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Short Communication

Quaternary ammonium polyethylenimine nanoparticles for treating bacterial contaminated water

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ABSTRACT

This study highlights the potential application of antimicrobial quaternary ammonium nanomaterials for water disinfection. Quaternary ammonium polyethylenimine (QA-PEI) nanoparticles (NPs) were synthesized by polyethylenimine crosslinking and alkylation with octyl iodide followed by methyl iodide quaternization. Particles modified with octyldodecyl alkyl chains were also prepared and evaluated. The antimicrobial activity of QA-PEI NPs was studied after anchoring in non-leaching polymeric coatings and also in aqueous suspension. Particles at different loadings (w/w) were embedded in polyethylene vinyl acetate and polyethylene methacrylic acid coatings and tested for antimicrobial activity against four representative strains of bacteria in static and dynamic modes. Coatings embedded with fluorescent labeled particles tracked by Axioscope fluorescence microscope during the antimicrobial test indicates no particles leaching out. Coatings loaded with 5% w/w QA-PEI exhibited strong antibacterial activity. Aqueous suspension was tested and found effective for bacterial decontamination at 0.1 ppm and maintains its activity for several weeks.

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1. Introduction

Waterborne diseases remain a major cause of death in many countries. Over one billion people lack access to safe water [1,2]. Chemical disinfectants commonly used by the water industry such as free chlorine, chloramines and ozone can react with various constituents in natural water to form disinfection byproducts (DBPs), many of which are carcinogens [3]. The rapid growth in nanotechnology has generated interest in new materials and composites for environmental applications [4]. Recently, several nanomaterials have been reported to possess antimicrobial activity, including chitosan, silver nanoparticles (nAg), photocatalytic TiO₂, fullerol, aqueous fullerene nanoparticles (nC60) and carbon nanotubes (CNT) [5–10]. Unlike conventional chemical disinfectants, these antimicrobial nanomaterials are not oxidants or consumable, and not expected to produce harmful side effects. If properly incorporated into treatment processes, they have the potential to replace or enhance conventional

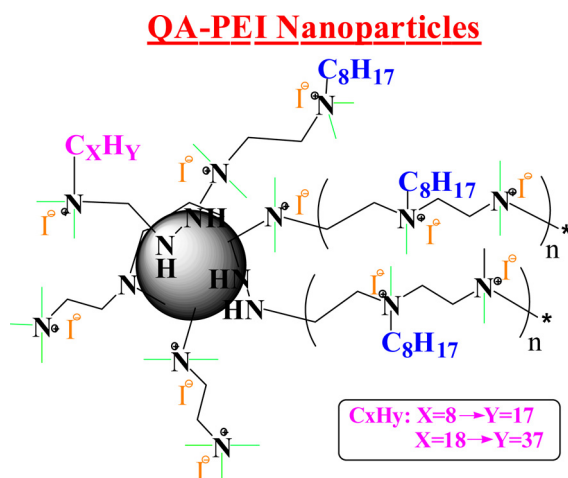
disinfection methods [11,12]. However, several challenges exist for efficient application of antimicrobial nanomaterials in drinking water treatment, primarily concerning dispersion and retention of nanomaterials and the sustainability of antimicrobial activity [4]. Quaternary ammonium (QA) functionalized materials, as antibacterial agents, have received much attention as they provide effective protection against bacterial colonization with long term durability and environmentally friendly performance. They demonstrated an ability to kill a wide spectrum of bacteria by contact [13,14].

In the present work, we report preparation of active antimicrobial surfaces using different methods, based on our previously described QA polyethylenimine nanoparticles (QA-PEI NPs) C₈ alkylated [15,16], and C₁₈ modified, where these NPs embedded in polyethylene vinyl acetate (PEVA) and polyethylene methacrylic acid (PEMA) coatings and these coatings were tested for their antibacterial activity against representative bacteria, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Heterotrophic plate count*, in static and dynamic modes, for potential application in self-sterilization coatings and large water containers. In this study, QA-PEI NPs were also analyzed for their activity in aqueous suspension in comparison to aging period for waste water reuse as in reuse systems.

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Scheme 1. Chemical structure of C₈/C₁₈ alkylated quaternary ammonium polyethylenimine (QA-PEI) crosslinked nanoparticles (Scheme 1S Supporting Information, SI).

2. Materials and methods

2.1. Materials

Polyethylenimine (PEI), molecular weight of 600 K–1 MDa was purchased from Fluka (Rehovot, Israel). Iodoctane, diiodopentane, iodomethane, sodium bicarbonate, anhydrous dichloromethane and dansyl chloride were all purchased from Sigma–Aldrich (Rehovot, Israel). Ethanol, ethyl acetate and chloroform (HPLC grade) were purchased from J.T. Baker, Holland. All solvents and reagents were of analytical grade. Tween 20 and span 60 purchased from Dexcel Pharma (Jerusalem, Israel). PEVA 28 (28% VA) and 46 (46% VA), PEMA were purchased from DuPont™ Elvax®, Switzerland. Bacterial strains: clinically isolated *Escherichia coli* and *Pseudomonas aeruginosa* (Maurice and Gabriela Goldschleger School of Dental Medicine at Tel-Aviv University, Israel). *Staphylococcus aureus* ATCC 8639 were used in this study. Heterotrophic plate count bacteria, HPC (mixed bacteria from tap water).

