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Kinetics and equilibrium adsorption of nano-TiO_2 particles on synthetic biofilm

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ABSTRACT

Understanding the environmental behavior of nanoparticles includes their interaction with biofilms, which is a covering on the surface of a living or nonliving substrate composed of microorganisms. This study focuses on nano-TiO_2 sorption mechanism by synthetic biofilm that was prepared as superporous spherical beads from agarose, using batch stirred flasks kept at room temperature. The pH plays an important part in these phenomena, by its influence on the nanoparticles and biofilm chemistry, where the biofilm nanoTiO_2 uptake at neutral pH was enhanced over acidic conditions. Hydroxylation of TiO_2 nanoparticles, dependent on pH and the salinity of the solution, influences the stability of colloids, the sorption kinetics via the nature of limiting phases: diffusion through the boundary layer or intrabiofilm mass transfer and the sorption mechanism. The sorption follows pseudo first-order adsorption kinetics with estimated average rate constants of 2.2 (min^{-1}). Equilibrium isotherms were evaluated using Langmuir and Freundlich isotherms to obtain the maximum uptake at different solution pH and the free energy of the adsorption. The adsorption is apparently irreversible because biofilm limits diffusion of particles out of the pores and the complexation active binding sites on the surface hydrated biofilm to the hydrophilic TiO_2 nanoparticles.

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1. Introduction

Biofilms referred to as Extracellular Polymeric Substance (EPS) are aggregates of bacteria and other microorganisms embedded in a hydrogel matrix consisting of a mixture of polymeric compounds, primarily polysaccharides, proteins, humic substances, surfactants, lipids, glycolipids, membrane vesicles, and ions such as calcium ions, and DNA [1–3]. Over 99% of microorganisms on earth live within these biopolymers and the biofilm matrix is believed to be hydrated, containing up to 97% of water [3,4]. Bofilms are characterized by the environmental conditions and surfaces that favor their formation, the gene products that are required for their formation, the architecture of the biofilm, and the types of extracellular products that are concentrated in the biofilm matrix [5,6].

There is an increasing interest in the EPS of microorganisms in biotechnology due to their wide structural diversity and their physical and other unique properties such as complex nature with enormous binding sites [5]. One of the expanding areas of the biofilm application is in the remediation of environmental effluents produced by industries, and in wastewater treatment plants to degrade contaminants [7–17].

As EPS are a complex mixture of different biopolymers, they are slow to grow and their composition depends on the different environmental conditions under which the biofilms exist. A simpler alternative approach can be to synthesize artificial biofilm that simulates the natural biofilm in the laboratory [18]. Artificial models of defined composition and structure can be helpful to mimic natural biofilm. Agarose based polymers simulate EPS since they are easy to assemble and have well-defined structural parameters [19]. Agarose is a neutral polysaccharide derived from red purple seaweeds and the biofilms made from this material are composed of network agarose chains with water filled porous structure [20]. Some important physico-chemical properties of the artificial EPS matrix models, like solubility, water retention, swelling behavior and simulation of protective effects against biocides have been reported [18,19]. The simulation helps to understand the protective effects of the artificial EPS matrix against toxic substances like biocides in comparison to known protective effects of the EPS of native biofilms. Agarose biofilms provide a flexible, cell membrane-like environment and a large outer surface on which target analytes can be attached in solution. They are characterized by their large flow pores that allow rapid equilibration of the inner part of a particle with the chromatographic flow, giving the material excellent separation properties [21–23]. Because of this excellent biocompatibility, these biofilms have demonstrated their analytical potential in detecting various analyte classes in a homogeneously scattered medium and as solid phase separation tools for DNA detections and immunoassays, and hydrophobic interaction chromatography [20,22,24,25].

There have been rising developments of nanotechnology and potential increase in their production and applications in agricultural, environmental and industrial sectors ranging from fabrication of molecular assemblies to microbial array chips. At the same time, there is an increasing concern regarding the risks of synthetic nanoparticles

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on the environment and their likely impact on the human health [26–32]. In general, the environmental fate of nanoparticles is strongly influenced by sorption processes [33,34]. Therefore, it is important to understand the underlying nanoparticle sorption to the natural systems such as biofilms as the EPS can release the nanoparticles on decomposition leading to remobilization of pollutants. However, little is known about the adsorption capacity of biofilms for nanoparticles [35]. There have been few reports on the interactions and subsequent effects of some nanoparticles on natural biofilms. Interacting silver nanoparticles with *Pseudomonas putida* biofilms and important factors, which affect the adsorption of nanoparticles on biofilms such as the presence of ions present in the system, were previously reported. Authors reported aggregate formation and the cell response to the existence of nanoparticles in biofilm [36,37]. Some fluoride containing nanomaterials have shown antimicrobial activity and they were able to restrict biofilm formation of common bacterial pathogens [38]. Nitrogen-doped TiO_2 and ZrO_2 antibacterial effects on *Escherichia coli* and biofilm heterotrophic bacteria under solar light illumination were reported [39]. Influence of biofilm on the transport of fullerene (C-60) nanoparticles in porous media demonstrated that EPS have a great influence on C-60 deposition [40]. But, the potential toxicity of carbon nanotubes to biological processes in wastewater treatment has been documented in the literature [41].

