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Bactericide glasses developed by Na^+/Ag^+ ionic exchange

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ABSTRACT

The action of bacteria and fungi in residential, industrial and hospital environments offers high risk to human health. In this context, the development and use of antimicrobial materials has been an efficient method of handling risk situations. This work presents preliminary results of powdered glass showing bactericide effect obtained by ionic exchange between sodium ions, present in the glass composition, and silver ions, present in the ionic exchange medium. Powdered glass was submitted to ionic exchange in an ionic medium containing different concentrations of silver species. The bactericide effect was dependent on $AgNO_3$ concentration in the ionic medium. The Agar Diffusion Test on *Escherichia coli* bacteria, EDS and ICP-MS analyses were applied to the samples; the results showed that a critical concentration of silver ions incorporated into the powdered glass occurred and a limit to the bactericide effect. Tests and analyses revealed that 6 wt.% of $AgNO_3$ in the ionic medium was the critical concentration.

1. Introduction

The action of bacteria and fungus in residential, industrial and hospital environments offers high risk to human health. These microorganisms present the potential to proliferate in many environments used by people, representing a major concern in public health programs [1,2]. In this context, the development and use of antimicrobial materials has been an efficient way of handling risk situations. In recent years many works have been developed related to biocide materials applied to polymer and ceramic materials. These works deal with studies regarding biocide addition efficiency, methodologies for the production of bactericide and fungicide materials and the optimization of biocide properties [3–13].

Nowadays, glass materials are a special class of biocide materials developed with keen interest due to the extended duration of their bactericide action. Present in the glass structure are ionic specimens with active principles that are gradually released, providing a long active period of bactericide action for these products [10,14–16]. These materials have been applied in the production of coverings for ceramics parts with bactericide properties for use in residential, hospital and laboratory environments and in many others applications. These glass materials in powder form can be applied as additives in many products, for example, as polymeric additives, in inks, as composite additives and in ceramic products [14–18].

One method of developing biocide properties in these materials consists of incorporating metallic ions capable of eliminating bacteria (bactericide elements) and/or fungi (fungicide elements) into the glass structure. Biocide properties are the material ability to promote microorganism death. In particular, bactericide properties promote bacteria death. The bacteria death mechanisms are complex and comprise many processes. An interesting process comprises the absorption of specific metallic ions by the bacteria that harm the vital functions of the microorganism. Bactericide glass materials can contain ionic specimens in the glass structure with biocide characteristics that gradually are liberated during long times, providing the material bactericide action [10,16].

Some metallic ions present oligodynamic properties and are used by industries in the production of biocide materials. The oligodynamic properties are manifested by the action of these ions on microorganisms, through reproduction inhibition or death. Some ions present the required proprieties and those most studied are: silver, titanium, mercury and copper [3,11–13].

The activity of metal complexes increases with their concentration in the biocide material. This enhancement in the activity can be explained on the basis of chelation theory [11]. Cu complexes show higher antifungal activity than other complexes in all concentrations; Co complexes show higher antibacterial activity, except at low concentrations; Zn complexes show higher antibacterial effect at medium concentrations [11–13].

Many works report the use of ionic exchange processes incorporating Ag^+ and Cu^{++} into glass structures [16–21]. A major problem faced in these methods is the incorporation of metal species in the ionic state, in which the maximum biocide efficiency occurs. The

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Table 1
Glass formula according Angioletto et al. [16], all values in wt.%.

Al_2O_3	SiO_2	Li_2O	Na_2O
3.0	72.0	5.0	20.0

incorporation of Ag^+ ions produces bactericide materials and Cu^{++} incorporation produces fungicide materials; these ions are the most commonly used for biocide purposes [16,19].

In order to obtain ionic exchange characteristics the studied materials are submitted to ionic exchange in specific ionic media. The ionic exchange mechanism usually occurs between many specimens. However, for ion-exchange processes involving glass materials, Na^+, K^+, Li^+, Mg^{++}, Ca^{++} are usually used in the glass structures and oligodynamic specimens, such as Ag^+, Cu^+, Ce^{++}, Zn^{++} and others, are used in the ionic media [10–16].

Ag^+ and Na^+ ions possess a similar ionic radius and equivalent valence. Many works have indicated the sodium ion as the best exchanger specimen with the silver ion [16–18,20,21] and that during this process the quantity of other specimens, like Al, Ca, Mg and K, remain constant [16]. Ahmed [15] showed that Li^+ is the second best option in an exchange with sodium ions; if both elements are present in the glass structure, the exchange process will occur preferentially between Na^+ and Ag^+.

Recently, Angioletto et al. [10,16] developed a ceramic material with bactericide properties using ionic exchange processes between Ag^+ and Na^+ in an ionic medium containing $AgNO_3$ compound as a silver source. This material was crushed and incorporated in a ceramic glaze. The microbiological analysis showed excellent results regarding bactericide properties.

