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Design and preparation of carbendazim-loaded alumina nanoparticles as a controlled-release biocide for wood protection

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ABSTRACT

Biocide delivery systems are intelligent strategies towards improving the efficiency of biocides over time. Here, we have developed a biocide system by loading alumina nanoparticles with carbendazim through surfactant-assisted ball milling. The obtained biocides were further validated by their impregnation into pinewood, followed by *in vitro* fungi tests. Fourier-transformed infrared spectroscopy stated physical adsorption of carbendazim on alumina, while the thermogravimetric analysis revealed its adsorption in a pseudo-molecular level. The carbendazim loading efficiency was improved after surfactant addition, which was also fundamental to effectively impregnate the pinewood. The biocide release profiles could be described using the parabolic-diffusion and Korsmeyer-Peppas kinetic models, which fitted the experimental data with determination coefficients over 0.9. After 600 h, the biocide systems have released 42–76% of carbendazim, where systems with higher biocide content released faster. The pinewood solid samples were completely impregnated with the prepared biocides; however, it tended to concentrate on the wood surface. A biocide retention of only 0.4 kg m^{-3} of sufficient to increase in 10 times the decay resistance of the pinewood, indicating very promising results.

1. Introduction

Biocides are essential to improve the decay resistance of biomass-derived materials, especially wood. Currently, the wood protection against fungi and xylophage insects is based on creosote, pentachlorophenol, arsenic, copper, zinc naphthenate and borate derivatives. Due to the severe restrictions and upcoming federal regulations, attempts for substitution of these traditional biocides are already in place (Cao and Jiang, 2014; Harandi et al., 2016; Lebow et al., 2015; Schultz and Nicholas, 2011). A driving factor that justifies the use of alternative chemical preservatives with reduced toxicity is the need to minimize contamination of inhabited areas, which if not attended, will increase the known risks to human health (Mercer and Frostick, 2014). Considering that the decontamination of areas and wastes containing toxic wood preservatives is expensive, complex, and only partially successful (Cecchin et al., 2017; Kartal et al., 2015), the most effective approach is to design and deploy new protection systems that are proven safer to mammalians and the environment.

Organic biocides such as the azoles, carbamates, cupric, aromatics and halogenated heterocycle compounds have become options in this replacement policy. Particularly, carbendazim (CBZ) is a broad-spectrum benzimidazole fungicide, which is well-known for its high efficiency against a wide variety of fungi (Marei et al., 2012). However, CBZ has poorly water solubility which makes it often inappropriate as antifungal agent (Ge et al., 2012).

As an attempt to avoid the bioaccumulation of biocides, many research groups have put significant efforts in developing suitable platforms to delivery bioactive molecules in a controllable rate (Ding et al., 2011; Erich and Baukh, 2016; Liu et al., 2003; Sorensen et al., 2010). Many materials could be applied as carriers for biocides delivery; however, synthetic polymers have been the mostly addressed. It is understandable since most of the knowledge on such delivery systems was developed in the pharmaceutical sector for drug delivery by using polymeric capsules (Siepmann and Siepmann, 2012, 2008). Currently, the materials scientists have used these well-consolidate polymeric capsules to design biocide delivery systems as well. Nevertheless, the utilization of polymeric capsules for biocides delivery may not be as efficient as they are for drug delivery since they are thermally, dimensionally and chemically unstable. These disadvantages compromise their application in a wide range of wood products. Besides that, to keep the

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controlled release biocides competitive, their synthesis and manufacture needs to be simple and up-scalable (Lvov et al., 2008), which may not be the case of the polymeric-based systems.

By using inorganic supports, such as Al_2O_3, it will be possible to overcome some instabilities related to the carrier and its interaction with the surrounding environmental, leading to a more stable biocide delivery system. The application of these systems in wood-based materials would be even more appealing if the carrier apply to control the biocide release also prompted in parallel improvements for the material properties, which could be the case of Al_2O_3. Nanometric Al_2O_3 when applied as filler or coating has shown multiple improvements in the mechanical, thermal and UV-resistance properties of wood-based materials (El-Meligy et al., 2012; Grison et al., 2015; Kumar et al., 2013; Nikolic et al., 2015; Sow et al., 2011).

Thus, here we aimed to design and synthetize biocide delivery systems with controlled release by loading CBZ into alumina nanoparticles via surfactant assisted ball milling. By doing so, we expect to improve the bioactivity of a poorly water soluble molecule by promoting its slow delivery in water. CBZ was chosen as active ingredient due its broad-spectrum antifungal properties and as an attempt to make it suitable as antifungal agent against decay fungi, once its bioactivity against mold and stain fungi is well-known (Ge et al., 2012; Kositchaiyong et al., 2014). Alumina was selected as nanometric support due its high thermal, dimensional and chemical stability. The ball milling for biocide loading was applied looking for a possibility to further up-scale this methodology. We also investigated the effect of surfactant on the biocide loading, as well as its release out from the alumina.

2. Materials and methods

2.1. Design and preparation of the CBZ-loaded alumina nanoparticles

Aluminum oxide (>98%, #CAS 1344-28-1), carbendazim (97%, #CAS 10605-21-7) and sodium dodecyl sulfate (>99%, #CAS 151-21-3) were purchased from Sigma-Aldrich.

