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Potent antifouling silver-polymer nanocomposite microspheres using ion-exchange resin as templating matrix

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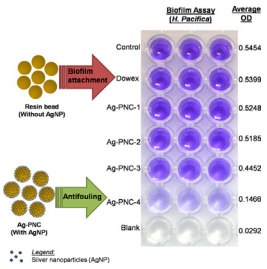
HIGHLIGHTS

- Synthesis and physical characterization of Ag-polymer nanocomposite.
- Ag-polymer nanocomposite with Ag particle size between 20 and 60 nm.
- Static biofilm assay on *Halomonas pacifica*, common marine biofilm forming bacteria.
- Higher biofilm inhibition with higher Ag loading.
- Up to 76% decrease of biofilm attachment.

GRAPHICAL ABSTRACT



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ABSTRACT

Biofouling of marine surfaces is a significant and complex problem especially in the shipping industry. This study seeks to develop a silver-polymer nanocomposite (Ag-PNC) system by synthesizing highly dispersed silver nanoparticles with narrow size distributions using Dowex protonated copolymer ion exchange resins as a templating matrix. Ag ions were introduced into the copolymer microbeads through an ion exchange process with silver nitrate, followed by chemical reduction using sodium borohydride to form metallic Ag on the surface of the microbead structure. Scanning electron microscopy (SEM) imaging revealed the uniform distribution of Ag nanoparticles with diameters between 20 and 60 nm on the surface of the microbeads, while UV–visible (UV–VIS) analysis showed the characteristic surface plasmon resonance for Ag nanoparticles ranging from 406 to 422 nm. Thermal stability of the nanocomposites was enhanced with the incorporation of Ag nanoparticles, with significant degradation occurring at 460 °C compared to 300 °C for the copolymer microbead, while the glass transition temperature of the Ag-PNCs increased from 130 °C to 323 °C. Significant inhibition of biofilm formation by *Halomonas pacifica*, a common marine bacteria responsible for initial marine fouling process, was observed, following treatment with Ag-PNC. Biocompatibility testing with human lung fibroblast and human keratinocytes show no significant toxicity to human cells. Toxicity testing of the Ag-PNC material with non-target marine microalgae *Dunaliela tertiolecta* and *Isochrysis* sp. also displayed no significant morphological changes, with cytostatic growth inhibition. These results strongly suggest that Ag-Dowex nanocomposites

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possess great potential to be an alternative to other antifouling agents due to their affordable, accessible and high yield production method.

1. Introduction

Marine biofouling is a natural process of accumulation of micro- and macro-organisms through their constant interactions in the complex marine environment. Biofouling of marine surfaces affect ship hulls [1], aquaculture cages [2], oil pipelines [3], and water desalination systems [4]. Particularly, the attachment of fouling organisms will lead to degradation of the affected parts, with loss of functional efficiency and increased operation costs [5]. It was estimated that an unprotected ship hull could accumulate up to 200 tons of foulant, increase fuel consumption by 40%, and incur cost increases of at least 70% in the overall cost of sailing [5–7].

To date, the majority of the antifouling technology for marine surfaces is based on biocidal coating formulations incorporating environmentally toxic substances such as tributyl tin [8], copper metal oxides, and booster biocides including Irgarol 1051 (2-methylthio-4-tert-butylamine-6-cyclopropylamine-s-triazine), Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea), Sea-nine™ 211 (member of 3(2H)-isothiazolone), zinc pyrithione, copper pyrithione, Zineb, dichlofluanid, and chlorothalonil [9,10]. These biocidal compounds have been found to cause deformations in the reproductive organs of molluscs [11], possess toxic effects on fish larvae [12], and have been found to accumulate to lethal concentrations in aquatic vegetation, crustaceans and fish [10].

Silver nanoparticles are the subject of intense research in recent years due to their antimicrobial properties against up to 650 microbes [13]. The potency of silver nanoparticles is attributed to the small size of the particle which is capable of entering the microbial cellular structure and interfering with the integral cellular processes [14]. However, silver nanoparticles are prone to agglomeration due to their high surface area to volume ratio [15]. Agglomerated silver nanoparticles reduce its availability of active surface areas and hence reduce its antimicrobial efficiency. Several strategies have been developed to synthesize and maintain the nanostructure of silver nanoparticles including their immobilization on polymer substrates [16–19], dispersion in a colloidal polymeric matrix [20–22], and using inorganic frameworks as host materials, such as microporous zeolites [23] and mesoporous carbons [24].