2.2. Methods

2.2.1. Preparation of QA-PEI NPs

The synthesis of QA-PEI nanoparticle was previously described [15–17]. In brief, 10 g of PEI dissolved in 100 ml ethanol was crosslinked with diiodopentane (4% per primary amine in PEI) under reflux for 24 h. N-alkylation with iodoctane was conducted at amine:iodooctane 1:0.25 molar ratio under reflux for 24 h. After 24 h, excess sodium bicarbonate (1.25:1 mole ratio, NaHCO₃/iodooctane) was added to neutralize released HI; neutralization reaction was continued for 3 h under the same conditions. Thereafter, methylation of these particles was carried out by reacting with methyl iodide at 1:3 mole ratios (PEI/methyl iodide) at 42 °C for 48 h. HI released was neutralized by adding molar equivalent of sodium bicarbonate per PEI, and the reaction was continued under the same conditions for additional 24 h. Formed NaI salt, excess of unreacted NaHCO₃, and traces of the unreacted iodoctane and methyl iodide were removed by washing with hexane and DDW. The average yield was 80% (mol/mol) (Scheme 1) (Scheme 1S, Supporting Information, SI). QA-PEI particles with more hydrophobic nature with C₁₈ alkylated, were also prepared by the same procedure except an extra alkylation step for 24 h were performed before C₈ alkylation step. Particles with ratio between alkylation agents C₁₈:C₈ 1:9, 2:8 and 3:7 respectively, of total 25% alkylated

amine groups were prepared and tested (Scheme 1) (Scheme 1S, SI).

2.2.2. QA-PEI NPs analysis

IR spectra were recorded on Perkin-Elmer System 2000 FTIR. Particles size and Zeta-potential were measured using a Zetasizer 2000 (Malvern, UK), measurements were done in double deionized water (DDW) in triplicate. Hydrophobicity (C/N) was estimated by elemental microanalysis of nitrogen (%N), carbon (%C) and iodine (%I) using a Perkin-Elmer 2400/II CHN analyzer. Thermal analysis was determined on a Mettler TA 4000-DSC differential scanning calorimeter, calibrated with zinc and indium standards, at a heating rate of 10 °C/min (typical sample weight was 10 mg).

2.2.3. Degree of alkylation and quaternization

Degree of alkylation of PEI particles is the percent of substituted ethyleneimine units with an appropriate alkyl halide. The degree of alkylation of QA-PEI NPs was determined as follows:

$$\text{Degree of Alkylation\%} = \frac{(\text{Carbon/Nitrogen})_{\text{Found}}}{(\text{Carbon/Nitrogen})_{\text{Calculated}}^{\dagger}} \times 100 \quad (1)$$

[†]The values were calculated by using ChemDraw Ultra 7.0

Degree of quaternization is the percent of quaternized polyethylenimine based particle. The degree of quaternization with an appropriate alkyl halide and with methyl iodide of QA-PEI NPs was determined as follows:

$$\text{Degree of Quaternization\%} = \frac{\text{Halide content}_{\text{Found}}}{\text{Halide content}_{\text{Calculated}}^{\dagger}} \times 100 \quad (2)$$

[†]The values were calculated by using ChemDraw Ultra 7.0

2.2.4. Fluorescence labeling of QA-PEI

Previously freeze-dried PEI (2 g, 12.2 mmol of ε-NH₂) was dissolved in 10 ml of anhydrous dichloromethane. To this solution 1 ml (0.12 mmol equivalent to 1% mol/mol to ε-NH₂) of dansyl chloride in anhydrous dichloromethane was added. The mixture was stirred at room temperature for 3 h. To this solution 265 μl of dibromopentane at 1:0.04 mole ratio (monomer units of PEI/dibromopentane) were added. Crosslinking was continued at reflux conditions for 24 h. During crosslinking step, labeled PEI was precipitated, filtered and washed with several amounts of dichloromethane. The crude was dried overnight on NaOH pellets. Further steps such as alkylation and methylation were repeated as described in the typical procedure (see Section 2.2.1). These labeled particles were used for tracking the particles onto the surface of the polymeric coating using Axioscope fluorescence microscope. Labeling of the quaternary ammonium polyethylenimine with the above dye did not affect the biological activity of the polymer.

2.2.5. Quaternary ammonium (QA) coatings preparation

Different polymer coatings were applied and evaluated using polyethylene vinyl acetate (PEVA, 28% and 46% VA, DuPont™ Elvax®) and polyethylene methacrylic acid (PEMA, DuPont™ Elvax®), QA-PEI particles were suspended in polymers solutions at 1% w/v in chloroform or ethyl acetate. Stable homogenous suspension with minimal particle aggregates was obtained by mixing the QA-PEI particles with polysorbate 20 (Tween 20) and sorbitan monooleate 60 (Span 60) at 1:1 and 1:0.3 w/w, respectively, followed by 10 min probe sonication with an amplitude of 60 Hz. Coatings with 5, 15 and 30% w/w particles were prepared. These coatings were made by two methods: cast or spray coating. For cast coating, 24 wells plates were used, each well was filled with 200 μl of the QA-PEI suspension followed by fast evaporation at 50 °C to prevent particle precipitation or aggregation (Fig. 1S, SI).

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