



# Titanium dioxide/zeolite integrated photocatalytic adsorbents for the degradation of amoxicillin



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## ABSTRACT

Integrated photocatalytic adsorbents (IPA) prepared from TiO<sub>2</sub> and natural zeolite were applied to amoxicillin (AMX) degradation. The acid-alkali pre-treated zeolite annealed at 300 °C under nitrogen resulted in the best degradation of AMX. The superior performance of this IPA material was explained using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD). SEM analysis showed an uneven surface as a result of TiO<sub>2</sub> cluster deposition, which provides more active sites for adsorption and degradation. XRD results revealed that peaks from more photoactive anatase were more prominent in this IPA material. EDS analyses also confirmed the presence of high amounts of TiO<sub>2</sub>. Despite their large TiO<sub>2</sub> loadings, comparison experiments with untreated zeolite suggested that the pores are still available for adsorption. The overall performance of the IPA material for the degradation of AMX was thus attributed to the adsorption capability of the zeolite carrier, the photocatalytic activity of TiO<sub>2</sub> coating and acid-catalyzed hydrolysis ('capture & destroy'). Degradation products resulting from TiO<sub>2</sub>/zeolite IPA-induced hydrolysis were identified by liquid chromatography-mass spectrometry (LC-MS) prior to photocatalytic treatment. AMX and its thermal degradants were almost completely removed after 240 min of irradiation. The efficiency of the developed TiO<sub>2</sub>/zeolite material provides a potentially economical way of degrading pharmaceutical compounds and recovering photocatalysts simultaneously.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) has been intensively studied as a heterogeneous photocatalyst and has demonstrated its potential for the degradation of organic compounds in aqueous systems [1,2]. A major difficulty encountered with this material is the time-consuming and uneconomical recovery of TiO<sub>2</sub> and the necessity for high photocatalyst loadings [3]. These drawbacks have limited the widespread technical application of heterogeneous photocatalysis in water treatment. To achieve pre-concentration of pollutants and improve the separation of TiO<sub>2</sub> particles, immobilization of TiO<sub>2</sub> on an adsorbent or an inert support to create integrated

photocatalytic adsorbents (IPAs) has been proposed [4,5]. Using IPAs, degradation of pollutants can be achieved by the simultaneous effects of physical adsorption by the adsorbent and photochemical degradation by the immobilized TiO<sub>2</sub> ('capture & destroy'). To achieve this TiO<sub>2</sub> particles are typically dispersed on inert and high surface area supports such as activated carbon [5,6], zeolite [7,8], organic polymers [9] or alginate [10]. Of these materials, natural zeolites are especially promising for IPA syntheses as they are abundant in nature and inexpensive. Zeolites are hydrated aluminosilicate minerals consisting of three-dimensional structures of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedrally linked by oxygen atoms to form a cage-structure [11]. They are characterized by good adsorption abilities, uniform channels and regular pores [12]. The exact composition and consequently the physicochemical properties of natural zeolites vary with geographic location. Pre-treatment is thus commonly applied to enhance their adsorption efficiency. Ion exchange with inorganic salts and alkali bases as well as acid treatment and calcination at high temperature has been utilized to modify the surface structure of zeolite particles [13]. Due to their acidic nature,

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zeolites are frequently used as solid acid catalysts [14]. This feature makes them interesting materials for the photodegradation of pollutants by targeted pH-alteration [15]. Likewise,  $\text{TiO}_2$  can be readily supported in the existing cage-structure or channels of the zeolite particles. Studies of  $\text{TiO}_2$ /natural zeolite IPAs mostly report on organic compounds such as dyes [16–18] and humic acids [7]. In contrast, these materials have not been studied for the degradation of pharmaceutical compounds, which have recently emerged as significant environmental pollutants [19–21].

Amoxicillin (AMX) [22], a  $\beta$ -lactam antibiotic, was selected for the current study as it is a widely human and veterinary medicine [23]. Due to its slow rate of metabolism in humans, oral administration of 500 mg of AMX in humans has resulted in the excretion of  $86 \pm 8\%$  in the urine within two hours of consumption [24]. Although sensitive towards hydrolysis under a variety of pH conditions [25,26], AMX is difficult to degrade completely and it can be found in both urine and faeces, along with its hydrolysed and metabolised by-products [27]. In Australia, AMX has emerged as one of the most frequently prescribed medicines and has been reported to be present used in river water and hospital effluents in ng/L levels [28]. Only partial removal of antibiotics is generally achieved by conventional urban wastewater treatment plants (WWTPs), making this class of drugs important pollutants [29]. The widespread usage of AMX and its frequent detection in the environment highlights the need for its removal.

Most advanced oxidation processes for the degradation of AMX in water matrices have focused on Fenton/photo-Fenton [30–36], ozonation [37,38] or  $\text{UV}/\text{H}_2\text{O}_2$  [39]. Photocatalysis studies have reported the use of  $\text{TiO}_2$  [24,33,40–44] or ZnO [45] for the removal of AMX. A study by Klauson et al. utilized doped and undoped titania [44], while a  $\text{TiO}_2$ /activated carbon (AC) derived IPA was investigated by Basha and co-workers [6] for its degradation. In the latter study, results showed that 10%  $\text{TiO}_2$ /AC produced the highest removal of 87% for a 150 mg/L AMX solution after 150 min of irradiation.

