

Waste-derived inosilicate carrier for antimicrobial Zn²⁺ and Ag⁺ ions

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1. Introduction - Recent research by the authors has demonstrated that the inosilicate, lithium metasilicate (Li₂SiO₃), can be prepared by hydrothermal synthesis from waste green container glass (GCG) [1,2]. This study investigated the potential of this material to be ion-exchanged with antimicrobial Zn²⁺ or Ag⁺ ions for use as a filler in polymer composites. Antimicrobial polymer composites are an advantage in applications where the communication of pathogenic bacteria poses a problem, such as hospitals, abattoirs and food-processing factories. The naturally-occurring biodegradable mucopolysaccharide derivative, chitosan, was used as a model polymer in this study. The lithium metasilicate product was synthesised from GCG in LiOH_(aq) and ion-exchanged with either Zn²⁺ or Ag⁺ ions *via* batch sorption. The *in vitro* antibacterial properties of solvent-cast metasilicate-chitosan composite membranes were then evaluated by zone of inhibition against *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

2. Experimental - Impure lithium metasilicate (LS) was prepared from discarded GCG bottles by heating 3.0 g of ground glass (< 125 µm) and 60 cm³ of 4M LiOH_(aq) in a PTFE autoclave at 100 °C for 5 days. The products were washed with deionised water to pH ~8, dried in air at 60 °C and characterised by powder X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Ion-exchanged lithium metasilicate phases (LS-Zn and LS-Ag) were, respectively, obtained by exposure to 5 mM Zn²⁺ or Ag⁺ nitrate solutions at a mass:volume ratio of 1:4 g dm⁻³ for up to 24 h. Metal-uptake from solution was monitored by inductively coupled plasma spectroscopy (ICP). LS, LS-Zn or LS-Ag and chitosan were blended in 2% aqueous acetic acid solution, at a mass ratio of 1:5, cast onto polycarbonate surfaces and dried in air at 60 °C. Composite membrane discs (8 mm diameter) were placed on nutrient agar plates spread with *E. coli*, *P. aeruginosa* or *S. aureus* (at ~10⁶ CFU cm⁻³). Zones of inhibition were measured following incubation at 37 °C for 24 h. All syntheses and analyses were carried out in triplicate.

3. Results and Discussion - Powder XRD data confirmed that the principal hydrothermal reaction product was lithium metasilicate with minor quantities of calcium hydroxide, calcite, lithium carbonate and tobermorite present below 5 wt%. SEM analysis indicated that the product was granular, in the size range 50 to 100 µm, with a blocky texture. During ion-exchange, the respective maximum uptakes of Zn²⁺ and Ag⁺ ions by LS were found to be 6.4 and 8.8 mmol g⁻¹ at 24 h. The extent of Zn- and Ag-loading of LS exceeded those of other synthetic silicates such as tobermorite, Ca₅Si₆O₁₆(OH)₂·4H₂O, (1.0 and 1.6 mmol g⁻¹, respectively) that have been shown to possess bactericidal activity [3]. Zone of inhibition analysis verified that the composite blended with LS-Ag asserted antibacterial action against all three pathogens, as distinct clear zones were observed in all cases. Bacteria failed to populate the surfaces of the composite containing LS-Zn indicating that this material afforded protection against direct biofilm formation. The control pure chitosan membrane and that blended with LS did not possess antimicrobial activity, as their surfaces were readily colonised by the pathogens.

4. Conclusions - An impure product of lithium metasilicate was obtained from green container glass and ion-exchanged with 6.4 or 8.8 mmol g⁻¹ of Zn²⁺ or Ag⁺ ions, respectively. Metasilicate-chitosan composites incorporating Ag⁺-exchanged metasilicate exhibited antibacterial action against *E. coli*, *P. aeruginosa* and *S. aureus*, and the Zn²⁺-bearing phase protected against biofilm formation.

5. References

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