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Enhancement of photocatalytic activity of TiO_2 by immobilization on activated carbon for degradation of pharmaceuticals

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ABSTRACT

This work evaluates the photocatalytic activity of bare TiO_2 and TiO_2 immobilized on activated carbon (TiO_2/AC) for degradation of pharmaceuticals. Four selected pharmaceuticals namely amoxicillin, ampicillin, diclofenac, and paracetamol were oxidized using solar irradiation. The TiO_2/AC composite was prepared by a temperature impregnation method. Characterization of TiO_2/AC by Brunauer–Emmett–Teller (BET) analysis, Fourier transforms infrared spectroscopy (FTIR), and scanning electron microscope (SEM) revealed successful immobilization of TiO_2 particles on activated carbon. Amoxicillin and ampicillin were completely degraded by TiO_2/AC, while 89% of amoxicillin and 83% of ampicillin were removed by bare TiO_2. Likely, TiO_2/AC attained higher removal of diclofenac (85%) and paracetamol (70%) as compared to bare TiO_2. Amortization and operating costs of full scale solar photocatalytic reactor were estimated. It was found that TiO_2/AC is more economic.

1. Introduction

The pharmaceutical industrial facilities produce various products which are used for human and animal medications [1]. Unfortunately, wastewater generated from pharmaceutical industries contains non-biodegradable organics such as drugs and antibiotics which are ineffectively removed by conventional wastewater treatment systems [2–4]. Therefore, treatment of pharmaceutical wastewater is urgently needed for prior treatment before being released into water streams in order to avoid serious environmental problems. Researchers have found that pharmaceuticals are not only found in pharmaceutical industrial wastewater but also low concentrations of different pharmaceuticals were detected in municipal wastewater, surface water and ground water [5,6]. Among all the pharmaceutical compounds that may be harmful to the environment, scientists expressed serious concerns about antibiotics and drugs because of their high consumption rate in both veterinary and human medication [7,8]. In addition, the widespread presence of antibiotics in low concentration leads to development of antibiotic resistant bacteria [9].

Biological treatment is preferable due to its low cost. However, the presence of toxic and bio-recalcitrant chemicals detracts the viability of biological treatment process for treatment of pharmaceutical wastewater [10,11]. Advanced oxidation processes (AOPs) have been realized as particularly efficient technologies for treatment of toxic wastewater and non-biodegradable organics [12–14]. In AOPs powerful reactive species like hydroxyl radicals ($^{\bullet}OH$) are generated by specific chemical reactions in aqueous solutions [15]. Hydroxyl radicals are able to destroy the most resistant organic molecules and break them down into relatively less persistent organics and end products such as CO_2 and H_2O [16]. Among AOPs, heterogeneous photocatalysis using artificial ultraviolet (UV) light source or solar irradiation has been recognized to be effective for the degradation of several types of persistent organics such as phenolic compounds, pesticides, and pharmaceuticals [17]. In heterogeneous UV/TiO_2 processes, ultraviolet light ($\lambda < 400$ nm) is utilized as an energy source and TiO_2 acts as a semiconductor photo-catalyst[18–20]. Nano-scale TiO_2 is distinctive with big surface area, good particle size distribution, high chemical stability, and the possibility of using sunlight as a source of irradiation [12]. In photocatalysis process, the photons with energies higher than the band-gap energy cause excitation of

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valence band (VB) electrons which then enhance the reaction of TiO_2 with organic molecules [21]. Illumination of the catalyst active sites with sufficient energy produces positive holes (h^+) in the valence band and in electrons (e^-) in the conduction band. The positive holes oxidize either the organic pollutants or H_2O to induce hydroxyl radicals [7,22].

Many researchers investigated immobilization of TiO_2 nano particles on different support materials to improve the photocatalytic activity and make the separation of treated effluent more effective [23–25]. Coating surfaces with TiO_2 has relatively low improvement on photocatalytic reaction because of the low particles dispersion and limited mass transfer between the pollutants molecules and the catalyst [26,27]. Catalysts can be more effective and easily separated from the effluent if they are supported on adsorbent surface such as powdered activated carbon (PAC) [28–30]. Activated carbon (AC) has no photocatalytic activity but it certainly enhances the photocatalytic reaction between TiO_2 and the contaminants due to the adsorption of pollutants on its surface [31,32]. Increased adsorption contributes to higher concentration of contaminants around TiO_2 active sites [33]. Activated carbon has a good developed pore structure, very large surface area, and high adsorption capacity. Therefore, it is widely used as an adsorbent for organic and inorganic pollutants [34]. The AC in the TiO_2/AC catalyst would act as a reaction station where organic molecules are adsorbed before transferring to the decomposition center [32,35]. Many researchers used Langmuir–Hinshelwood model to describe the kinetics of photocatalytic degradation of different organics in aqueous solutions [36]. The model basically relates the rate of degradation (r) and concentration of substrate (C) in water at reaction time (t) [37].

