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Review article

Controlled release for crop and wood protection: Recent progress toward sustainable and safe nanostructured biocidal systems

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ABSTRACT

We review biocide delivery systems (BDS), which are designed to deter or control harmful organisms that damage agricultural crops, forests and forest products. This is a timely topic, given the growing socio-economical concerns that have motivated major developments in sustainable BDS. Associated designs aim at improving or replacing traditional systems, which often consist of biocides with extreme behavior as far as their solubility in water. This includes those that compromise or pollute soil and water (highly soluble or volatile biocides) or those that present low bioavailability (poorly soluble biocides). Major breakthroughs are sought to mitigate or eliminate consequential environmental and health impacts in agriculture and silviculture. Here, we consider the most important BDS vehicles or carriers, their synthesis, the environmental impact of their constituents and interactions with the active components together with the factors that affect their rates of release such as environmental factors and interaction of BDS with the crops or forest products. We put in perspective the state-of-the-art nanostructured carriers for controlled release, which need to address many of the challenges that exist in the application of BDS.

Chemical compounds considered in this article

Tebuconazole (PubChem CID: 86102)
Carbendazim (PubChem CID: 25429)
Imidacloprid (PubChem CID: 86418)
Paraquat (PubChem CID: 15938)
Azadirachtin (PubChem CID: 5281303)
Chlorothalonil (PubChem CID: 15910)
Iodopropynyl butylcarbamate (PubChem CID: 62097)
Salicylic acid (PubChem CID: 338)

1. Applications of nanostructured systems for crops and wood materials protection

Derived from research focusing on the development of drug delivery systems (DDS) in the biomedical field, controlled release formulations have recently attracted interest in the protection of agricultural crops and wood materials. This is owing to the fact that living environments and agrochemical-free food production has become a predominant concern [1–3]. For biomedical applications, DDS have been developed continuously over the past 70 years. However, the number of new, successful clinical applications has slowed down since associated requirements have become more stringent, specialized and sophisticated [4,5]. Consequently, some of the vast knowledge accumulated in this area is being transferred and adapted in agricultural release systems. Here, the use of environmentally friendly and low toxicity compounds for crop protection, for example in biocide delivery systems (BDS), is a considerably less constraining field of application when compared with DDS. It can be expected that transfer of knowledge to this area will only increase in the future. Nevertheless, although less stringent for technical applications of BDS, soil properties together with climatic conditions need to be considered as they can significantly affect release properties or potential long term hazardous effects of BDS. For instance, these environment-associated factors have been observed to play an important role in the degradation and stability of pesticides when applied to crops [6,7]. Additionally, answers to the many challenges pertaining the development of new agrochemicals [8] may exploit synergies with novel BDS that can have a particularly large socio-economic impact, highly interrelated to human health and to the development of a sustainable bioeconomy.

Interest in the formulation of BDS arises because traditional methods of biocide-based protection in the agriculture fields usually

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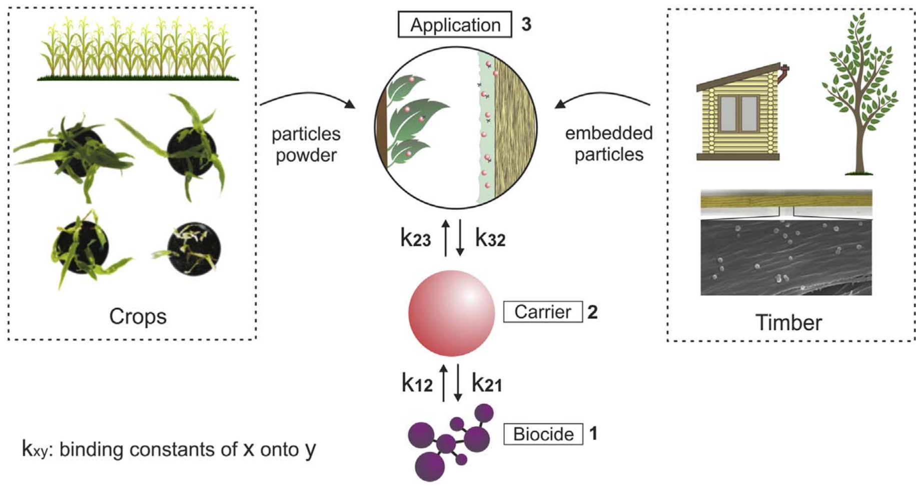

