



Visible-light-driven photocatalytic removal of acetaminophen from water using a novel MWCNT-TiO₂-SiO₂ photocatalysts

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ABSTRACT

The presence of acetaminophen (APAP) in water and wastewater indicates its low susceptibility to conventional treatment. The application of new TiO₂ nanocomposites containing pristine carbon nanotubes (MWCNT, 0.15–8.78 wt%) prepared by solgel method in acetaminophen removal from water was tested. The studied nanocomposites possessed a high surface area (348–421 m²g⁻¹) with uniform framework-confined mesopores (primary mesopores) with an average pore width of about 3 nm. TiO₂ was present as anatase with crystal size ~ 5–6 nm. The nanocomposites had an exposed more graphitized MWCNT surface with a lower content of C–O and O=C–O– surface groups.

The addition of MWCNT reduced the band gap of TiO₂ from 3.2 eV to 2.82 eV. Dark adsorption resulted in insignificant changes in APAP concentration. The greatest changes in APAP concentration during Vis irradiation over the tested nanocomposites were observed using CNT10 (Fig. 10B). The highest efficiency was exhibited by the nanocomposite containing 1.72 wt% of MWCNT that enabled 81.6 ± 0.6% removal of APAP from water. Generally, an increase of MWCNT concentration up to 1.72 wt% in the nanocomposites induced APAP removal. The nanocomposites possessing higher MWCNT addition were, however, not so efficient (63.2 ± 2.4% and 62.2 ± 4.2% removal). The enhanced photocatalytic activity of different nanocomposites is observed only in the narrow range. The obtained results confirmed that photogenerated holes and, to a lower extent, 'O₂' and 'OH radicals played the key role in photocatalytic APAP removal over MWCNT-TiO₂-SiO₂. The studies using *Vibrio fischeri* have confirmed that photocatalytic oxidation is an effective method for reducing water toxicity.

1. Introduction

The ubiquitous occurrence of traces of new emerging contaminants, including pharmaceuticals and personal care products (PPCPs), in environmental matrices has an adverse effect on human and animal health [1,2]. Acetaminophen (C₈H₉NO₂, N-acetyl-p-aminophenol, known as paracetamol or APAP, logK_{ow} 0.460, pK_a = 9.38 [3] – 9.5 [4]), is a widely used over-the-counter non-steroidal anti-inflammatory drug applied for the treatment of pain and fever (analgesic, antipyretic, and anti-inflammatory effect) [5,6].

According to literature data, 20% of APAP is excreted unchanged and the most known metabolites are sulfate conjugates (30%) or paracetamol cysteine or mercapturate (5%) [3]. The environmental concentrations of PPCPs are up to hundreds of ppb [4]. APAP concentration in wastewater influent was measured at 6924 – 492.340 ng·L⁻¹ depending on the source [4,7]. The studies of Gros et al. [7] showed that APAP was noted in all studied wastewater influents in North East of Spain, in 93% of wastewater effluents, and in 89% of river

water samples. In other studies conducted in the UK, the concentration of APAP in a wastewater treatment plant (WWTP) was up to 281 ng·L⁻¹, and then up to 264 ng·L⁻¹ in the Thames (the final destination of treated wastewater from the WWTP), or even 555 ng·L⁻¹ in a small river close to the WWTP [8]. Acetaminophen is known as a very safe drug, but only in limited doses with the narrow margin of safety. The toxicity of APAP manifests itself as dose-dependent liver injury or nephrotoxicity [4,5].

The increasing consumption of drugs, including APAP, will definitely result in their increased concentration in wastewater, as wastewater is the main route of introduction of PPCPs into the environment [3,9,10]. The persistence of pharmaceuticals in WWTPs is associated with their low (if any) adsorption onto activated sludge or they require a longer retention time (slower microbiological decomposition) [7]. Although the removal of APAP during wastewater treatment is high relative to other PPCPs [3], the APAP concentrations in fresh water were as high as 2.382 ng·L⁻¹ [3], indicating that new more effective methods of wastewater treatment need to be developed.

