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ZnO nanoparticles in complete photo-mineralization of aqueous gram negative bacteria and their organic content with direct solar light

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ABSTRACT

For the first time, pristine ZnO nano-particles can be used as effective catalyst for water disinfection by killing and complete mineralization of two gram negative bacteria with direct solar light. Just like in earlier studies, pristine nano-size ZnO particles have shown anti-bacterial activity against two types of gram negative bacteria, *E. coli* and *P. aeruginosa*, where up to 20% of the former and 25% of the latter have been killed in the dark. Under direct solar radiation, the pristine ZnO particles readily catalyzed bacterial photo-degradation. While earlier studies were mostly limited to bacterial death and growth inhibition by pristine ZnO particles, the results describe for the first time how bacteria and their organic content can be completely photo-mineralized by direct solar radiations in 60 min. Only the bacterial cell wall fragments resisted the photo-degradation process. Under the reaction conditions, the degradation occurred by the UV tail of the direct solar light, where the ZnO nano-particles behaved as photo-catalysts. The results show the added value of using ZnO nano-particles as photo-catalysts in water disinfection strategies, leaving no resulting organic molecules in water.

1. Introduction

Continued contamination is making fresh healthy water a challenge, as only about 1.1% of natural waters are safe to drink [1]. Water is contaminated by different chemical and biological contaminants. Biological contamination by different types of pathogenic bacteria, protozoa and viruses, is a real threat to human beings causing different diseases [2]. Lack of control on human wastes is one serious cause for contamination [3]. Drinking water contamination with different types of bacteria is documented [2]. One class of widely known bacteria is *E. coli,* which belongs to gram-negative rod-shaped bacteria, with typical dimensions of ~2 μm in length and ~0.5 μm in width. *E. coli* may be hazardous (causing diarrhea and gastroenteritis) or harmless, depending on their types [4–6]. *P. aeruginosa* bacteria are other gram negative bacteria capable of causing serious infections in insects, plants and animals. *P. aeruginosa* is a major cause of nosocomial infections and causes chronic lung infections that affect cystic fibrosis [7]. *P. aeruginosa* is well known for its resistance to anti-bacterial agents [8]. Both bacteria are hazardous and should thus be completely removed from drinking waters.

Disinfecting drinking waters is a globally common practice. Different methods of disinfection are being used. Chlorination (with Cl_2, NaOCl, $Ca(OCl)_2$, chloramines or chlorine dioxide) is commonly used, but causes the production of chlorinated organic compounds in the municipality drains [9,10]. Other disinfection methods, are also used such as UV radiation and ozonolysis [11]. Such methods are effective but could be costly if used at large scale processes.

Nano-particles have been widely described as tools to kill micro-organisms [12–14]. Huang et al. reported that "*Cell wall damage, followed by cytoplasmic membrane damage, leading to a direct intracellular attack, has therefore been proposed as the sequence of events when microorganisms undergo TiO_2 photo-catalytic attack*" [15]. ZnO nanopowders have been reported for killing *E. coli*, *S. aureus* and *Bacillus atrophaeus* [16,17], although Adams *et al.* ruled out any effect for ZnO nano-particles against *E. coli* [18]. Zhang reported that ZnO particles exhibited activity with certain sizes [19,20]. The effect of

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pH on ZnO activity against bacteria was also reported [21]. Effect of ZnO particle storage, under different conditions, on their antibacterial activity against *E. coli* was investigated by Zhang et al. [20]. Doping the ZnO particles with other elements further enhanced their antibacterial activity [14].

Bacterial death and growth inhibition are thus well documented. A mechanism to explain the effect of ZnO particles on bacteria, based on electrostatic interactions with their surfaces, was also proposed. Another mechanism based on disruption of the cell membrane and oxidative stress in the bacteria was proposed [22]. Based on earlier reports, nano-size ZnO particles have antibacterial activities by causing death or growth inhibition. Biological mechanisms of such activities have also been widely described and need not be rigorously described again here. Effects of different parameters on the disinfection process have also been thoroughly investigated in detail. In a recent review [23] the mode of action of nano-size ZnO particles has been surveyed. ZnO particles caused bacterial death and growth inhibition in the dark and under radiation. Bacterial inactivation by photo-catalytic processes has also been reported [24–26]. Antibacterial photo-catalytic activity of ZnO nano-particles with UV radiations and visible light has been recently investigated [27,28]. Hu et al., reported the anti-bacterial activity of ZnO/SiC nano-particles with no UV radiations [29].

Killing or inhibiting bacteria by ZnO particles, in the dark or under radiation, is assumed to yield a complex mixture of different organic compounds, which could themselves be hazardous. Despite the sizable number of reports on disinfection with ZnO nano-particles, to our knowledge, the issue of remaining organic matter after bacterial death in water has not been described in earlier literature [17,23,27,30–32]. TiO_2 particles can photo-degrade bacteria and their organic content, on the particle surfaces in the air [33], but in water the fate of the resulting organics has not been studied.

