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Solar light and metal-doped TiO_2 to eliminate water-transmitted bacterial pathogens: Photocatalyst characterization and disinfection performance

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ABSTRACT

The present study deals with the inactivation of *Escherichia coli* and *Klebsiella pneumoniae* in water by means of heterogeneous photocatalysis under simulated solar irradiation. For this purpose, novel Mn-, Co- and Mn/Co-doped TiO_2 catalysts were prepared. A straightforward, simple and inexpensive process has been developed based on a co-precipitation method for the synthesis of metal-doped catalysts, which were subsequently assessed in terms of their disinfection efficiency. The effect of various operating conditions, such as metal dopant (Mn-, Co- and Mn/Co), dopant concentration (0.02–1 wt%), catalyst concentration (25–250 mg/L), bacterial concentration (10^2–10^8 CFU/mL), treatment time (up to 60 min), toxic effects on bacteria and photon flux (4.93–5.8 $\times$ 10^{-7} Einstein/(L s)), was examined under simulated solar irradiation. Metal-doped TiO_2 samples were prepared reproducibly and doping shifted the optical absorption edge to the visible region. Their activity was superior to the respective of commercially available P25 titania. The reference strains of *E. coli* and *K. pneumoniae* proved to be readily inactivated during photocatalytic treatment of aqueous samples, since disinfection occurred rapidly (i.e. after only 10 min of irradiation) with the dopant concentration affecting the overall process to a certain extent. Disinfection follows a pseudo-first order kinetic rate in terms of both bacteria removal. Inactivation of the bacteria is attributed to the oxidative degradation of their cells and increase of their cell permeability and not to the potential toxicity of the metal-doped semiconductors, which did not exhibit any bactericidal properties. It has been shown that the improved activity of the Mn-, Co-, and binary Mn/Co doped TiO_2 is accredited to the fact that they can be activated in the visible part of the spectrum, in the absence of UV light (i.e. >420 nm).

1. Introduction

Occurrence of bacterial pathogens and fecal contamination in surface water may pose high health risks, as they are considered major agents of waterborne diseases. Given that potable water is an essential requirement, efficiency of disinfection techniques is imperative for the adequate inactivation of microorganisms and the protection of public health [1]. The most popular disinfection techniques nowadays involve chemical compounds, filtration or radiation (e.g. chlorination, ozonation, UV irradiation, etc.), which may act by different means like inhibition of enzymatic activity or destruction of cellular components [2]. However, considerable disadvantages including toxic by-products generated during chlorination, high cost of ozonation and action limitation depending on source-water turbidity when UV irradiation is applied, have led to the development of alternative methods [3,4].

Semiconductor photocatalysis has emerged as a promising technique for microbial inactivation in various aqueous matrices, including diverse types of bacteria, fungi, viruses, and spores [5–7]. Titanium dioxide (TiO_2) is widely used as a photocatalyst in

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these processes due to its high efficiency, low toxicity, physicochemical stability and low cost [2,6,8,9]. A drawback, regarding most commercially available TiO_2 catalysts, is that they are mainly active under UV spectral range because of the high required band gap energy (~3.2 eV) for excitation of the semiconductor. Therefore, the bactericidal potential of TiO_2 photocatalysis has been extensively studied with the use of UV light, which is a small fraction of the total solar-light spectrum, excluding solar source of energy, which is abundant and free of cost [5,10–12].

For this purpose, over the last decade, research interest has been focused on the use of solar irradiation for photocatalysis and thus the exploitation of the visible light energy. The photocatalytic efficiency of TiO_2 has been improved by many different strategies, which have been adopted for either morphological or chemical modifications of the catalyst [2,8,13]. The latter involve incorporation of additional components in the TiO_2 structure, like non-metal or/and noble and transition metal deposition. Doping the TiO_2 by several metals such as copper, cobalt, manganese, etc. broadens the absorption spectrum of these semiconductors toward the visible light region, as new energy levels are formed between the valence and conduction band [1,12–19]. The nature and the amount of the doping agent usually play an important role concerning the photocatalytic activity. On the other hand, some possible limitations have been reported like photo-induced corrosion and promoted charge recombination at some metal sites [2,8,20].

Up until now, various studies have been conducted in terms of the evaluation of disinfection efficiency of doped catalysts during water treatment under visible light, using mostly *Escherichia coli* as a model microorganism [3–5,10,14,16,18,21–24]. In most cases, inactivation of bacteria has been attributed to the decomposition of bacterial outer membrane due to phospholipid peroxidation of the membrane, caused primarily by hydroxyl radicals, generated during treatment [25–27]. Apart from *E. coli*, the information regarding the behavior of other bacteria is very limited. The bacterial content of water consists of many groups and species, which exhibit variable tolerance in disinfection as a result of differences in cellular structure. *Klebsiella pneumoniae* is considered as an emerging human pathogen and can be transmitted through water consumption, but it has been merely studied as far as its resistance against disinfection is concerned [28,29].

