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Remediation of wastewater: Role of hydroxyl radicals

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ABSTRACT

The photocatalytic oxidation of wastewater with TiO_2 and coupling effect of different advanced oxidation processes onto the oxidation of wastewater has been studied. A basic mechanism involved during oxidation has been reported. The role of hydroxyl radical in the breakdown of the wastewater is elucidated through determining the degradation rates, kinetics, analyzing transformation intermediates and studies using computational chemistry methods. In order to realize a complete mineralization of wastewater COD, BOD and TOC analysis has been carried out.

1. Introduction

The toxicity and persistence of pollutants can directly impact on to the health of an ecosystems and present a threat to humans through contamination of drinking water supplies [1]. In response it has become a challenge to achieve the effective removal of persistent organic pollutants from wastewater effluent to minimize risk of pollution problems. Conventional purification systems are generating wastes during the treatment of contaminated water, which requires additional steps to avoid secondary waste. Heterogeneous photocatalysis is a promising new alternative method among advanced oxidation processes (AOPs) which generally includes UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for oxidative removal of organic pollutants and inactivation of microorganisms in water [2–3].

Recently, much effort has been devoted to study TiO_2 as a very promising semiconductor for photocatalytic degradation of water pollutants. But, it has numerous shortcomings such as recombination of photogenerated electron–hole pair, low quantum yield, surface morphology of the films, which obstruct commercialization of the photocatalytic process [4]. Consequently, it has enormous attention in improving the photocatalytic activity by appropriate modification. One approach is to fabricate it in various 1D, 2D and 3D nanostructures etc with high specific surface areas [5–6]. Other interesting approach is to dope the transition metals (Ga, Al, In), non-metals (N, F, C), alkaline and rare earth metals in order to reduce the band gap energy and improve charge separation between photogenerated electrons and holes [7]. However, insufficient light harvesting especially in the visible-light region and inefficient energy conversion [8–9], still remain two great challenges to us. So development of efficient photocatalysts is a critical breakthrough in global energy and environmental issues. Saverini et al. [10] studied the effect of (±)α-pinene, (+)β-pinene, (+)3-carene, and R-(+)limonene terpenes in wastewater of a citrus transformation factory by using Solid Phase Micro-extraction (SPME) followed by GC analyses. Tanvir et al. [11] developed an enzyme based biosensing method for evaluating the toxicity of solutions treated by titanium dioxide photocatalysis. The method is based on the potential of rat liver microsomal glutathione transferase ability (mGST) to get enhanced in the conditions of chemical and oxidative toxicity. Stambolova et al. [12] reported the preparation of nanostructured TiO_2 films with higher photocatalytic effectiveness and longer exploitation life. Interesting result of the work is the reduction of toxicity after photocatalytic treatment of RB5 with TiO_2, which was confirmed by the lower percentage of mortality of Artemia salina. Shinde et al. [13] reported the photocatalytic degradation of the sea water using photoelectrochemical (PEC) reactor module consisting of nine photoelectrochemical cells equipped with spray deposited TiO_2 catalysts under solar light and its physicochemical and bacteriological analysis.

Very recently, N–TiO_2 thin films have attracted much attention in the photocatalytic processes owing to its high photocatalytic activity in the degradation of organic contaminants because of the large content of oxygen vacancies and strong absorption of OH^- ions on the surface of the catalyst [14–15]. In this paper, we reported the photocatalytic oxidation of sugarcane factory wastewater with N–TiO_2 photocatalyst. Coupling behavior and mechanism of different advanced oxidation processes for wastewater oxidation has been reported. Analysis of water sample is carried out for their COD, BOD and TOC tests in order to analyze extent of the degree of complete mineralization.

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2. Experimental

Firstly, fluorine doped tin oxide (FTO) conducting substrates were prepared onto the corning glass substrates using preparative parameters [16–17]. The substrates of size ($10 \times 10 \times 0.15\ \text{cm}^3$) were cleaned using chromic acid and methanol treatment and again rinsed with double distilled water. Prior to using FTO as substrates for N–TiO_2 (NTO) deposition, they were first cleaned with acetone ethanol and DI water (1:1:1 v/v/v). N-doped titanium oxide thin films were prepared onto the corning glass substrates by using chemical spray pyrolysis technique. To deposit N (5 at%) doped TiO_2 thin films, Titanium acetylacetonate (AR grade, 98.8% pure) supplied by Alfa Aser, and N,N-Dimethylformamide ($H{\cdot}CO{\cdot}N(CH_3)_2$, AR grade, 99% pure) supplied by THOMAS BAKER were used as initial ingredients. To attain N doping, N,N-dimethylformamide ($H{\cdot}CO{\cdot}N(CH_3)_2$) was mixed in to the solution. Analytical reagent grade potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4) and silver sulphate all obtained from Loba Chemie were used with required concentrations without further purification. The photodegradation reactor module consists N–TiO_2 electrodes coated on a conducting glass substrate was used as photoanode and a stainless steel plate at a distance of 0.1 cm, facing the photoanode, acted as cathode. The surface area of these electrodes in contact with the electrolyte was $576\ \text{cm}^2$ (identical to the illuminated area). Backside irradiation (through the FTO substrate) was used, utilizing solar light with manual inclination and azimuth tracking. The external bias was applied with the help of PV silicon solar cells. The diluted wastewater of sugarcane industry was used as water pollutant source for degradation studies under solar light illumination in the absence and in the presence of photocatalysts. 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 $8.4\ \text{l h}^{-1}$ (flow velocity $2.92\ \text{cm s}^{-1}$) using a Gilson MINIPLUS peristaltic pump, France with silicon tubing. Using aliquots withdrawn from the reaction mixture at some intervals, the concentrations of impurities in the solutions were determined by measuring the UV–Vis absorbance (extinction) using a 119 SYSTRONICS UV–vis spectrophotometer. TOC was measured using the aliquots after acidification with phosphoric acid and purging out IC (inorganic carbon, CO_2) by catalytic combustion, using a Photometer model 400D. Aliquots extracted from the solutions at various intervals during the degradation reaction were also used for determining chemical oxygen demand (COD) using the standard method of oxidation with an excess of dichromate in concentrated sulfuric acid by digestion at 140 °C. The concentration of the impurities was calculated from the dichromate extinction at various wavelengths using equations [18].