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The removal of APAP was conducted using ozonation [11], ultrasounds [12], oxidation [13], adsorption [14,15], and membranes [16]. Among new techniques, photocatalysis is often tested [17–20] as it enables most of organic pollutants to be removed from the water matrix [17]. TiO_2 is the most studied and traditionally used photocatalyst because of its low price, availability, high thermal stability, and activity [18,21]. The UV activity of TiO_2 , however, excludes it from widespread use [19]. The relatively low surface area of the commercially available P25 photocatalysts (ca. $50 \text{ m}^2 \text{ g}^{-1}$) and low utilization of visible light are responsible for the development of new TiO_2 based photocatalytic materials [22–24]. The key parameter of TiO_2 photocatalytic activity is to obtain a material that will combine two main features: high surface area and Vis activity. One of the ways of enhancing TiO_2 Vis activity is doping with carbon materials [25] and carbon nanotubes (CNT), among others [26]. The role of CNTs, both multi-walled (MWCNT) and single-walled ones (SWCNT), is to narrow the band gap energy and introduce a new surface for adsorption of contaminants [27]. The mechanism of synergetic enhancement in CNT- TiO_2 composites is connected with i) inhibited recombination, ii) photosensitizing of TiO_2 (e^-/h^+ generation onto CNT), and iii) introduction of impurities (Ti–O–C bonds) [25]. In our previous studies, MWCNT-COOH- TiO_2 - SiO_2 nanocomposites (SiO_2 was used as the factor controlling TiO_2 crystallization [28]) possessed high UVA and UVC activity [29]. Simultaneously, Wanag et al. indicated that a similar role may be ascribed to the presence of carbon in TiO_2 nanocomposites as decreased transformation to rutile was observed [30]. The role of MWCNT-COOH was not exactly the enhancement of the available surface active sites (MWCNT acted as admixture up to 4 wt% or as the support above 4 wt%) but rather the inhibition of e^-/h^+ recombination and increase in the number of $\cdot\text{OH}$ radicals formed (a photosensitizer). As the properties of MWCNTs are influenced by their functionalization [31], it seems that the properties of MWCNT- TiO_2 nanocomposites will differ depending on MWCNT functionality.

The analytical methods of APAP determination in different matrices (e.g. pharmaceutical tablets and biological fluids) include chromatography [32] or spectrophotometry [33]. The application of electrochemical sensors, including a metal and Nafion film modified boron-doped diamond electrode [34], enables low concentrated samples to be analyzed. The main advantage of these methods is their high sensitivity, low cost, and quick response [35].

The aim of the present study was to evaluate the effect of pristine MWCNT doping on TiO_2 Vis activity. The photocatalytic activity of MWCNT- TiO_2 - SiO_2 nanocomposites was tested in the removal of APAP from water. The mechanism of APAP removal (the impact of photo-generated radicals) was also estimated.

2. Materials and methods

2.1. Materials

Titanium butoxide (TBOT) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich (Poland). Carbon nanotubes (MWCNT, outer diameter 20–30 nm, length 10–30 μm , surface area $165.6 \pm 5.0 \text{ m}^2 \text{ g}^{-1}$) were purchased from Timesnano (China). Butanol and ethanol were supplied by POCH (Poland). A pollutant solution was prepared using 10 mg L^{-1} of acetaminophen (Sigma Aldrich) in distilled water. Isopropyl alcohol, benzoquinone and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were purchased from Sigma-Aldrich and POCH (Poland).

The sulphuric acid (0.1 mol L^{-1}) used as a supporting electrolyte in voltammetric measurements was prepared from a reagent purchased from Merck. Nafion (5% solution) was obtained by diluting a reagent purchased from Aldrich with ethanol (from POCH) in order to obtain a 3% concentration. The standard solution of Bi(III) was purchased from Merck.

