university of aveiro
theoria poiesis praxis

ciceco
centre for research in ceramics & composite materials

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

Fábio Silva, Ricardo Pinto and Tito Trindade

Chemistry Department-CICECO, Aveiro Institute of Nanotechnology, University of Aveiro, 3810-193 Aveiro

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

Vegetable cellulose (VC)

- *In situ*
- Layer-by-Layer (LbL)

VC/silver nanocomposite

Bacterial cellulose (BC)

- *In situ*
- Diffusion of NPs

BC/silver nanocomposite

Nanocomposites characterization

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

Table 1 – Cellulose/silver nanocomposites prepared and final silver content determined from elemental analysis using ICP.

Method	Substrate	Sample code	Ag content (mg/g)
In situ	VC	VC_Ag_bor	0.15
	BC	BC_Ag_bor	0.57
LbL	VC	VC_Ag_LbL	1,76
Diffusion	BC	BC_Ag_dif	2.15

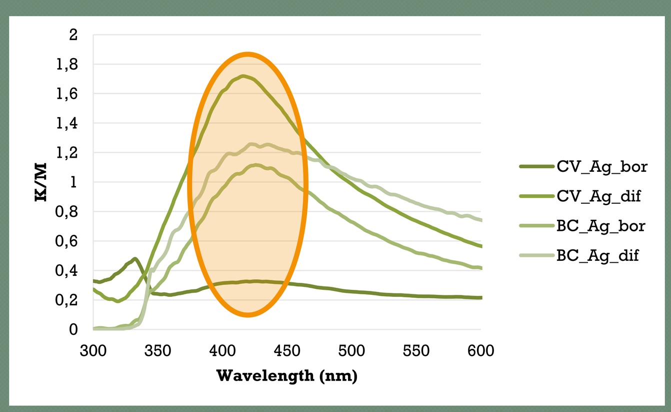

Fig. 1 – UV-vis spectra of the cellulose/silver nanocomposites.

The diffuse reflectance spectra confirms for all nanocomposites the presence of Ag^0 (typical absorption band at 425 nm).

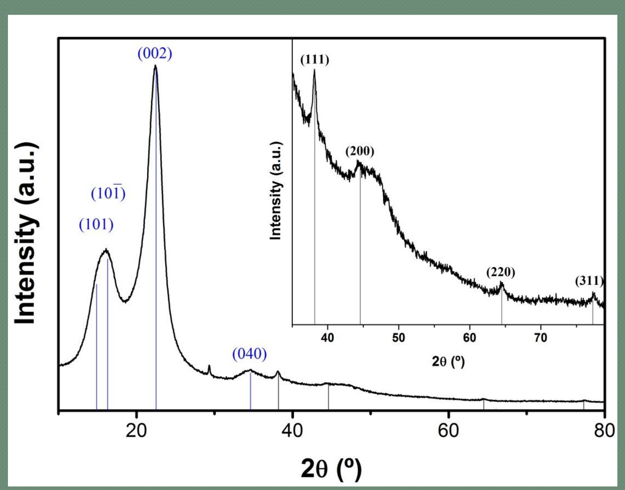

Fig. 2 – XRD patterns of CV_Ag_LbL nanocomposite. The markers refer to CV (blue) and Ag (black) phases.

Besides the peaks assigned to the phases of cellulose the diffraction peaks observed at 2ϑ 38.2° (111), 44.6° (200), 64.5° (220) and 77.3 ° (311) are characteristic face-centered cubic (fcc) silver .

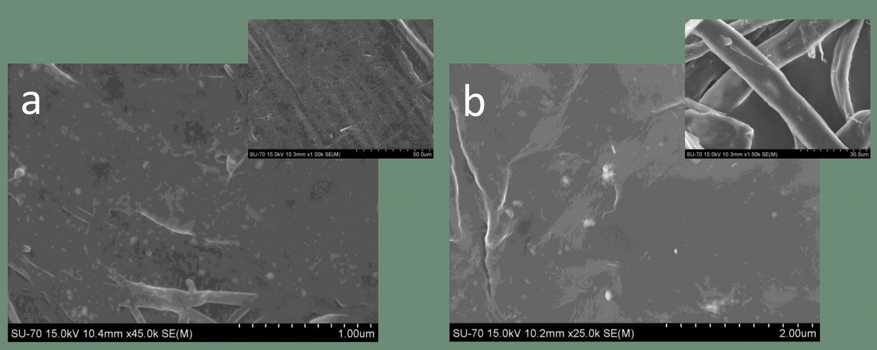

Fig. 3 – SEM images of a) BC_Ag_bor and b) CV_Ag_bor nanocomposites at different magnifications.

SEM images show the presence of silver NPs in all of the nanocomposites.

