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# Adsorption and photocatalytic detoxification of diazinon using iron and nanotitania modified activated carbons

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ABSTRACT

Diazinon is used as an insecticide for different types of cultivation. It is considered to be a toxic pollutant. In this work, we present a comparative study of diazinon detoxification by two methods: adsorption and photocatalytic degradation. Chemically activated carbon (AC) was prepared from flamboyant pods. AC was modified with iron (Fe-AC) to be used as a solid adsorbent for diazinon. $TiO_2$ and $TiO_2$-AC, as photocatalysts for degradation of diazinon, were prepared by the sol–gel method. Textural and surface characterizations of the prepared solid samples were carried out using nitrogen adsorption at −196 °C, scanning electron microscopy (SEM), $pH_{PZC}$ and the Boehme titration method. Adsorption of diazinon was investigated on AC and Fe-AC considering the effects of pH, time, adsorbent dosage and concentration. The results showed that the adsorption capacity of Fe-AC is three times higher than that of AC. Furthermore, as the adsorbent dosage increases, the diazinon removal percentage increases, and adsorption follows pseudo-first- and pseudo-second-order equations. The diazinon photocatalytic degradation efficiency for $TiO_2$-AC is higher than that for $TiO_2$; the diazinon degradation percentage reaches 95% in the case of $TiO_2$-AC and only 55% in case of $TiO_2$ after 80 min.



## 1. Introduction

Pesticide pollutants are introduced into the environment from different sources, such as industrial effluents, chemical spills and agricultural runoff. They exist in surface water, underground and potable water. Diazinon is a phosphorothioate that was introduced in 1952 and is used as commercially an insecticide for various types of cultivation, such as trees of fruit, sugarcane, rice, corn and tobacco. Diazinon (*O*, *O*-diethyl *O*-[2-isopropyl-6-methylpyrimidine-4-yl] has been associated with toxicity to aquatic organisms at a concentration of 350 mg/L [1]. Diazinon is relatively water soluble, persistent in the soil, and fatal to humans at doses in the range of 90–444 mg/kg, and hence, it is considered to be a toxic pollutant. Removal of pesticide residue from the aquatic environment is therefore considered important and serves as an attractive case study. There are various methods for the removal of pollutants from wastewater, such as membrane filtration, [2–4] ion exchange, [5,6] electro-deposition, [7], biological process, [8,9] oxidation, [10,11] photocatalysis [12–14] and adsorption [15,16]. Adsorption has proven to be an effective and reliable method for pollutant removal from wastewater. Activated carbon is the most convenient solid adsorbent, owing to its highly developed porous structure, high degree of surface reactivity, higher adsorption capacity and easy chemical modifiability [17–19]. However, photocatalysis is an advanced and convenient method to remove pollutants by advanced oxidative processes in which toxic organics are converted directly into harmless substances in wastewater without the use of chemicals thereby avoiding sludge production and its disposal. Irradiation of $TiO_2$ with UV radiation can decompose a wide range of organic compounds, and as a result, it is the most popular semiconductor photocatalyst. In addition, $TiO_2$ is chemically inert, easy to prepare, able to catalyze oxidative chemical reactions, usable without risks to human health, photocatalytically stable and inexpensive. $TiO_2$ particles cannot be separated from solution after treatment, which is one of the major disadvantages of using $TiO_2$ in these types of applications [20]. It has been observed that the combination of activated carbon and $TiO_2$ results in fast decantability compared with $TiO_2$ alone, and the rate of organic removal by $TiO_2$-activated carbon is

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six times higher than that with $TiO_2$ alone [21]. To the best of our knowledge, there have been no studies in the pertinent literature reporting a comparison between adsorption and photocatalytic methods using iron-modified activated carbon or inserting titanium dioxide for removal of the insecticide diazinon. Furthermore, flamboyant pods, an agricultural solid waste, have rarely been considered previously as a source of the activated carbon.

This work presents a comparative study of diazinon insecticide detoxification by two different methods. The first method is adsorption of diazinon onto ferric-modified zinc chloride activated carbon (Fe-AC) produced from flamboyant pods, as agricultural solid waste. The second method is based on the photocatalytic degradation of diazinon using titanium oxide loaded onto activated carbon ($TiO_2$-AC) in the presence of ultraviolet radiation. Textural and chemical characterizations of the prepared solids were performed using different techniques. In this work, the influences of time, concentration, pH, and adsorbent dosage during the adsorption and photocatalytic degradation process were studied. Photolysis and kinetic parameters were considered during photocatalytic degradation.

## 2. Experimental

### 2.1. Materials

Analytical grade diazinon and titanium (IV) isopropoxide were purchased from Sigma-Aldrich and used without further purification. Zinc chloride, isopropanol and ferric chloride were purchased from Alfa Aesar. Flamboyant pods were collected from public garden.

