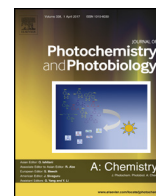




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Invited feature article

## Photocatalytic degradation of paracetamol over magnetic flower-like TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> core-shell nanostructures<sup>☆</sup>

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## ABSTRACT

The presence of pharmaceutical residues and their metabolites in water, even in low concentrations, is of significant concern due to their effects on aquatic environment. The application of new recyclable photocatalysts with high photocatalytic activity and stability for water treatment has received increasing attention in recent times. In this work, photocatalytic degradation of paracetamol (PA) has been investigated in aqueous solution over magnetically separable flower-like TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> core-shell photocatalysts using 450 W medium pressure mercury lamp. SEM, TEM, N<sub>2</sub> sorption (BET method), XRD, FTIR, Raman spectroscopy and VSM were used to characterize the prepared photocatalysts. Results showed that photodegradation and photomineralization of paracetamol was increased with increasing TiO<sub>2</sub> content in the TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> core-shell. GC and GC/MS were used to identify the intermediate products formed during the degradation of paracetamol. 4-Acetamidoresorcinol, 4-acetamidocatechol, hydroquinone, 1,2,4-benzenetriol in addition to aliphatic acids were identified in the photolysate mixture. The 33% TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> core-shell photocatalyst showed high photocatalytic efficiency for the degradation of paracetamol after four repeated cycles which demonstrates the high stability of the prepared photocatalyst. A pseudo first order rate was demonstrated for the photocatalytic degradation process of paracetamol.

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## 1. Introduction

Over the past few years, pharmaceuticals, personal care products and endocrine disruptors (known as emerging environmental contaminants) have emerged as a significant class of water contaminants for which public and scientific concern are increasing steadily because of their potential impact on human health and the environment [1–3]. Pharmaceutical drugs, for example, have recently been detected in sewage effluents [4,5], surface and ground water [5], and even in drinking water [3,5] in levels rarely exceed the µg/L levels [6]. However, their presence at low or high concentrations could bring about harmful toxicological

consequences [7]. Therefore, several efforts have been made to find out ways for eliminating or inactivating this class of substances in surface or wastewater.

Paracetamol (*p*-acetamidophenol, *N*-acetyl-*p*-aminophenol, 4-hydroxyacetanilide, PA), for example, is one of the top 200 prescriptions overall the world, which is widely used as pain relief due to tension headache, migraine headache, muscular aches, backache, neuralgia, joint pain, general pain, rheumatic pain, toothache and teething pain and as antipyretic. It is also used as an important material for the manufacturing of azo dyes and photographic chemicals [8]. PA and its metabolites are continuously introduced into the aquatic environment by consumer use

**Abbreviations:** PA, paracetamol; TBAB, tetrabutylammonium bromide; BSTFA, *N,O*-bis(trimethylsilyl)trifluoroacetamide; TMCS, trimethylchlorosilane; EG, ethylene glycol; TTIP, titanium(IV) tetraisopropoxide; VSM, vibrating sample magnetometer; SEM, scanning electron microscope; TEM, transmission electron microscope; EDX, energy-dispersive X-ray spectroscopy; XRD, X-ray diffraction; BET, Brunauer-Emmet-Teller; BJH, Barrett-Joyner-Halenda; FTIR, fourier transform infrared spectroscopy; NDIR, nondispersive infrared; TOC, total organic carbon; UV, ultraviolet; UV-vis, ultraviolet-visible; GC, gas chromatography; FID, flame ionization detector; GC/MS, gas chromatography-mass spectrometry; Ms, saturation magnetization; Mr, remnant magnetization; Hc, coercivity; FWHM, full width at half-maximum; AOP, advanced oxidation process.

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and disposal, and hospital waste [9]. Muir et al. have demonstrated that PA and its metabolites are excreted from the body in 58 – 68% during therapeutic use [10]. Concentration levels in the range of 1–6  $\mu\text{g/L}$  have been detected in the European sewage treatment plant effluents [6], up to 10  $\mu\text{g/L}$  in water samples from natural sources in the USA [11] and more than 65  $\mu\text{g/L}$  in the Tyne river in the United Kingdom [12].

Various advanced oxidation processes (AOPs) such as electrochemical oxidation [13], ozonation and  $\text{H}_2\text{O}_2/\text{UV}$  oxidation [14,15] in addition to biodegradation [10] have been employed to remove paracetamol from water. In particular, semiconductor heterogeneous photocatalysis, one of the most promising AOPs, receives significant attention for the treatment of contaminated streams because of its high degradation and high mineralization efficiency, low toxicity, low cost, and ability to function under ambient conditions [16]. When a semiconductor is illuminated with light energy equal to or greater than its band gap energy, excited high-energy states of electron and hole pairs ( $e^-/h^+$ ) are produced. The photogenerated electrons could reduce the organic substrate and the photogenerated holes can also oxidize either the organic molecule directly, or the  $\text{OH}^-$  ions and the  $\text{H}_2\text{O}$  molecules adsorbed on the catalyst surface to the strong oxidizing  $\cdot\text{OH}$  radicals [17].

A variety of metal oxides semiconductors such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$  and  $\text{WO}_3$  have been used as photocatalysts. In addition, combining two metal oxides (e.g.  $\text{WO}_3/\text{TiO}_2$ ,  $\text{TiO}_2/\text{Fe}_2\text{O}_3$ ,  $\text{WO}_3/\text{ZnO}$ ) could improve photocatalytic activity [18–20]. Among these catalysts,  $\text{TiO}_2$  catalysts are the most promising candidates, owing to their superior redox ability, chemical and biological inertness, non-toxicity, and comparatively low cost, as well as their excellent photochemical corrosion-resistant stability [21,22].

