

Analytical reagent grade salicylic acid ($C_6H_4(OH)COOH$)), 4-chlorophenol or 4-CP ($HOC_6H_4Cl$), benzoic acid ($C_6H_5COOH$), N,N-dimethyl formamide and oxalic acid ($H_2C_2O_4{\cdot}H_2O$) were obtained from Sigma–Aldrich and s.d. fine Chem. Ltd. Other chemicals such as potassium dichromate ($K_2Cr_2O_7$), sulfuric acid ($H_2SO_4$) and perchloric acid ($HClO_4$) all obtained from Loba Chemie were used with required concentrations without further purification. All the solutions were prepared using ultrapure water from Millipore water system (Milli-Q). The anatase $TiO_2$ electrodes used in this study were deposited by spray pyrolysis onto large area (10 cm × 10 cm × 0.125 cm) conducting glass plates (spray deposited fluorine doped tin oxide on glass, FTO, with sheet resistance of 10–20 $\Omega\ sq^{-1}$). Preparation and structural, optical and photoelectrochemical characterization of the $TiO_2$ electrodes have been reported elsewhere [12]. Briefly, FTO substrates were cleaned ultrasonically in acetone, ethanol and double distilled water for 20 min. The precursor solution consisted of 0.1 M titanyl acetylacetonate in methanol and then 5at% N,N-Dimethylformamide as a dopant. Then prepared solution was sprayed through a pneumatic glass nozzle using compressed air as a carrier gas onto FTO substrates maintained at a fixed temperature 470 °C. The spraying rate was 4.5 ml/min and the quantity of the spraying solution was 150 cc. Solar light was used as a source of illumination. The schematic photodegradation module, as shown in Fig. 1, was used for experiment. Each photoelectrochemical cell encloses a '5at%N-$TiO_2$ electrode coated on FTO substrate' serving as photoanode and a stainless steel disc as a cathode at a distance of 0.1 cm facing the photoanode. The surface area (circular) of these electrodes in contact with the electrolyte was 576 $cm^2$ (identical to the illuminated area). The term "bias" was used for the voltage applied between the two electrodes. The 5at%N-$TiO_2$ electrodes were illuminated from backside (through the transparent FTO substrate), employing solar light with manual inclination and azimuth tracking.

The appropriate concentrations of salicylic acid, 4-CP, benzoic acid and oxalic acid were used as model pollutants in water for degradation studies under solar light illumination in the absence and in the presence of 5at%N-$TiO_2$ photocatalyst. A fixed amount of electrolyte, the major part of which contained in an external reservoir, was recirculated through the photoelectrochemical cells with a constant flow rate of 8.4 $l\ h^{-1}$ (flow velocity 2.92 $cm\ s^{-1}$) using a Gilson MINIPLUS peristaltic pump, France with silicon tubing. Using aliquots withdrawn from the reaction mixture at some intervals, the concentrations of organic impurities in the solutions were determined by measuring the UV–Vis absorbance (extinction) using a 119 SYSTRONICS UV–Vis spectrophotometer (for the

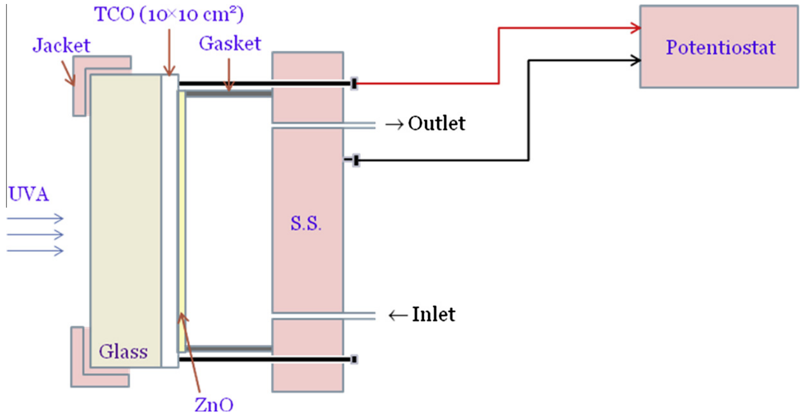

**Fig. 1.** Schematic diagram of a photodegradation module.