### 2.2. Preparation of activated carbon and Fe-modified activated carbon

Flamboyant pods were first washed with deionized water to remove any surface impurities and then dried at 110 °C for 24 h, ground and sifted to obtain particle sizes ranging from 1 to 2 mm. The $ZnCl_2$-(AC) sample was prepared via a one-step method. Dried pods particles were soaked in an aqueous zinc chloride solution (1:2, precursor: $ZnCl_2$ weight ratio) for 48 h at room temperature. The mixture was then dried at 110 °C for 24 h. The last dried mixture was carbonized for 6 h in a stainless reactor (60 × 4 cm) at a rate of 10 °C/min up to 600 °C. The prepared sample was washed several times with deionized water to remove zinc cations, then dried at 110 °C, and finally stored in a clean and dry glass bottle (AC).

Fe-AC was prepared by mixing 2 g of AC with 200 mL of a 200 mg/L ferric chloride solution for 24 h, then filtered to remove the solid, and gently washed with deionized water. Then, the solid was dried at 80 °C for 24 h

### 2.3. Synthesis of photocatalysts

$TiO_2$ was prepared by the sol–gel method, in which 15 mL of titanium isopropoxide was mixed with 60 mL of isopropanol under vigorous stirring. A solution of isopropanol/HCl/$H_2O$ (1:100:50) was precisely added drop-wise within a stirring reaction mixture. The supernatant liquids were evaporated using a rotary evaporator, and the gel was dried and then calcined at 500 °C. $TiO_2$-AC was prepared by the addition of 10 mL of titanium isopropoxide to 4 g of AC (suspended in 40 mL of isopropanol). A solution of isopropanol/HCl/$H_2O$ (1:100:50) was added drop-wise within a stirring reaction mixture and stirred for 30 min. The mixture was heated to 45 °C in a water bath and supernatant removed by rotary evaporator. The sample was then washed with deionized water to remove the non-deposited titanium compound and then calcined in an inert atmosphere for 4 h at 500 °C.

### 2.4. Characterization of the prepared adsorbents and photocatalysts

The specific surface area ($S_{BET}$, $m^2/g$), total pore volume ($V_T$, mL/g), and average pore radius ($\bar{r}$, nm) were determined via nitrogen adsorption at −196 °C using a NOVA2000 gas sorption analyzer (Quantachrome Corporation, USA). Prior to adsorption, the catalysts and adsorbents were degassed at 200 °C for 6 h under a reduced pressure of $10^{-4}$ Torr. The morphological structure of the investigated samples was examined using a JEOL JSM-6510LV model SEM. The concentrations of basic and acidic functional groups on the surface of samples were determined by the Boehme titration method [22]. The point of zero charge ($pH_{PZC}$) of solid adsorbents was determined by the following procedure. Initially, 50 mL of 0.01 M NaCl were placed into several closed Erlenmeyer flasks. The pH within each flask was adjusted between 2 and 12 by adding HCl (0.01 M) or NaOH (0.01 M). Then, a portion of the adsorbent sample (0.15 g) was added to each flask, the flasks were agitated for 48 h, and the final pH was then measured. The $pH_{PZC}$ is the point where $pH_{final} = pH_{initial}$ [23].

### 2.5. Adsorption and photocatalytic degradation of diazinon

Batch equilibrium adsorption experiments were performed at 25 °C by mixing a known adsorbent dosage (0.1–0.4 g/L) with 50 mL of a solution with a definite concentration of diazinon in a 250 mL Erlenmeyer flask. Then, the mixture was filtered and the residual diazinon concentrations were measured at a wavelength of 247 nm using a UV–vis spectrophotometer Unicam UV/VIS 5625. The adsorbed amount $q_e$ (mg/g) was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where $C_o$ and $C_e$ (mg/L) are the concentrations of diazinon at the beginning and at equilibrium, respectively, $V$ is the volume of solution (L), and $W$ is the mass (g) of dry adsorbent. The effect of pH was determined via batch adsorption using solutions of diazinon with pH ranging from 2 to 10, using a solution with a concentration of 40 mg/L, 50 mL in volume and 0.2 g/L adsorbent dosage. The effect of time was determined in 100 mL bottles by mixing 0.01–0.04 g of adsorbent with 100 mL of 40 mg/L diazinon aqueous solution. After definite time intervals, the concentration of diazinon was determined in solution. The adsorption capacity of the adsorbent at time $t$; $q_t$ (mg/g) was calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where, $C_t$ (mg/L) is the liquid-phase concentration of diazinon at time $t$.

Photocatalytic degradation of diazinon was examined using a Pyrex reactor with 10 cm length and 20 cm width containing 200 mL of 40 mg/L diazinon solution and 0.3 g catalyst. The reactor was illuminated with UV radiation (8 W) at a wavelength of 254 nm. The degradation was determined by removal of 2 mL of solution at different time intervals and the residual diazinon concentration at 247 nm was determined as described above.

## 3. Results and discussion

### 3.1. Characterization of adsorbents and photocatalysts

The textural properties of the solid adsorbents and photocatalysts were calculated from nitrogen adsorption at −196 °C. Surface area ($S_{BET}$, $m^2/g$), total pore volume ($V_T$, mL/g) and the average pore radius ($\bar{r}$, nm) could be calculated using the following equation:

$$V_T\,(mL/g) = V(cc/g)\ \text{near saturation} \times 15.5 \times 10^{-4} \quad (3)$$

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