Photocatalytic degradation of paracetamol in aqueous  $\text{TiO}_2$  with UV light irradiation has been studied by some authors [23–26]. However, in practical, problems of separation and recycling of fine photocatalyst nanoparticles from water has been encountered. Fortunately, Magnetic photocatalysts could be effectively separated and recycled by applying an external magnetic field [27,28]. Magnetic photocatalysts composed of magnetic core  $\text{Fe}_3\text{O}_4$  and  $\text{TiO}_2$  shell were used for the first time by Beydoun and co-workers [29]. The magnetic  $\text{TiO}_2/\text{Fe}_3\text{O}_4$  and  $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$  nanoparticles

(NPs) catalysts were used for photocatalytic degradation and mineralization of paracetamol from aqueous solutions [30].

In the present work, magnetic flower-like  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  core-shell nanostructure catalyst was prepared and used instead of  $\text{TiO}_2/\text{Fe}_3\text{O}_4$  due to the photostability of  $\text{Fe}_2\text{O}_3$  compared to  $\text{Fe}_3\text{O}_4$ . The effect of various parameters, reusability and efficiency of the used catalyst were also assessed.

## 2. Experimental

### 2.1. Materials

The following reagents, iron (III) chloride ( $\text{FeCl}_3$ , Riedel-de Haën), urea ( $(\text{NH}_2)_2\text{CO}$ , Nice chemicals), tetrabutylammonium bromide (TBAB, Aldrich), titanium dioxide ( $\text{TiO}_2$  P25, Degussa) titanium(IV) tetraisopropoxide 97% (TTIP, Aldrich), ethylene glycol (EG, SDFCL), isopropanol ( $(\text{CH}_3)_2\text{CHOH}$ , Sigma-Aldrich), absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , Sigma-Aldrich), acetonitrile ( $\text{CH}_3\text{CN}$ , Merck), paracetamol 98% ( $\text{C}_8\text{H}_9\text{NO}_2$ , Alfa Aesar), 4-nitrocatechol 97% (Sigma-Aldrich), 1,2,4-benzenetriol 97% (Alfa Aesar), succinic acid (Adwic, Egypt), oxalic acid (Adwic, Egypt), maleic acid (Nice chemicals), tartaric acid (Adwic, Egypt), malic acid (Adwic, Egypt) and N,O-bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane (BSTFA+TMCS 99:1, Supelco, USA) were used as received. Deionized water was used in all experiments.

### 2.2. Instrumentation

X-ray diffraction (XRD) patterns were recorded on a Philips diffractometer (Model PW2103). FTIR spectra were recorded with a Thermo-Nicolet-6700 FTIR spectrophotometer.  $\text{N}_2$  sorption isotherms at 77 K were obtained using a Quantachrome (Nova 3200 series) multi-gas adsorption apparatus. SEM images were taken by a Quanta 250 FEG (FEI Company, Netherlands) scanning electron microscope attached with EDX unit, at an accelerating voltage of 30 kV. TEM images were taken by a TECNAI  $\text{G}^2$  spirit TWIN transmission electron microscope at an accelerating voltage of 120 kV and conducted by VELETA camera. Magnetic measurements of the prepared samples were carried out at 300 K temperature using a Lakeshore 7410 vibrating sample magnetometer. Raman

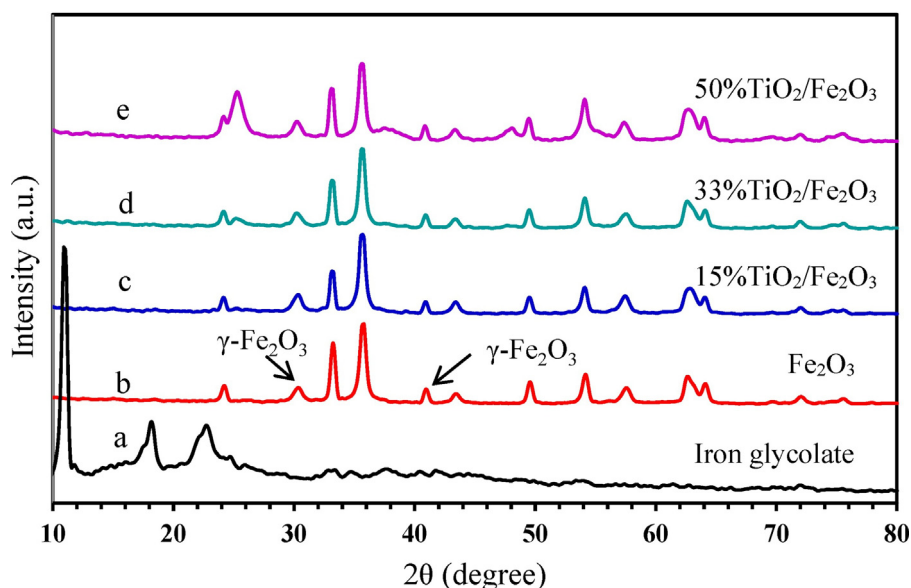


Fig. 1. XRD patterns for iron glycolate, pure  $\text{Fe}_2\text{O}_3$  microflowers and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  core-shells.

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