Fig. 1. Schematic representation of the incorporation of biocides (1) that are integrated with carriers (2) in delivery systems displaying a number of interaction (k_{xy}) relevant to crop and wood protection (3). The left panel illustrates controlled release herbicides (for example, paraquat-loaded chitosan nanoparticles for managing crop health). The right panel shows a wood protecting coating that incorporates amphiphilic, self-assembling particles (for example, chitosan/PMMA nanoparticles containing tebuconazole).
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imply high-volume application of active molecules at high initial dosages (and often require repeated use). Furthermore, delivery is often uncontrolled, which results in short-time biocidal protection and increased bioaccumulation. In fact, excessive toxins concentration in ground and surface water has led to acute health problems and water purification costs [9]. In this context, the preparation and application of engineered nanoparticles for controlled release of biocides, *i.e.* "nanoagriculture", represent an effective answer that, among others, may involve 'on-demand' modes of action. In turn, BDS may take advantage of efficient methods that minimize or completely avoid repeated application of agrochemicals, which impact positively any effects related to environmental pollution and food poisoning. A representative example of efforts in this area includes the European program Horizon 2020, the biggest EU Research and Innovation effort ever, with nearly €80 billion funds available over 7 years (2014 to 2020). Horizon 2020 addresses the most important challenges in nanotechnologies to achieve health and wellbeing, efficient energy, food, sustainable agriculture, forestry, water and the future bioeconomy [10]. In sum, there is no doubt that the objectives of BDS will benefit from new developments in agricultural nanotechnologies.

In agricultural applications, nano- and micro-particulate biocides, including those that display nanometric features (*i.e.*, nanostructured), are some of the most promising ones for achieving sustainability, high payload and high efficiency. This is in part due to the functions that emerge in nanometric materials, usually associated to their high surface area, which have been applied to impart new physical, mechanical, electrical/electronic, catalytic, and optical properties [11–14]. For example, high surface area, superstructures associated with nano-organized architectures offer a mean to increase the density of the active sites in order to improve levels of detection, reactivity and selectivity [15]. While less evident, many possibilities exist for the application of nanotechnologies in agriculture, silviculture and wood protection. Among these, the most impactful applications include crop protection and efforts to improve plantation yields, water management, early diagnostics, plant breeding and the isolation of nanomaterials from plants [16].

Despite of the remarkable advantages of nanotechnology in the agricultural sector, the few efforts that exist have not been as prominent as in other industrial sectors. The biggest obstacle that has prevented a wider adoption is the high initial investments, which is encountered with a demand for materials in large scales. Indeed, from the onset of their application, most nanotechnology products need to display a clear positive impact while being economically viable [16]. The use of nanotechnology may be a solution to the increased food needs (for example, grains and others), given the growing worldwide consumption and the pressure to achieve high yields [17]. In this scenario, food demand is expected to double in the following decades [18]. However, limits in cropland expansion implies that future strategies will likely focus in improving agricultural operations. For example, this can be achieved by drastically reducing the crop losses to pests *via* efficient and prolonged exposure to safe biocide [19]. In addition, nanostructured controlled release biocides can bring benefits at large scales in silviculture and in wood protection and preservation [20,21]. This is especially the case if they offer alternatives that are safe and meet the requirements and regulations that are in place, which limit or forbid the application of some otherwise traditional systems. In this context, popular wood preservatives have included creosote, pentachlorophenol, and waterborne chromate copper arsenate [22]. Among biggest incentives to replace highly-toxic chemical preservatives one can include the risk of contamination of inhabited areas and associated negative effects to human health [23]. A solution to address these issues includes the utilization of organic biocides. However, they may be either too soluble [21], promoting high soil and water contamination or, otherwise, poorly soluble, which often entails a lower bioavailability [24]. Thus, a better strategy is that of controlled release, for example, in fertilizers to improve cereal production [25,26]. Their development closely matches that of BDS since the technologies are developed in parallel for a common goal. This has recently been reviewed by Naz and Sulaiman [25], and Azeem et al. [26].

The scope of this review is focused on the use of sustainable biocides and carriers as means of protection from harmful organisms. Here, we discuss the most significant and recent breakthroughs reported in the literature in relation to controlled release of fungicides, herbicides, and insecticides, with focus on biocidal activity (Fig. 1). These systems have changed conceptually over the years, introducing new carriers, biocides and methods of preparation. We first expand on the fundamental thermodynamics driving the delivery of biocides through complex carrier-biocide-environment interactions. Following, we explore how the architecture and morphology of carrier materials affect the release profile of biocides and consider the parameters affecting their performance in given applications. Then we broaden the scope for biocide delivery systems and highlight recent developments in BDS designed and synthesized bottom-up, from renewable or mineral resources. Finally, the highlighted reports are critically discussed and put in perspective in order to bring forward important necessary considerations for future BDS developments.

2. Carrier-biocide-water interactions in controlled release systems

Fundamentally, controlled release systems involve competitive interactions between the carrier or vehicle, the biocide and the environment to which it will be released (Fig. 1). Controlling the associated balances is key in the design of sustainable biocides delivery systems. In this section, we briefly introduce the thermodynamics of underlying