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Plant-derived metallic nanoparticles: environmental safety and colloidal behaviour

Ratul Kumar Das and Satinder Kaur Brar

Plant-derived metallic nanoparticles (MNPs) have emerged as an important alternative to chemically synthesized MNPs for various environmental applications. However, such applications must ensure eco-friendliness during various stages of fate-determining processes in the environment. This issue is of global concern, but has not been addressed so far. This necessitates delving into the environmental fate and role of surface-capped plant molecules of plant-derived MNPs in nano-specific fate processes and applicability of colloidal science principles.

In recent years, the performance of plant-mediated green route of metallic nanoparticles (MNPs) synthesis has been impressive due to the efforts and tenacity of the research community. Vast arrays of newly explored plant species capable of reducing metallic ions into neutral atoms are continually being introduced. This approach seems to deliver the message of applicability of green-synthesized MNPs. However, it is highly desirable to put this green route into practice for the safety of environment. The fate of engineered nanomaterials (ENMs) in terrestrial and aquatic environments has been well studied with conclusive evidences. The principles of colloidal science have illustrated most of the fate-determining steps for ENMs¹. A pertinent question is whether the principles of colloidal science can be applied to plant-derived MNPs. Release (anthropogenic) of plant-derived MNPs to the terrestrial and aquatic environments and their fate should be analysed for the interpretation of green synthesis.

MNPs with non-biodegradable metal core (e.g. gold, silver, platinum, etc.) are of recalcitrant nature and become persistent in the environment. Plant-derived MNPs have capped phytochemicals that are claimed to be responsible for reducing the potential toxicity of otherwise naked metal core of nano dimensions². In the terrestrial environment, plant-derived MNPs coming in contact with soil microorganisms can have different effects on the capped phytochemicals and metal core. In general, plant debris is gradually decomposed by soil microorganisms. The fate of plant debris can end up in soil organic matter (SOM) or mineralization into CO₂, minerals and H₂O, or transformation into complex organic matter. SOM can further transform into humus by non-enzymatic chemical reactions and

accumulate in the soil. Complex organic matter is of recalcitrant nature³. Figure 1 presents a schematic depiction of the fate of the surface-capped phytochemicals in terrestrial environment. It is obvious that the surface-capped plant molecules belong to different classes (e.g. alkaloids, terpenoids, phenolics, etc.) of phytochemicals and are source (plant species)-dependent. However, the final fate of the capped plant molecules may not be controlled by these two factors (class of phytochemicals and plant species). Microbial decomposition of the surface-capped plant molecules will render the surfaces of plant-derived MNPs naked. This is of serious concern to the terrestrial environment, as the metal cores of MNPs are recalcitrant and become persistent. It thus can be ascertained that plant-derived MNPs are susceptible to fate-determining steps and transformed into MNPs of recalcitrant nature. In this regard, the environmental toxicity concern of chemically synthesized and plant-derived MNPs seems to remain unaltered.

The fate of plant-derived MNPs can also be discussed in reference to the aquatic environment (Figure 1). The theoretical background of colloidal science illustrates the behaviour of ENMs in the aquatic environment⁴. Moreover, physicochemical properties of ENMs influence their behaviour and fate. Specifically, surface properties (e.g. surface charge and energy, surface coating, etc.) can drastically change the fate of ENMs. It is of importance to analyse whether the surface-capped plant molecules can alter the nano-specific fate processes (dissolution, surface modification, homoaggregation, heteroaggregation and sedimentation) of plant-derived MNPs in the aquatic environment. To explain this further, dissolution kinetics of colloidal science can

be applied to plant-derived MNPs. In general, dissolution of ENMs in the aquatic environment can be expressed by the equation¹

$$\frac{dM}{dt} = -kSA, \quad (1)$$

where M is the amount (kg) of ENM dissolved in unit time (sec), A the Total surface area (m²) of ENM, S the water solubility of the chemical (kg/m³) and k is the dissolution rate constant (m/s).

For plant-derived MNPs, it is obvious that dissolution of the metal core will proceed only after the removal of surface-capped plant molecules. This will delay the dissolution of MNPs, and it can be ascertained that the capping behaviour (fully or partially capped) will play a key role. Moreover, the dissolution kinetics of the surface-capped molecules might not be governed by the factors mentioned in eq. (1) and warrants further studies.

Apart from dissolution kinetics, it is also important to consider other nano-specific fate processes such as aggregation and sedimentation for plant-derived MNPs. However, there is a large knowledge gap in the behaviour of plant-derived MNPs in the aquatic environment and hence adequate modelling for aggregation and sedimentation is a challenging task. For instance, accurate data on radius and density of MNPs are required to apply Stokes law for sedimentation modelling. Moreover, determination of thermal energy barrier is necessary for the application of Boltzmann's law in aggregation modelling^{5,6}. Surface capping can influence the radius and density of plant-derived MNPs compared to chemically synthesized ones of the same metal composition.

As the nano-specific fate processes determine the ecotoxicity behaviour of

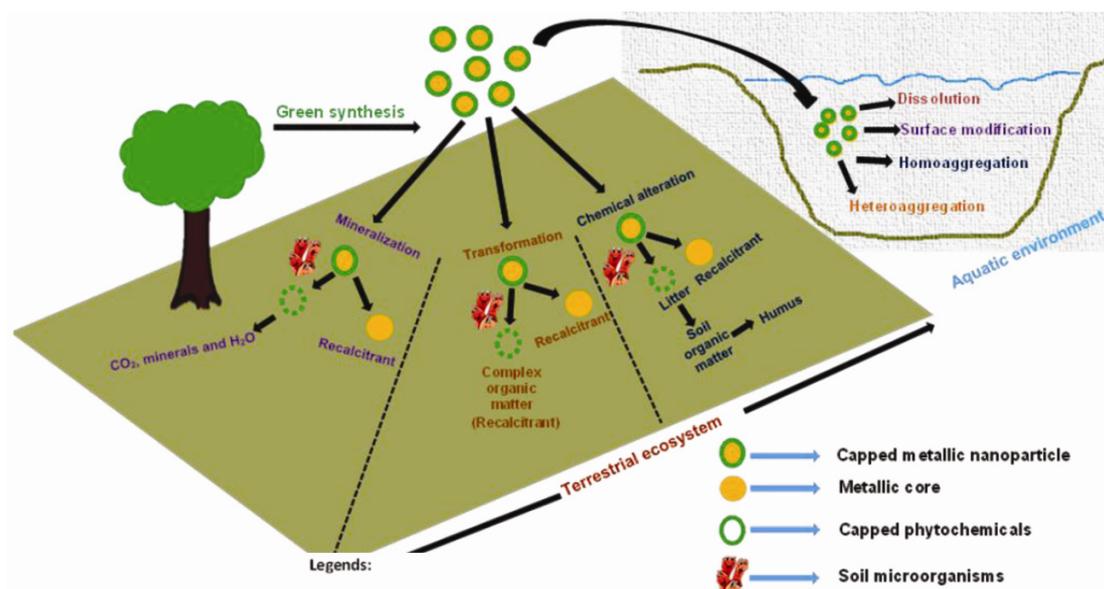


Figure 1. Schematic depiction of the fate of plant-derived metallic nanoparticles in terrestrial and aquatic environments.

ENMs and plant-derived MNPs are not proven for environmental safety concerns, it is a timely need to delve into the theoretical background of colloidal science applicable for plant-derived MNPs and evaluate environmental safety concerns.

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