The main objective of this investigation is to assess the efficiency of solar photocatalytic oxidation process using TiO_2 versus TiO_2/AC for degradation of pharmaceuticals. Two antibiotics namely amoxicillin and ampicillin and two prevalent drugs (diclofenac and paracetamol) were used as model substrates. TiO_2/AC catalyst characterization was carried out and factors affecting on the photo degradation process such as pH and catalyst loading were extensively studied. Furthermore, the pseudo-first order kinetic reaction was tested according to the Langmuir–Hinshelwood model.

2. Materials and methods

2.1. Chemicals

Amoxicillin, ampicillin, paracetamol, and diclofenac were purchased from Glaxo Smith Kline. The TiO_2 and powdered activated carbon (AC) with bulk density of 0.37 g/cm^3 in Nano scale was obtained form from Acros and Adwic respectively.

2.2. Catalyst preparation

Immobilization of TiO_2 on activated carbon (AC) was executed according to the high temperature impregnation method described by El-Sheikh et al. [38]. A slurry of 20 g TiO_2 was heated and stirred with 300 mL of distilled water at a temperature of 70° C. AC was added with a ratio of TiO_2 being 1:2 respectively. The mixture was continuously stirred for 120 min at a temperature of 70° C. The dark black color of AC and white color of TiO_2 were observed at the beginning at which the mixture was gradually changed into a gray color. This observation implies that the interaction between AC and TiO_2 certainly occurred. The mixture was settled for 15 min and then the supernatant was decanted and the precipitate was dried in the oven at a temperature of 200° C for 12 h.

2.3. Photocatalysis experiments

Photocatalysis experiments were carried out using a solar reactor equipped with compound parabolic collectors (CPCs). The reactor was placed at the city of Borg Alarab, Egypt (Latitude 30°52′, Longitude 29°35′). The reactor consists of six borosilicate tubes (0.36 m^2) with a diameter of 2.5 cm and a length of 75 cm mounted on curved polished aluminum sheets with radius of curvature 9.2 cm. The module was fed with pharmaceutical mixtures in a closed cycle. The feed stock of pharmaceuticals solution was continuously circulated in a closed cycle in the module. A schematic diagram of the experimental set-up is shown in Fig. 1. The reactor was initially fed with 4 L of a pharmaceutical solution (50 mg/l) for a period of 210 min. The first 30 min was used to assess the adsorption process without illumination and 180 min for photocatalytic process. TiO_2 or TiO_2/AC were used as catalysts. Effects of pH values, TiO_2 and TiO_2/AC dosage were investigated. The pH value of the mixture was changed from 3 to 10 using H_2SO_4, and NaOH (50%). TiO_2 and TiO_2/AC dosages varied from 0.2 to 0.8 and from 0.4 to 1.6 g/L respectively. The solar irradiation was measured by Met, one Portable Weather Station (Model Number 466A). The normalized illumination time (t_{30w}) was used to compare between photo-catalytic experiments instead of exposure time (t). The normalized illumination time was calculated by the following equations [16,39]:

$$t_{30w,n} = t_{30w,n-1} + \Delta t_n (UV/30)(V_i/V_t) \quad (1)$$

$$\Delta t_n = t_n - t_{n-1} \quad (2)$$

Where t_n: contact time, UV: average solar ultraviolet radiation (W/m^2) measured during Δt_n, t_{30W}: the normalized illumination time, which refers to a constant solar UV power of 30W/m^2 (typical solar UV power on a perfectly sunny day around noon), V_t: the total reactor volume and V_i: the total irradiated volume.

2.4. Analytical methods

The concentrations of pharmaceuticals were quantified by Shimadzu HPLC using C-18 phenomenex reverse phase column, degasser (20A5), pump (LC-20AT), and prominences Diode Array Detector (SPD-M20A). The samples were filtered by micro syringe

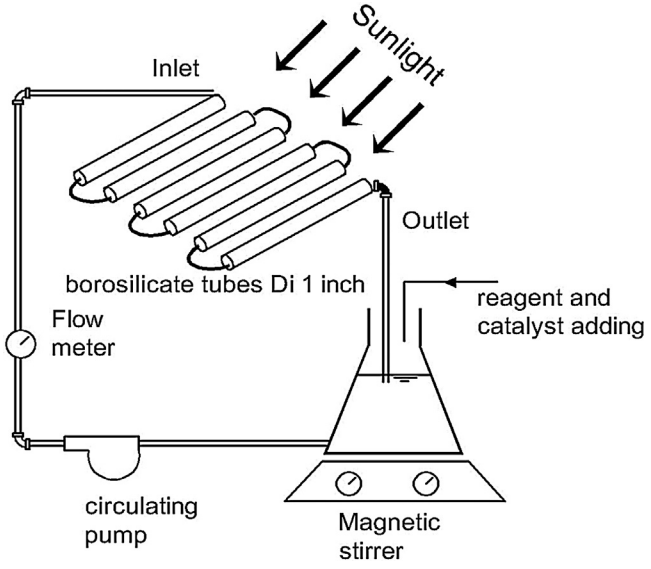

Fig. 1. Schematic diagram of the solar compound parabolic collectors reactor.