BIOACCUMULATION AND BIODISTRIBUTION OF SILVER AND TITANIUM DIOXIDE IN MARINE SEAWEED FOR HUMAN CONSUMPTION

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INTRODUCTION

The increasing use of engineered nanomaterials (ENMs) for commercial and industrial purposes gives rise to concerns regarding possible environmental impacts. Their extensive use and application will inevitably lead to their release into the aquatic environment and their bioaccumulation in aquatic organisms, ultimately posing a risk to human health [1]. Silver nanoparticles (AgNPs) and titanium dioxide nanoparticles (TiO2NPs) are among the most used ENMs due to their unique physicochemical properties [2]. Their predicted environmental concentration in water bodies ranges from mg/L for TiO2NPs to ng/L of total silver for AgNPs [3]. Their bioaccumulation in some molluscs (e.g. mussels) and fish has been reported recently [4]. Unfortunately, very few works have thus far addressed the potential bioaccumulation of these ENMs in seaweed. This data could be important because seaweeds have been identified as promising food resources due to their rich nutrient content and sustainability, besides being the major organism responsible for coastal environment equilibrium [5, 6].

METHODOLOGY

In this work, two different species of marine seaweed, Ulva fenestrata (green seaweed) and Palmaria palmata (red seaweed) were exposed to 0.1 mg/L and 1 mg/L AgNPs and TiO2NPs during bioaccumulation experiments for 28 days. In order to study the NP biodistribution, we analysed ultrathin sections of fixed, resin-embedded seaweed by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) coupled with X-ray spectroscopy (EDS) in order to localise and identify the ENMs associated to seaweed tissue. In addition, scanning electron microscopy (SEM) in combination with EDS has been employed to characterise external tissue morphology and possible ENM interaction with seaweed surfaces. Elemental content was analysed by inductively coupled plasma-mass spectrometry (ICP-MS) after a microwave-assisted acid digestion. TiO2NPs were extracted from seaweed in basic media with TMAH in an ultrasound bath, whereas AgNPs were extracted enzymatically using the Macerozyme R-10® enzyme complex after tissue disaggregation using an ultrasonic probe. Single-particle

ICP-MS (spICP-MS) was used to quantify and characterise the size distribution of NPs in the extracts.

RESULTS

Quantification results indicate that there is a very significant accumulation of both ENPs in each of the seaweed studied. Ti concentration increased with the dose and time of exposure in Palmaria palmata, with a maximum observed concentration of 30.6 µg/g (day 28, dose 1 mg/L), a value smaller than that measured in Ulva (48.0 µg/g, day 28, 1 mg/L). The number of TiO2NPs also increased with sampling time up to a maximum of 1.1×1010 part/g (day 28, 1.0 mg/L) in Palmaria palmata, whereas a plateau was reached in Ulva at day 14 (7.0 ×109 part/g, 1 mg/L). In the case of Ag, the concentration increased with dose and exposure time until reaching a plateau, with the greater concentration measured in Palmaria palmata (0.79 µg/g, day 14, 1 mg/L). Preliminary results showed the accumulation of AgNPs with time and dose (maximum concentration: 1.4×109 part/g, day 28, 1 mg/L). EM analysis shows that both AgNPs and TiO2NPs are accumulated in the seaweed: AgNPs seem to penetrate deeper into the tissue with the time of exposure, reaching the cell membrane. The size of the primary AgNPs (15 nm) decreases inside the seaweed. However, TiO2NPs are accumulated on the surface in the medium times of exposure (14 day).

DISCUSSION

Seaweed is a well-established source of food in Asia and an increasingly popular one in Europe due to its high nutritional value, the fact that it is a non-animal food and its high availability. However, seaweeds are prone to concentrate metals and due to their large surface area, their exposure to the contaminants present in water is very high. The presence of ENMs, in particular the highly produced ones, in surface waters has been demonstrated and could pose a risk to the environment and a source of seafood contamination, ultimately entering the human food chain. Here, we demonstrate for the first time the potential bioaccumulation of ENMs in seaweed used for human consumption. Both AgNPs and TiO2NPs are accumulated in both species of seaweed, but the amount and their biodistribution differs; AgNPs penetrate deeper in the tissues, being able to reach the cell membrane while decreasing in size, while TiO2NPs seems to accumulate on the surface of the seaweed and become trapped in the cell wall at longer exposure times. Future studies should determine what transformations those NPs are undergoing after being processed in the food industry.