Artificial biofilm models, therefore, could show promise and are likely to provide an excellent platform wide applications in biotechnology and separation science [42]. In this we report the work inspired by using artificial biofilm models to mimic important aspects of real biofilms, which allow studying the adsorption and interaction of nanoparticles with biofilms. This paper details the results of interactions of manufactured TiO_2 nanoparticles (Degussa) with biofilms. This work allows us to gain an insight on the kinetics and thermodynamic on the adsorption of TiO_2 on biofilms, and understanding of the nanoparticle-biofilm adsorption would offer developing a technique for efficient water treatment membrane filtration.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

Agarose SFR™ (gelation point 35 °C) was obtained from AMRESCO®. Tween 80 (polyoxyethylenesorbitan monooleate, code) and Span 85 (sorbitan trioleate, code) were obtained from Sigma Aldrich. TiO_2 nanoparticle was purchased from Degussa and was obtained from Fluka. All the chemicals used were of analytical grade. High-purity water (Milli-Q system) was used for all the applications.

2.1.2. Characterization of TiO_2 nanoparticles

Transmission electron microscopy (TEM) image of TiO_2 nanoparticles was acquired on a JEOL JEM-2010 transmission electron microscope, operated at 200 kV. TEM sample was prepared by casting drops of dilute dispersion of TiO_2 nanoparticles in methanol on 100-mesh silicon monoxide supported copper grids. The Zeta potential measurements (by means of the electrophoretic mobility) were performed on a Malvern ZS equipment. Each measurement of Zeta Potential versus pH was done after magnetic stirring for 20 min followed by an ultrasonic treatment of 5 min of the suspension. Characterization of the particle size distribution was performed by Dynamic Light Scattering (DLS). The size distribution of the TiO_2 nanoparticles was measured at pH 6.5 and 1 mM NaCl ionic strength.

2.1.3. Preparation of synthetic agarose biofilm

The super-porous synthetic biofilms were fabricated using water in-oil emulsification–thermal regeneration method, following prior published protocol [18,19]. Agarose SFR™ (8 g) was added in 200 ml deionized water with gentle mixing for 15 min. The mixture was heated to 90–95 °C on a hot plate until it became a clear suspension with subsequent cooling to 55 °C. A pre-warmed solution (to 50 °C) of 6 ml Tween 80 with 80 ml of cyclohexane was added to the clear agarose solution and the mixture was left to emulsify by stirring (1200 rpm) for 5 min. Additional pre-warmed solution (to 50 °C) of 24 ml of Span 85 and 600 ml of cyclohexane was added to the emulsion of agarose and Tween 80, and while stirring at 500 rpm for 10 min. Thereafter, spherical white beads were obtained after 2 h continuous stirring at room temperature. The beads were washed twice using deionized water and were collected after decanting the solvent. This technique allowed formation of biofilm with diameter ranging from 350 to 800 μm. These beads were kept at 4 °C to minimize bacterial growth and were used as biofilm for the adsorption study [18,19].

2.2. Characterization of synthetic biofilm

2.2.1. Optical and electron microscope measurements

Fresh samples of superporous agarose biofilm were imaged using a digital microscope (VHX-600 Gen II, Keyence, Osaka, Japan). To evaluate the shape and surface characteristics of the freeze-dried biofilm and the biofilm with TiO_2 nanoparticles adsorbed, a Philips XL-30 ESEM (FEI, Eindhoven, Netherlands) was used to acquire micrographs. Samples were mounted on an aluminum sample holder using double-glued Scotch tape and coated with gold for 60 s, using a Desk II Cold Sputter Etch Coater (Denton Vacuum, Cherry Hill, New Jersey). For cross-sectioned micrographs, a stainless steel blade (Feather Safety Razor, Japan) was used to carefully split the freeze-dried biofilm, which were previously immersed, in liquid nitrogen. The distribution of elemental concentrations for the solid samples was analyzed using the mapping analysis of energy dispersive X-ray spectra (EDX Genesis).

2.3. Analytical procedure for batch adsorption studies

A commercially available TiO_2 (Degussa P25) was used to prepare nanoparticle dispersion. Standard dispersions of TiO_2 between 1 and 150 mg/L were prepared by dissolving the nanoparticles in deionized water to plot a calibration curve. All spectrophotometric measurements of TiO_2were done with a UV–vis spectrophotometer (Agilent Technologies, Deutschland GmbH, Waldbronn, Germany), using 3 ml matched open-top UV–vis quartz cuvettes at λ_{max} 480 nm. An Oakton digital pH/mV meter (pH/CON 510 series) was used for all pH measurements. Studies of adsorption were conducted varying the TiO_2 concentration from 10 to 50 mg/L with initial pH 3, 6.5 and 10, and with initial ion strength 1 and 100 mM NaCl. Samples were sonicated for ca. 10 min prior to adsorption study. Hydrogel of agarose (4% w/v) was used to coat the biofilm on stainless steel sheets (2″ × 3″). Adsorption tests were carried out by taking 724 mg biofilm adsorbent and 1 L of solution containing TiO_2 nanoparticles with varying solution chemistry. All experiments were carried in agitation at 20 °C. In addition, control experiments were performed for each set of runs using the same experimental parameters without the use of biofilm in the solution. Changes in the nanoparticle concentration because of adsorption on artificial biofilm were analyzed by collecting liquid samples from the dispersion between 30 min to 2 h time intervals. The concentrations before and after adsorption study were measured by UV–vis spectrophotometer. Desorption study carried out by immersing the bead loaded samples into dispersions contained 50 mg/L TiO_2 in 1 mM NaCl, with three pHs, 3, 6.5 and 10. The biofilm on stainless steel plates were left in the dispersion until equilibrium was attained. Thereafter, the plates removed and immersed in to deionized water solution with adjusted initial pH and ion strength, which were the same as the initial nanoparticles containing dispersion. The concentration of the solution was then monitored as time increased and until the desorption equilibrium reached. Solution

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