In addition, several methods to prepare polymer/silver nanocomposite microspheres have been reported previously. These include the suspension polymerization of poly(vinyl acetate) in the presence of Ag nanoparticles [25], Ag nanoparticles crosslinkers coated with 4-mercaptomethylstyrene [26] and polystyrene-core/polyacrylic acid brush/Ag [27]. However, the complex polymerization synthetic procedures of these methods, variation in Ag nanoparticle size range, high cost and low yield remained a challenge to their production at the industrial scale. Although other supporting matrix material such as silica, zeolites and carbon have also been used to formulate silver nanoparticles, the purification step which requires high-speed centrifugation or ultrafiltration remained the major limitation in industrial production.

Ion exchange resins have been shown to allow the immobilization of charged metal complexes ion exchange sites through non-covalent electrostatic interactions [28]. In addition, the micron-sized and specific shapes of ion exchange resins can be recovered easily by simple filtration or decantation, suitable for industrial scale production. Furthermore, the use of ion exchange resins as an insoluble support material also possess several advantages over other matrix materials, including their ease of handling, ease of recycling, negligible levels of metal leaching, and their compatibility with water and other reaction solvents [28].

Several synthetic routes of ion exchange resins have been described previously including reaction of styrene and divinylbenzene monomers via a surfactant reverse micelles swelling method [29] or by conventional radical suspension polymerization method [30]. In the present study, we sought to develop a system to synthesize highly dispersed silver nanoparticles with narrow size distributions on the surface using a commercially available ion exchange resin (i.e. Dowex) for antimicrofouling applications.

2. Materials and methods

2.1. Preparation of Ag-polymer nanocomposite (Ag-PNC)

The Dowex 50WX8-400 copolymer resin beads (Sigma–Aldrich, USA) were incorporated with silver ions through an ion exchange process with silver nitrate solutions of various concentrations, and the metallic Ag nanomaterials were obtained by chemical reduction with sodium borohydride (Table 1). In a typical synthesis, 2 g of Dowex 50WX8-400 was mixed with 10 ml of $AgNO_3$ aqueous solution (ranging from 1 mM to 1 M; Sigma–Aldrich, USA) and magnetically stirred at 26 °C in the dark for 1 h to allow ion exchange to occur. 10 ml of 2 mM–2 M sodium borohydride (Sigma–Aldrich, USA) was added to the mixture at room temperature under continuous stirring. The Ag-PNCs were obtained by centrifugation at 4000 rpm and washed 3 times with deionized water followed by drying at 80 °C for 10 h.

2.2. Characterization of Ag-PNC

The surface plasmon excitation of Ag-PNCs was measured using a Varian Cary 50 Conc UV-visible spectrophotometer (Varian Inc., USA). The Ag-PNCs were dispersed in ultrapure water by sonication for 1 h. 2 ml of sample with concentration of 0.1 mg/ml was loaded into a 10 mm quartz cell and subjected to the irradiation of 800–200 nm wavelength using a Xenon lamp. The morphology of the Ag-PNCs was observed under an FEI Quanta 400F scanning electron microscope (SEM) (FEI, USA). The Ag-PNCs were dried and gently crushed into powder form before being mounted on carbon tape for SEM viewing. Using the same samples from SEM viewing, the elemental compositions of the Ag-PNCs were evaluated using an Oxford Instruments X-Max with a 20 mm^2 EDX detector (Oxford Instruments, United Kingdom). The crystalline properties of the Ag-PNCs were measured using a PANalytical X'Pert PRO X-ray diffractometer (PANalytical B.V., The Netherlands), equipped with Cu Kα radiation (λ = 0.15406 nm), in the 2θ range from 5° to 80°, with a step increment of 0.02° s^{-1}. The thermal properties of the nanocomposite microspheres were investigated using a TGA/DSC thermal system (Mettler-Toledo, Switzerland). 10 mg of samples were inserted in an alumina crucible and heated in a nitrogen atmosphere from 25 to 1000 °C at a heating rate of 10 °C/min.

2.3. Evaluation of antimicrofouling behavior against H. pacifica

The marine fouling bacterium, *Halomonas pacifica* (ATCC® 27122), a gram negative bacterium, was obtained from American