Study of the silver release

For the this study 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

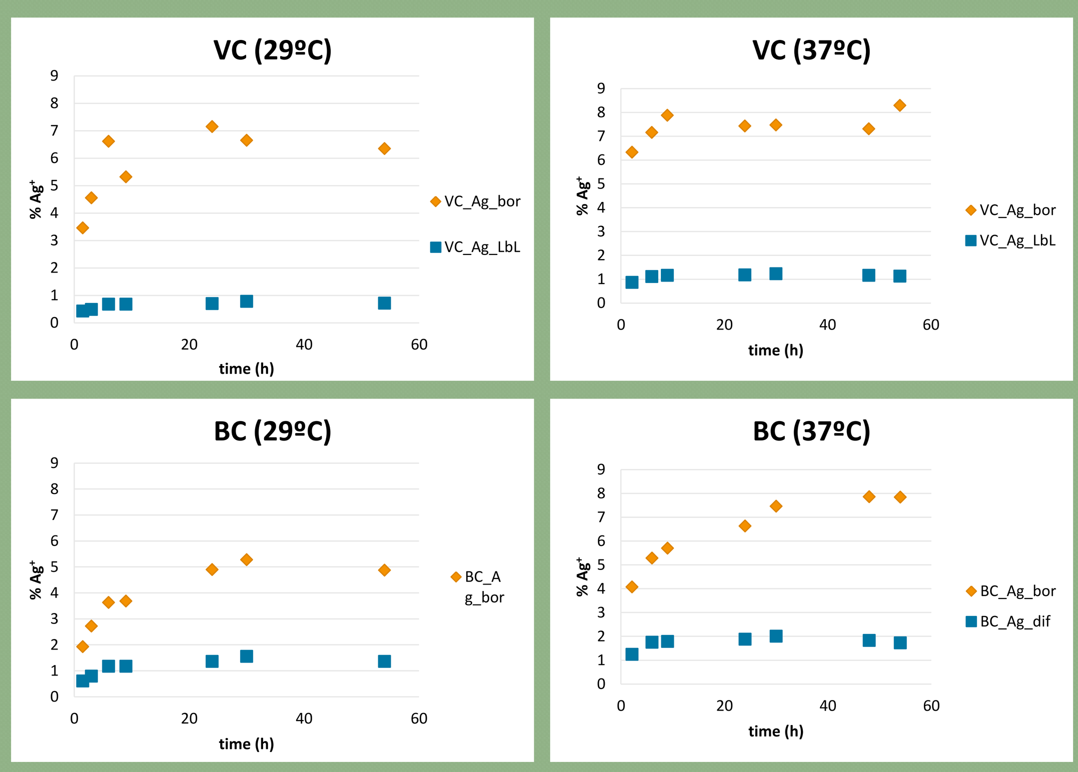

Fig. 4 – Percentage of Ag^+ release in function of time for the VC/Ag and BC/Ag nanocomposites obtained using two different temperature (29 and 37 ºC).

- The percentage of ionic silver released is higher for the nanocomposites with VC, mainly due to the particles being onto the surface of the fibres, while in the BC nanocomposites, the silver nanoparticles are inside the fibres network and water needs to diffuse into the fibres network in order to reach the nanoparticles.
- It can be noticed a direct relationship between the release temperature and the ionic silver release, mainly in BC, since the water diffusion into the fibres network can be promoted be the increase of the temperature.
- The nanocomposites synthesised by the *in situ* method shows the higher percentage of ionic silver release, both for VC and BC.

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.

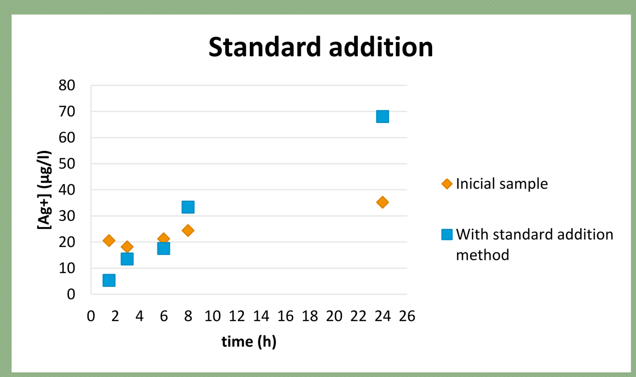

Fig. 5 – [Ag+] release in function of time (37 ºC) for a VC/Ag nanocomposite with ionic silver release below the detection limit.

III. Validation studies using ICP

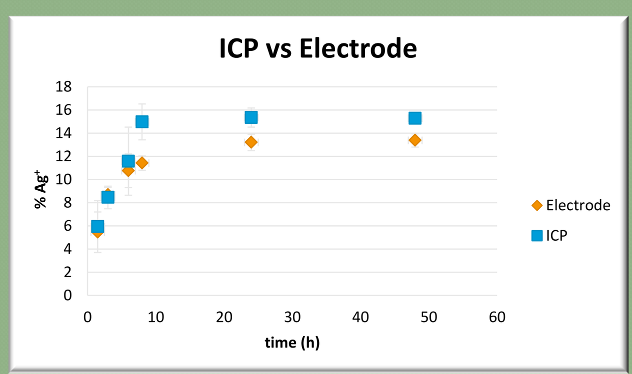

Fig. 6 – Percentage of Ag^+ release in function of time for the VC_Ag_bor nanocomposite at 37 ºC mesured by potentiometry and by ICP.

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 cellulosic 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 perspective 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

[1] R. Pinto, P. Marques, C. Pascoal Neto, T. Trindade, S. Daina and P. Sadocco, "Antibacterial activity of nanocomposites of silver and bacterial or vegetable cellulosic fibers", Acta Biomater. vol.5 pp. 2279-2289, 2009

[2] R. Kumar and H. Munstedt, "Silver ion release from antimicrobial polyamide/silver composites", Biomaterials Vol. 26, pp. 2081-2088, 2005.

[3] T. Maneerung, S. Tokura and R. Rujiravanit, "Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing", Carbohydr. Polym. vol. 72, pp. 43-51, 2008.