3. Results and discussion

3.1. Photocatalysis

Mimicking the elaborate architectures and basic principles to design and make more reliable and efficient materials or systems is highly appealing. One of the most promising materials that have been synthesized is N-doped TiO_2. Since the pioneering work nitrogen-doped TiO_2 has received a lot of attention, because the implantation of nitrogen modifies the electronic structure by introducing localized states to the top of the valence band, narrowing the band gap which enhances photocatalytic activity. Fig. 1 depicts the WWS degradation on NTO under sunlight illumination (a) plot of extinction as a function of degradation time, (b) kinetics of degradation (extinction taken at 276 nm). It is seen that, the concentration of WWS decreases due to its decomposition (photochemical oxidation) with reaction time. It is further used to study the reaction kinetics by plotting $\ln(c/c_0)$ as a function of reaction time. Linearity of this plot shows first order reaction kinetics and slope gives rate constant ($-k$). The analysis of kinetic parameters due to surface trapping and recombination has been shown in Table 1. The photocatalytic reaction is totally inhibited due to strong binding of the anion to the active sites thereby preventing the adsorption of WWS. Previous literature has shown that this in situ generated radical can sufficiently act as strong oxidizing agent or initiate the formation of hydroxyl radical [19]. Using NTO photocatalyst we have degraded the WWS up to 82.3% in 320 min. The improvement in efficiency is described as, defect energy state newly formed due to N-doping in the host lattice. The electrons, generated in the VB from the light irradiation, can first transfer to the defect energy state, and then further transfer to the CB by absorbing less energy than that of the first step transition. This means that the electron transition from VB to CB in TiO_2 semiconductor, generally produced by UV irradiation, can be fulfilled even with the lower energy of visible irradiation since a defect energy state is formed.

3.2. Sonolysis

To degrade wastewater, many techniques such as adsorption treatments with activated carbon, biological treatments and advanced oxidation processes (AOP) such as ozonation treatment, Fenton reactions, photolysis and radiolysis [20–21] have been studied. Strong ultrasonic wave generation in water brings about the formation of small bubbles. During the collapse, local reaction site of several thousand (degree) temperature and (atmosphere) pressure is produced due to the quasi-adiabatic collapse [22], while the bulk liquid temperature hardly changes. Sonochemical degradation proceeds via a reaction with OH radicals, which are formed from water pyrolysis in bubbles and at the interface. For the volatile pollutants, the degradation proceeds with the OH radicals as well as direct pyrolysis reaction.

Reaction mechanism for the high-frequency ultrasound oxidation treatment is as follows [23]:

$$H_2O + \rangle\rangle\rangle \rightarrow OH^{\cdot} + H^{\cdot} \tag{1}$$

$$H^{\cdot} + O_2 \rightarrow {}^{\cdot}HO_2 \rightarrow OH^{\cdot} + \frac{1}{2}O_2 \tag{2}$$

$$O_2 \rightarrow 2O^{\cdot} \tag{3}$$

$${}^{\cdot}O + H_2O \rightarrow 2OH^{\cdot} \tag{4}$$

$$2OH^{\cdot} \rightarrow H_2O_2 \tag{5}$$

$$2{}^{\cdot}HO_2 \rightarrow H_2O_2 + O_2 \tag{6}$$

Fig. 2 shows the WWS degradation under sonolysis treatment (a) plot of extinction as a function of degradation time, (b) kinetics of degradation. The degradation of WWS under sonochemical reactions agreed remarkably first-order kinetics. It is due to the accumulation of solute in bubbles and at the interface, indicating that the concentration of solutes becomes inhomogeneous in solution [24]. It was considered that most of the solutes are relatively hydrophobic compared with water, so they tend to accumulate at the gas–liquid interface of the bubbles and decrease the surface free energy of the bubbles. Sonolysis treatment degrades the WWS up to 16.3% after 320 min i.e. it is very slow process as compare to other process. Fig. 3 shows the WWS degradation with coupling of sonolysis and H_2O_2 treatment (a) plot of extinction as a function of degradation time, (b) kinetics of degradation. It is seen that the concentration of WWS decreases quickly with reaction time as compared to only sonochemical and H_2O_2 oxidation. Influence of H_2O_2 in sonolysis process enhances the degradation efficiency of WWS up to 34.8% while only H_2O_2 treatment can degrade up to 16.6% as shown in Tables 1 and 2.