This work presents an optimization study of $AgNO_3$ concentration in an ionic medium used to develop ionic exchange processes between sodium ions (glass composition) and silver ions (ionic medium), responsible for the glass bactericide properties. Ionic media containing different concentrations of $AgNO_3$ compound were prepared to evaluate the influence of $AgNO_3$ concentration. A powdered glass substrate was submitted to ionic exchange treatment and to microbiological analysis after a specific time. EDS and ICP-MS techniques were used to evaluate silver incorporation in the glass structure.

2. Materials and methods

2.1. Glass development

The glass formula was prepared following the composition and methodology developed by Angioletto et al. [10,16] (Table 1). The raw materials were first melted at 850 °C for 30 min with a heating rate of 10 °C/min, then at 1450 °C for 120 min at the same heating rate. In sequence, the glass obtained was crushed to particle sizes less than 40 µm and submitted to ionic exchange treatment in $AgNO_3$ ionic media at different concentrations. Although it is known that the particle size affects the exchange area, a single particle size distribution was opted for to simplify this work. As a consequence, the exchange area was considered constant in this work. The particle size distribution was based on previous work [16].

2.2. Ionic exchange treatment

The ionic exchange treatment between the prepared glass (containing sodium oxide) and the ionic medium (containing silver ions) was carried out using $AgNO_3$ as a silver source and $NaNO_3$ as a melted medium (Reagan, 99.9% purity). The powdered glass was immersed in the ionic medium and submitted to 430 °C for 4 h in a muffle oven. Both processes were carried out in different ionic media, maintaining the sodium concentration constant, but varying $AgNO_3$ concentration. Table 2 presents the compositions used as ionic media systems.

Table 2
Composition of ionic media systems: concentration constant for $NaNO_3$ and varied for $AgNO_3$ in the ionic exchange medium.

Sample	Powdered glass (±0.01)g	Ionic medium		
		$NaNO_3$ (±0.01)g	$AgNO_3$ (±0.01)g	$AgNO_3$ wt.%
01	23.00	3.00	0.10	0.43
02	23.00	3.00	0.20	0.86
03	23.00	3.00	0.30	1.29
04	23.00	3.00	0.40	1.72
05	23.00	3.00	0.50	2.15
06	23.00	3.00	1.00	4.30
07	23.00	3.00	1.50	6.45
08	23.00	3.00	2.00	8.60
09	23.00	3.00	2.50	10.75

After the ionic exchange treatment, the powdered glass samples were washed and kept in deionised water for two days. This procedure was used to dissolve the sodium residues incorporated on the glass surfaces during the ionic exchange process. The powdered glass samples were then dried in a vacuum system and crushed again to particle sizes less than 40 µm. The particle size distribution was controlled by sieving (#325 ASTM, 44 µm).

2.3. Microbiological tests

The powdered glass materials shown in Table 2 (samples 01 to 09, containing different silver concentrations in the glass structure) were submitted to microbiological analysis to evaluate their bactericide effects. The Agar Diffusion Test was used for each sample and applied to *Escherichia coli* bacteria.

All tests were conducted at 36 °C and the bacteria were submitted to an 18 hour incubation period. For all samples, microbiological tests were carried out to evaluate the ionic medium influence on the production of a biocide glass; the tests were conducted in Petri dishes containing 0.30 (±0.01)g of powder glass [15,16].

To evaluate the efficiency of the bactericide action of the powdered glass samples in liquid medium, the microbiological tests Minimum Bactericide Concentration (MBC) and Minimum Inhibitory Concentration (MIC) were realized with the bacteria *Staphylococcus aureus* (SA), *E. coli* (EC) and *Pseudomonas aeruginosa* (PA). To evaluate the effect of the concentration of the silver specimens in the exchange medium on different bacteria, samples were prepared at two concentrations, 1.0% and 1.5%, of $AgNO_3$ in the ionic media.

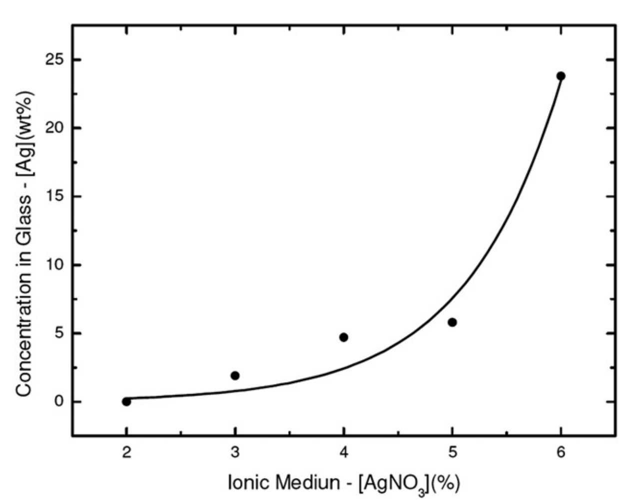

Fig. 1. ICP-MS results for the powdered glass submitted to ionic exchange between Na^+ and Ag^+ ions in the ionic medium containing different concentrations of $AgNO_3$.