Release behaviour of Ag(I) in synthetic silver/cellulose nanocomposites

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Introduction

The association of Ag nanoparticles (NPs) to biopolymers, such as cellulose, represents an interesting approach to developing new nanocomposites that might find a variety of new applications. The use of biopolymers is an excellent choice due to their renewable nature, non-toxicity and potential biocompatibility. Silver exhibits strong cytotoxicity towards a broad range of microorganisms and its use as an antibacterial agent is well known [1]. Metallic silver in aqueous environments promote silver ions release. Various studies have been undertaken in order to study this behavior due to the released kinetic and the release mechanism of the Ag ions be essential to understand the permanence of the antibacterial activity over time and/or after this immersion in aqueous environments. In order to have an efficient and long time activity, the release of silver ions at a suitable concentration with longer periods of time is crucial; a too slow or a too fast release of Ag ions would be inappropriate for many applications [2-3].

Very often the cationic silver release studies involve as main instrumental techniques ICP, AAS and ASV, which are expensive techniques, and in many work contexts cannot provide on-time results. In this work, we present the study of silver ion release of cellulose/silver nanocomposites and, at the same time, the possibility of implementation of potentiometric studies when using this type of materials.

Synthesis of cellulose/silver nanocomposites

Cellulose/Ag nanocomposites have been prepared with VC and BC fibers by in situ or post-deposition methodologies using sodium borohydride as reducing agent (table 1).

<table>
<thead>
<tr>
<th>Method</th>
<th>Substrate</th>
<th>Sample code</th>
<th>Ag content (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in situ BC</td>
<td>VC_Ag_bor</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>LBL</td>
<td>BC_Ag_bor</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>Diffusion</td>
<td>BC</td>
<td>VC_Ag_dif</td>
<td>2.15</td>
</tr>
<tr>
<td>Diffusion</td>
<td>BC</td>
<td>BC_Ag_dif</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Besides the peaks assigned to the phases of cellulose the diffraction peaks observed at 2θ 18.2° (111), 44.6° (200), 65.4° (220) and 77.3° (313) are characteristic face-centered cubic (fcc) silver.

Study of the silver release

For the this aqueous suspensions of the samples were prepared and then placed on an orbital shaker at a temperature of 29 or 37 °C, performing measurements of [Ag+] along the time. The [Ag+] was determined by potentiometry using a silver selective electrode and for selected samples these values were compared with determination by ICP.

I. Effect of substrate, temperature and methodology

The percentage of total silver released is higher for the nanocomposites with VC, mainly due to the particles being on the surface of the fibers, while in the BC nanocomposites, the silver nanoparticles are inside the fibers network and water needs to diffuse into the fibers network in order to reach the nanoparticles.

II. Standard addition to the samples

Since some nanocomposites presents very low values of ionic silver release [lower than detection limit of the electrode] it was tested the use of the method of standard addition.

Silver release profile of samples with [Ag+] below the detection limit are similar to the obtained to samples with ionic silver released within detection limit.

III. Validation studies using ICP

In order to validate the results obtained the samples are measured by potentiometry and after by ICP analysis. The values of ionic silver release obtained by ICP measurements are practically identical to the ones obtained using the potentiometric analysis.

Conclusions and future work

A series of nanocomposites of cellulose/Ag, using CB and CV, by numerous preparative techniques have been achieved. The release of Ag+ in the tested conditions depended on several parameters namely the type of cellulose substrate used, the preparative methodology and the temperature of release.

The results obtained have been collected by a simple potentiometric method using a Ag ISE thus open up the possibility to implement this methodology in a routine basis. Future work will involve kinetics and modeling studies in order to predict the behavior of these nanocomposites in variable conditions.

References