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Removal and regrowth inhibition of microalgae using visible light photocatalysis with ZnO nanorods: A green technology

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ABSTRACT

Algal biofouling can be a major problem during membrane filtration processes reducing membrane efficiency. Removal of microalgae by visible light photocatalysis using zinc oxide (ZnO) nanorods was studied in this work. ZnO nanorods were grown on polypropylene support substrates. The treatment unit was constructed by incorporating ZnO nanocoated substrates in a glass tube. Anti-algal activity of the treatment units were tested using green microalga, *Dunaliella salina*, of 10^7 cells/mL concentration, which is higher than the concentration of cells during algal blooms. Nearly total algal cell inactivation was achieved within 2 h of continuous visible light illumination in the presence of nanocoated support substrates, as determined by flow cytometry analysis (98%) and trypan blue staining (95%). Uncoated support substrate under light illumination did not lead to algal cell mortality (1.7%). Complete inhibition of any regrowth of algal cells treated with nanocoated substrates was confirmed as no significant changes in the total number of cells were observed even after 2 weeks of incubation of the treated culture. The anti-algal activity of ZnO nanorods was attributed to the formation of reactive oxygen species (ROS) through photocatalytic processes. ZnO nanorod coated substrates used in the treatment units could be a suitable green method to control membrane fouling in water treatment plants avoiding the utilisation of harmful chemicals.

1. Introduction

Water on earth is a valuable but finite resource. In developing countries more than 1.2 billion people lack access to clean and safe drinking water [1,2]. In arid regions, available drinking water is even more of a problem due to the scarcity of fresh water resources. Desalination technologies that alter saline water to fresh water have high potential to satisfy growing water demand which has led to massive reliance on membrane technologies for water desalination [3]. Membrane fouling is a major problem encountered in filtration processes, and is a major limitation that undermines the practical application of membranes for desalination and wastewater treatment [4,5]. Fouling of membranes in desalination plants compromises the efficiency of the treatment processes leading to higher production costs due to increased energy consumption [6].

Membrane biofouling occurs due to the attachment and subsequent growth of microorganisms such as bacteria and microalgae [7,8]. Algae are difficult to eliminate with conventional pretreatment methods. Also algal cells have tendency to deposit on the membrane surface which can reduce membrane lifetime [9]. Seasonal algal blooms can also affect water quality through the release of algal toxins and production of unfavourable odour rendering water unsuitable for drinking [10]. Thus, removal of algae is important for improved performance of membranes in water treatment plants. There are several microalgal species known to produce blooms that can even be potentially hazardous if they produce toxins [11]. Most reports available in the literature are related to the treatment of *Microcystis aeruginosa* [12] but few studies have considered other bloom forming species such as *Chlorella* or *Dunaliella*. The microalga *Dunaliella salina* is an organism that is commonly observed in salt lakes and marine environments which has tolerance towards variable salt concentrations [13].

Common practice to control biofouling involves the usage of high concentrations of chlorine. Longer contact of chlorine with organic matters in water leads to the formation of carcinogenic substances known as trihalomethanes [14]. In addition, chlorine breaks down natural organic matter to biodegradable products

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offering an additional nutrient source to remaining viable cells after the treatment, leading to transient effectiveness of chlorination [15]. Hence, multiple exposures of chlorine are required for effective treatment of fouling in membranes. Due to the problems accompanied with chlorination, numerous efforts have been made to develop novel, less toxic yet effective techniques for the prevention of membrane biofouling [16] including the use of ozone or ultraviolet (UV) treatments [14]. Also conventional biocide applications generates waste which have been demonstrated to lead to environmental, ecological and toxicological problems apart from being uneconomical [17].

Zinc oxide (ZnO) is a well-known semiconductor with a wide ranging application as a catalyst [18]. It is established that ZnO is a suitable visible light active photocatalyst capable of degrading harmful organic molecules [19,20] and to arrest bacterial growth [21,22] through the generation of reactive oxygen species (ROS) under visible light irradiation [23,24]. ZnO nanorod coatings have significant advantages over ZnO nanoparticles due to increased stability, lower toxicity and no added processing steps for the removal of nanoparticles from the treated water [25]. Moreover, it is feasible to modify any support material by ZnO nanorods growth due to low temperature (below 100 °C) synthesis process.

The purpose of the present study is to investigate activity of ZnO nanorod coated supports as a pre-treatment technology for the removal of the marine microalga *D. salina*. Specific objectives of the study include investigation of anti-algal activity of the nanocoated polypropylene substrate under continuous visible light irradiation and monitoring regrowth of algal cells after photocatalytic treatment.

2. Experimental

ZnO nanorods coatings were prepared by a two-step process. In the first step, a seed layer of ZnO nanoparticles were deposited on commercially available non-woven polypropylene support substrate (CUNO, CP 110, Oman). ZnO nanorods were then grown on these seeded substrates by utilizing simple hydrothermal route as described hereunder.