In this study,  $\text{TiO}_2$ /natural zeolite IPAs were prepared, characterized and subsequently evaluated for the degradation of AMX in water. The extent of mineralization was furthermore determined by measuring dissolved organic carbon (DOC). For the most efficient IPA material prepared, degradation by hydrolysis (during initial adsorption) and photocatalysis under several conditions was monitored by liquid chromatography-mass spectrometry (LC-MS).

## 2. Experimental

### 2.1. Materials and methods

Titanium (IV) isopropoxide ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ , TTiP, 95%, Alfa Aesar), absolute ethanol (AR grade, Univar, Australia), nitric acid (AR, BDH Chemical), hydrochloric acid (AR grade, Ajax Finechem Pty Ltd, Australia), sodium hydroxide (AR grade, Ajax Finechem Pty Ltd) and amoxicillin (R&D grade, Sigma–Aldrich) were used as received. Titanium dioxide P25 Aeroxide<sup>®</sup> (80% anatase and 20% rutile, BET surface area  $50 \text{ m}^2/\text{g}$ ) was supplied by Evonik industries. Natural Australian zeolite (Escott zeolite regular powder,  $<75 \mu\text{m}$ ) was obtained from Zeolite Australia Pty Limited (NSW, Australia). For the pH determination study, reverse osmosis water was prepared with a Millipore<sup>®</sup> Elix 10 from Millipore SAS. For all other applications, Milli-Q water from a Barnstead Nanopure Diamond water ion exchange system ( $18.2 \text{ M}\Omega\text{cm}$  resistivity) was used.

### 2.2. Preparation of integrated photocatalytic adsorbent

The raw Escott zeolite used in this study consisted of the zeolitic mineral clinoptilolite, with traces of mordenite, quartz, clay and

mica. The zeolite supplied was analysed for its composition by energy dispersive X-ray spectroscopy (EDS), which revealed  $\text{SiO}_2$  (72.3%) and  $\text{Al}_2\text{O}_3$  (11.6%) as the major constituents.

#### 2.2.1. Pre-treatment of natural zeolite

Zeolite (20 g/L) was vigorously stirred in deionized water for 5 h and the resulting suspension was allowed to settle prior to filtration and further washing with deionized water. Two types of treatments were performed on this zeolite sample: (i) an acid activation and (ii) a combination of acid-alkali activation. For the acid activation, the zeolite was treated with 1 M HCl for 24 h with continuous stirring. For the acid-alkali activation, the initial treatment was performed with 1 M HCl and was followed by 1 M NaOH. Contact times of zeolite with each reagent were kept to 5 h and vigorous stirring was applied. The pre-treated zeolite was continuously washed with deionized water and dried in a laboratory oven at  $70^\circ\text{C}$  for 24 h, followed by heat treatment at  $300^\circ\text{C}$  in a furnace oven (LABEC Model HTFS 60/13).

#### 2.2.2. Synthesis of $\text{TiO}_2$ /zeolite

$\text{TiO}_2$ /zeolite IPAs were synthesized following a modified procedure by Huang and co-workers [12]. TTiP (0.1 mol) was dissolved slowly in 100 mL of absolute ethanol. A white sol formed within 10 min. Concentrated  $\text{HNO}_3$  was added dropwise until the white precipitate disappeared and a transparent sol formed. The final pH of the transparent sol was adjusted to a pH value of 4 and stirred continuously for 6 h at room temperature to give a transparent yellow sol. The zeolite was added into the sol at a mass ratio of 1:5 (zeolite: $\text{TiO}_2$ ) and stirred until a gel was formed. The  $\text{TiO}_2$ /zeolite was aged at room temperature for 24 h. Subsequently, it was oven-dried at  $70^\circ\text{C}$  for 10 h and ground in a mortar to obtain a homogeneous material. These steps were performed for both acid activated and acid-alkali activated zeolites. The prepared  $\text{TiO}_2$ /zeolite samples were calcined at  $300^\circ\text{C}$  and  $450^\circ\text{C}$  in a nitrogen flow in a horizontal split tube furnace (LABEC Model HTFS 60/13) for 2 h. For comparison, pure  $\text{TiO}_2$  was also prepared, using the same procedure, but without the addition of pre-treated zeolite.

### 2.3. Characterization of $\text{TiO}_2$ /zeolite

Scanning electron microscopy (SEM) images of the  $\text{TiO}_2$ /zeolite materials were recorded using a JEOL scanning electron microscope (JSM-5410LV) at an accelerating voltage of 10 kV. The X-ray diffraction (XRD) patterns of the prepared materials were recorded on an X-ray diffractometer (Siemens D5000) using Ni filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406$ ) from  $2\theta = 2\text{--}65^\circ$ . EDS (JEOL JXA-8200) was used to characterize the synthesized IPAs and zeolite materials for their compositions.

### 2.4. Dark adsorption studies

AMX solutions of various concentrations (5, 10, 30 and 50 mg/L) were prepared and 100 mL of each solution was transferred into a 150 mL conical flask. IPA materials prepared by acid-alkaline treatment and calcined at  $300^\circ\text{C}$  (0.1 g) were added and the suspensions were agitated with exclusion of light for 24 h on an orbital shaker (Stuart Model SSL1). Aliquots were collected and filtered through a  $0.22 \mu\text{m}$  syringe filter prior to high-performance liquid chromatography (HPLC) analysis.

### 2.5. pH studies

An AMX stock solution (30 mg/L) was freshly prepared and 20 mL portions were transferred into 50 mL polypropylene centrifuge tubes. Zeolite,  $\text{TiO}_2$  or IPA materials (40 mg) were added and the suspensions were agitated with exclusion of light for a

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