In this perspective, the objectives of the present work were (i) to prepare novel cobalt- and manganese-doped titania materials and investigate their structural properties, and (ii) to study their potential to purify aqueous samples in terms of *E. coli* and *K. pneumoniae* reference strains removal under solar radiation. For this purpose, several operating parameters were investigated, namely catalyst type and loading, dopant concentration, initial bacterial concentration, as well as photon flux, which typically influence disinfection effectiveness. Furthermore, scanning electron microscopy (SEM) was employed to detect destruction of cellular structure induced by photocatalysis.

2. Experimental

2.1. Materials

Titanium (IV) oxysulfate hydrate ($TiOSO_4{\cdot}xH_2O$), manganese (II) acetate tetrahydrate ($Mn(CH_3COO)_2$), cobalt (II) acetate tetrahydrate ($Co(CH_3COO)_2$) and ammonium hydroxide (25% NH_4OH) purchased from Aldrich were applied. Commercially available titanium dioxide (TiO_2 P25) was purchased from Degussa – Evonik Corp. (physicochemical characteristics are anatase:rutile 75:25, particle size of 21 nm and BET area of 50 m^2/g) and was used as benchmark.

2.2. Preparation of metal-doped TiO_2

A co-precipitation method was used to prepare metal-doped TiO_2 nanoparticles with molar ratio in different concentrations in the range of 0.02–1 wt%. Doped titanium dioxide was precipitated at pH ~7 from aqueous solution of $TiOSO_4$ titanium (IV) oxysulfate hydrate and dopant (Mn or Co or Mn/Co) by the addition of ammonia. After aging the suspension overnight, the precipitate was filtered and dried under air at 373 K. The residue was crushed to a fine powder and calcined in a furnace at 973 K for 3 h. More details can be found in previous work [13].

2.3. Catalyst characterization techniques

Powder X-ray diffraction patterns were collected on a Rigaku D/MAX-2000H rotating anode diffractometer (CuKα radiation) equipped with the secondary pyrolytic graphite monochromator operated at 40 kV and 80 mA over the 2θ collection range of 10–80°. The scan rate was 0.05° s^{-1}. The average particle size (D in nm) of nanoparticles was calculated from the line broadening of the X-ray diffraction peak according to the Scherrer formula, as follows:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where k is the shape factor (~0.9), λ is the wavelength of the X-ray radiation (1.54 Å for CuKα), β is the full width at half maximum (FWHM) of the diffraction peak measured at 2θ, and θ is the Bragg angle.

The phase content of TiO_2 samples was calculated using the formula:

$$\%f_A = \left[\frac{1}{1 + 1.265 \times I_R/I_A}\right] \times 100 \quad (2)$$

where f_A is the content of anatase, and I_A and I_R are the integrated intensities of the anatase (1 0 0) and rutile (1 1 0) peaks, respectively.

The UV–visible diffuse reflectance spectra of the final powders were measured on a Perkin Elmer LAMBDA 950 with $BaSO_4$, as reference standard. The diffuse reflectance spectra were plotted as the Kubelka–Munk function, $F(R)$, versus wavelength based on the Kubelka–Munk equation:

$$F(R) = \frac{(1-R)^2}{2R} \quad (3)$$

where the reflectance $R = R_{sample}/R_{reference}$. The band gaps were then determined from the Kubelka–Munk function and the Tauc plots.

Surface morphology and elemental analysis of the samples were carried out using scanning electron microscopy (SEM) and an energy dispersive spectrometer (EDS) on a JSM-6390LV instrument. The microscopic nanostructures were studied by transmission electron microscopy (TEM) working at 200 kV (JEM-2100 instrument equipped with LaB6 filament).

2.4. Disinfection experiments

The bacterial strains used in the present study were *E. coli* ATCC 23716 (American Type Culture Collection, Rockville, MD, USA) and *K. pneumoniae* NCTC 5056 (Public Health England Culture Collections). Both reference strains were inoculated separately in 10 mL of nutrient broth (HiMedia Laboratories) and grown overnight at 37 °C. The concentration of bacterial cells in the suspension was estimated measuring its optical density at 600 nm (Shimadzu UV1240 spectrophotometer) where, according to McFarland scale, an absorbance of 0.132 corresponds approximately to a cell density of 1.5×10^8 CFU/mL. Plate counts were also performed for accurate bacterial count. In each case, suspensions were properly diluted to