2.2. Methods

2.2.1. Preparation of nanocomposites

MWCNT- TiO_2 - SiO_2 nanocomposites were prepared using ultrasonic assisted sol-gel method. TBOT (10 mL) and TEOS (1.64 mL) were sonicated for 10 min and then a proper amount of MWCNT was added (1–40 mol%). After sonication for 15 min the solution was hydrolyzed with an ethanol/butanol mixture (9:1). The next step was sonication for 30 min and hydrothermal treatment (60 $^\circ\text{C}$, 24 h). After decantation, the solid residues were washed with distilled water and dried (110 $^\circ\text{C}$, 12 h). The obtained nanocomposites were labelled as CNT1-CNT40, where the number corresponds to the molar ratio of MWCNT.

2.2.2. Characterization of nanocomposites

The obtained nanocomposites were characterized using several methods. BET surface area and porosity (pore volume and diameter) were estimated using low-temperature nitrogen adsorption-desorption method (AUTOSORB-1CMS, Quantachrome Instruments, USA). The pore size distribution was obtained from the desorption branch of the isotherm according to BJH procedure. The composition of nanocomposites was estimated using X-ray photoelectron spectroscopy (XPS, Prevac) and X-ray diffraction (XRD using Cu K α radiation, Empyrean, PANalytica). The morphology of nanocomposites was observed using Scanning Emission Microscopy (SEM, Quanta 3D FEG/FEI) and Transmission Electron Microscopy (TEM, Tecnai G20, X-TWIN, FEI). The Raman (inVia Reflex, Renishaw), Photoacoustic Fourier Transform Infrared Spectroscopy (FTIR-PAS, Nicolet 8700 A) and UV-Vis/DRS spectroscopy (Jasco V-660) were used for characterization of optical properties of the studied nanomaterials.

2.2.3. The photocatalytic test

The photocatalytic activity of the obtained nanocomposites was tested using acetaminophen as target molecule. The process of APAP removal (10 mg L^{-1}) from water was performed in an Heraeus photochemical reactor (0.7 L) using a doped high-pressure mercury lamp placed vertically inside the reactor vessel (with emission centered at 500–550 nm, intensity $7.31\text{--}7.53 \text{ mW cm}^{-2}$). The test was performed without modification of pH, as a nearly neutral pH was the most optimal for APAP photocatalytic degradation [36].

Prior to photocatalytic treatment, the nanocomposites were contacted with the APAP solution for 30 min in dark to obtain sorption equilibrium. The first sample was collected at the end of the “dark” period, and then samples were collected at regular intervals (after 5, 10, 15, 30, 45 and 60 min of photocatalytic treatment), filtered (0.45 μm syringe filters), and analyzed. The amount of by-products of APAP photocatalytic decomposition (Dissolved Organic Carbon, DOC) and the amount of dissolved organic nitrogen (DON) from APAP decomposition were estimated using DOC/DON analysis (DOC-N analyzer, Shimadzu). The removal of pollutants was presented as c/c_0 , DOC/DOC_0 or DON/DON_0 ratio (where c , DOC or DON is concentration, DOC_0 or DON_0 measured at time t , c_0 , DOC_0 or DON_0 is initial concentration of APAP, initial DOC or DON , respectively). To determine the impact of radicals, additional tests with radical scavengers were performed. The effect of $\cdot\text{OH}$, O_2^- and h^+ was tested using isopropyl alcohol (IPA), benzoquinone (B-Q), and EDTA-2Na, respectively.

2.2.4. The determination of APAP

All voltammetric measurements were performed on a $\mu\text{Autolab}$ analyser with GPES software (version 4.9) produced by Eco Chemie (the Netherlands). A three-electrode cell system consisting of a silver/silver chloride/potassium chloride ($\text{Ag}/\text{AgCl}/\text{KCl}$, 3 mol L^{-1}) reference electrode, a platinum wire as a counter electrode, and a modified boron-doped diamond electrode (BDDE, boron doping level of 1000 ppm, electrical resistivity of $0.075 \Omega \text{ cm}$) purchased in an inert polytetrafluoroethylene (PTFE, Teflon) body with an inner diameter of 3 mm (Windsor Scientific Ltd., United Kingdom) as the working

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