2.1. Synthesis of ZnO nanoparticles

Sol–gel synthesis of ZnO nanoparticles in ethanol medium was conducted by following a protocol reported earlier [26]. Briefly, 4 mM zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and 4 mM NaOH (MERCK, Germany) were prepared in 20 mL each of absolute ethanol solution under rigorous stirring. Then, the prepared zinc acetate solution was diluted with 20 mL of ethanol. Subsequently, freshly prepared NaOH solution was added drop wise under continuous stirring at room temperature. The mixture was then hydrolysed in a temperature controlled water bath at 60 °C for 2 h. The resultant ZnO colloidal solution was transparent, consisting of nanoparticles of 4–7 nm [27] (Supp. Info. Fig. S1).

2.2. ZnO nanoparticle seeding

Prior to hydrothermal growth of ZnO on the substrates, a pre-treatment step was introduced using the synthesized ZnO nanoparticulate colloid. The polypropylene substrates were modified following a procedure reported by Baruah et al [28]. First, the substrates were treated with 1% dodecanethiol solution in ethanol followed by heating at 100 °C for 15 min. The thiolated substrate surfaces help in the firm attachment of ZnO nanoparticles to polypropylene substrate. Subsequently, the substrates were dipped in colloidal suspension of ZnO nanoparticles for 15 min. The seeded polypropylene substrates were then dried at 150 °C for 15 min. This process was repeated five times in order to achieve a proper coverage of ZnO nanoparticles on the substrates and then dried and stored in a dehumidified chamber (25% RH) until further use.

2.3. Hydrothermal synthesis of ZnO nanorods

ZnO nanorods were grown in a sealed chemical bath containing an equimolar solution (10 mM) of zinc nitrate hexahydrate and hexamethylenetetramine (hexamine) (Sigma–Aldrich, USA) kept in an oven maintained at 90 °C. The precursor solution was changed every 5 h in order to replenish the depleted zinc ions [29,30] and the growth process was carried out for 15 h. Subsequently the samples were thoroughly rinsed with deionized (DI) water and kept in an oven at 90 °C overnight for drying.

Two different types of substrates were used throughout the experiment: uncoated substrates (only support substrates: non-woven polypropylene support substrate without ZnO nanorod coatings) and nanocoated substrates (support substrates: non-woven polypropylene support substrate coated with ZnO nanorods).

2.4. Characterization of nanocoated substrate

The modification of support substrates were studied using Fourier transform infrared spectroscopy (FTIR) (PerkinElmer Frontier 1, USA) spectrometer (Supp. Info. Fig. S2). Surface morphology of ZnO nanorods on support substrates were characterized by JEOL JSM-7200 (Japan) field emission scanning electron microscope (FESEM) working at 20 kV (working distance = 8 mm). ZnO crystal structure was studied by using X-ray diffraction (XRD) (Rigaku Miniflex 600, Japan) working at 40 kV, 15 mA with a scanning speed and step size of 10 deg/min and 0.02° respectively, for 2θ values from 20° to 80°. Zeta potential of the support substrates and nanocoated substrates were measured by streak potential technique using electro kinetic analyser (Anton paar, SurPASS, Austria). Specific surface area (m^2/g) measurements were conducted using NMR relaxation technique in a Xigo Nanotools equipment, with ethanol as the solvent [31,32]. In this system the spin magnetic moments of hydrogen nuclei are probed. A perturbation in the applied static magnetic field changes the total nuclear magnetization, whose relaxation back to equilibrium is registered as a function of time (comprising of longitudinal relaxation time T_1, defining the decay of spin alignment and the transverse relaxation time T_2, defining the decay of precession). In this work, transverse relaxation time (T_2) of the solvent in contact with pore surface was analysed by Acorn area software to extract the specific surface area (SSA) of the substrate in contact with the solvent. Active surface area (m^2) was subsequently calculated from the SSA by multiplying SSA (m^2/g) with weight of the support (g) substrate used for the experiment. Surface wettability measurements were carried out before and after photocatalysis for both uncoated and nanocoated support substrates using Theta Lite attention tensiometer (Biolin Scientific, Sweden). Water contact angle was measured at five random locations on each substrate using 5 μL DI water droplet and average values are presented with standard deviation. All other measurements were carried out in triplicates at room temperature.

2.5. Algal culture

Batch cultures of *D. salina* (Culture Collection of Algae and Protozoa, UK, CCAP 19/18) were grown in seawater of 35 ppt (parts per thousand) salinity and enriched with nutrients as described by Guillard and Ryther [33]. Cultures were grown in aerated Erlynmer flasks with continuous light irradiation of 150 μmol photons $m^{-2}\ s^{-1}$ at 30 °C. Growth rates were determined by the change in cell number over time by counting using the haemocytometer