The CBZ-loaded alumina biocides were obtained by ball milling. The submicrometric spherical alumina was turned into a nanometric irregular-shaped powder via ball milling, promoting the CBZ adsorption on the alumina fragments. Centrifugation was applied to agglomerate the nanometric fragments into irregular submicrometric particles with entrapped biocide (Fig. 1). Sodium dodecyl sulfate (SDS) was inserted to investigate its role in the biocide loading efficiency.

The ball milling was carried out in a Servitech equipment (Brazil) operating at 25 °C, 150 rpm, using 100 mL of ethanol:water 1:9 (pH ~7) containing alumina, CBZ and SDS in a HDPE vessel (1 L). Zirconia grinding elements, which were half with 5 mm and the other half with 1 mm in diameter, were added in a mass proportion of 1:1 considering the total mixture (solution, CBZ and alumina). The experiments were carried out using alumina:biocide ratio of 2:1 with (Al_2O_3:CBZ@2:1_S) and without surfactant (Al_2O_3:CBZ@2:1), as well ratio of 10:1 with (Al_2O_3:CBZ@10:1_S) and without surfactant (Al_2O_3:CBZ@10:1). The mass percent of the surfactant was based on the mass of the alumina.

After 24 h of milling and CBZ adsorption, the dispersions from each experiment were centrifuged at 10,000 rpm to re-aggregate, and oven-dried at 103 ± 2 °C until reaching constant mass. The experiments were triplicate to verify the reproducibility of the ball milling process.

2.2. Characterization of the CBZ-loaded alumina

The quantitative loading efficiency was calculated by difference between the mass loss of the alumina and the CBZ-loaded alumina at 1100 °C, by $LE\% = (ML\%_{bio} - ML\%_{alumina})/L_{max}$. Where $ML\%_{bio}$ is the mass loss of the CBZ-loaded alumina at 1100 °C; $ML\%_{alumina}$ is the mass loss of the alumina at 1100 °C, and L_{max} is the CBZ maximum load.

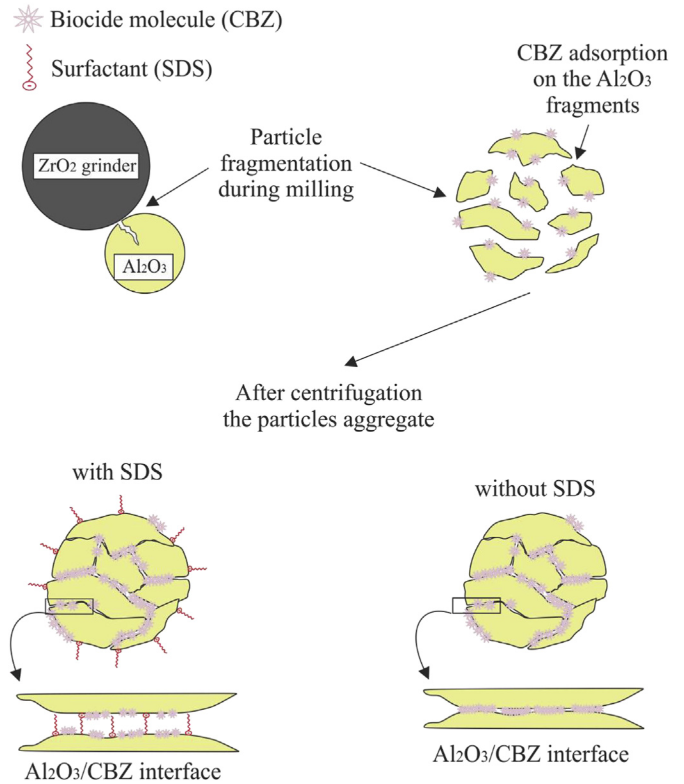

Fig. 1. Representative scheme for obtaining the CBZ-loaded alumina particles.

The morphological features of the as-received, ball-milled and the CBZ-loaded alumina samples were studied using a transmission electron microscope (TEM) JEOL, model JEM-1200 EXII. The specific surface area ($m^2\ g^{-1}$) of the samples was obtained in a Quantachrome NOVA 1200e using the Brunauer–Emmett–Teller (BET) multipoint model in the linear relative pressure range ($P\ P_0^{-1}$) from 0.05 to 0.35. The particle diameter (d_{BET}) was calculated considering a spherical isometric approach for the particles. To get closer of the real surface area of the alumina during the ball milling, we made a milling procedure of alumina and a 5 mL aliquot was taken after 24 h; after that, it was quickly frozen and then freeze-dried.

Thermogravimetric analysis (TGA) of the obtained biocides was carried out in a SETSYS Evolution TG/DSC (Setaram) equipment in argon atmosphere with gas flow of 20 mL min^{-1}, temperature range of 25-600 °C, and heating rate of 10 °C min^{-1}. Fourier-transformed infrared (FT-IR) spectra were acquired in a Bruker Tensor 37 equipment using KBr pellets by direct transmittance at a nominal resolution of 4 cm^{-1} for 32 scans in the range of 4000–400 cm^{-1}.

2.3. Release profiles and kinetic studies

The release profiles were acquired placing a known mass of the biocide systems (corresponding to 8 mg of CBZ) inside a filter paper immersed in 1 L of distilled water. The experiment was kept under room temperature (25±2 °C), and 3 mL samples were taken along 25 days. The calibration curve for CBZ determination was assembled by measurements of standard CBZ aqueous solutions – ranging from 2 to 8 mg L^{-1} – in a UV-VIS spectrophotometer Shimadzu UV-1800. The absorbance at 285 nm gave the best linear fit to measure the release of CBZ in water.