In a recent communication, we reported how dye sensitized ZnO nano-particles can be effectively used to kill *E. coli* and mineralize their organic content under visible radiations [34]. Despite the new findings, the tendency of the sensitizer to degrade under photo-electrochemical conditions, which needs continued addition of the dye to regenerate the sensitized catalyst, is a limitation for the sensitization technique. For wide scale practical purposes, it is necessary to use a robust catalyst system that functions under natural conditions with no need for continued regeneration.

It is assumed here that the ZnO nanoparticles will catalyze complete mineralization of bacteria and their organic contents in water under direct solar radiation. Such assumption will be tested in this work for the first time. ZnO nanoparticles were intentionally chosen here for a number of reasons. Firstly, ZnO is a non-hazardous material. Any Zn ion traces that may leach out of ZnO particles are non-hazardous to humans or to agriculture, as the World Health Organization (WHO) recommends using Zn as supplement [35–37]. Secondly the ZnO particles have band gaps (~3.2–3.3 eV) similar to other stable semiconducting materials such as TiO_2, with the advantage of having higher absorptivity toward the UV tail in the solar light [38–41]. Thirdly, the ZnO particles are easy to prepare in the nano-scale by simple methods from starting materials available in any laboratory. Moreover, ZnO exhibits soundly high photoconductive response which makes it useful in various applications [42]. It is widely described as a photo-catalyst for photo-degradation and other processes [43–46].

2. Experimental

2.1. Starting materials and solvents

Starting materials and other common lab chemicals, such as zinc chloride, barium chloride, nitric acid, sulfuric acid, ethanol, sodium hydroxide and hydrochloric acid were all purchased from either Sigma-Aldrich or Frutarom as analytical grade, and were used as received without further purifications.

2.2. Equipment

An AlaboMed Inc. spectrophotometer was used to quantitatively determine bacterial concentration using the turbidometric method. The suspensions were adjusted to the 0.5 M McFarland standard turbidity.

A Shimadzu UV-1601 spectrophotometer was used to measure the solid state electronic absorption (EA) spectra for the ZnO powders. The ZnO powder was cast onto the wall of a quartz cell.

A Perkin-Elmer LS50 luminescence spectrophotometer was used to measure the solid state photoluminescence (PL) emission spectra for ZnO powders in aqueous suspensions. The excitation wavelength was 325 nm.

Field emission scanning electron microscopy (FE-SEM/EDS) was measured on a Jeol Model JSM-6700F microscope. The service is available in the laboratories of ICMCB, University of Bordeaux, France.

X-ray diffraction (XRD) patterns were measured on a Philips XRD XPERT PRO diffractometer equipped with a Cu Kα radiation source (λ = 1.5418 Å). The service is available in the laboratories of ICMCB, University of Bordeaux, France.

Specific surface area measurement for the prepared solid ZnO was performed. The acetic acid adsorption method was used based on literature [35,47,48].

In the photo-catalytic experiments direct solar light was used as the irradiation source. Experiments were conducted under direct solar irradiation with average light intensity of 1000 lx (0.00015 W/cm^2). About 5% of the solar radiation is in the UV region 320–400 nm, while the major part (~95%) is in the visible and the IR regions [39,40].

Total organic content (TOC) was measured using a TELEDYNE TEKMAR TOC FUSION equipment, with a carbon detection limit range 2 ppb–10,000 ppm. The TOC method measures all organic carbon concentrations in the aqueous solution, including any living bacteria, bacterial surfaces and different organic compounds. Therefore, the TOC method gives an accurate measurement of all organic stuff remaining in the reaction mixture. Solid ZnO particles are not measured as they cannot be volatilized into CO_2 during oxidation, and remain in the oven.

Further analysis for the organic compounds, resulting from bacterial killing, was performed using gas chromatography/mass spectra (GC-MS). A Perkin-Elmer Clarus 500 GC/MS (2010) equipment, was used. The system is equipped with a SPME-GC/MS unit and an auto injector to directly analyze aqueous solutions. A capillary column (30 m in length and 0.25 mm in diameter) was used. Analysis conditions were as follows: starting with initial temperature 50 °C (for the first 10 min), the temperature was raised to 100 °C (ramp rate 2 °C/min) and kept for additional 20 min. The solid ZnO particles were filtered off from the aqueous mixture before injection into the GC/MS.

2.3. ZnO nanoparticles preparation

Nano-size ZnO particles were prepared as described earlier [49]. $ZnCl_2$ solution (0.45 M) was prepared by dissolving solid $ZnCl_2$ (15.23 g, 0.11 mol) in distilled water (200.00 mL). The solution was diluted to 250.00 mL. A solution of NaOH (0.90 M) was prepared by dissolving NaOH (9.00 g) in distilled water (200.00 mL) and diluting to 250.00 mL. The NaOH solution was then placed inside a 500 mL beaker and heated to ~55 °C. The $ZnCl_2$ solution was added drop-wise (within ~40 min) to the heated NaOH solution with vigorous magnetic stirring. The mixture was kept under these conditions for 2 h. The ZnO white precipitate was isolated, cleaned with deionized water and ethanol successively, and dried under air at ~60 °C. The prepared particles were characterized by UV–Visible absorption spectrophotometry, photoluminescence spectrometry, XRD and SEM as described below.