



## Toxicity of silver and gold nanoparticles on marine microalgae



Ignacio Moreno-Garrido\*, Sara Pérez, Julián Blasco

Institute of Marine Sciences of Andalusia (ICMAN-CSIC), Campus Río San Pedro, 11510 Puerto Real, Cádiz, Spain

### ARTICLE INFO

#### Article history:

Received 26 February 2015

Received in revised form

12 May 2015

Accepted 15 May 2015

Available online 16 May 2015

#### Keywords:

Nanoparticles

Gold

Silver

Microalgae

Environmental toxicology

### ABSTRACT

The increased use of nanomaterials in several novel industrial applications during the last decade has led to a rise in concerns about the potential toxic effects of released engineered nanoparticles (NPs) into the environment, as their potential toxicity to aquatic organisms is just beginning to be recognised. Toxicity of metallic nanoparticles to aquatic organisms, including microalgae, seems to be related to their physical and chemical properties, as well as their behaviour in the aquatic media where processes of dissolution, aggregation and agglomeration can occur. Although the production of these particles has increased considerably in recent years, data on their toxicity on microalgae, especially those belonging to marine or estuarine environments remain scarce and scattered. The literature shows a wide variation of results on toxicity, mainly due to the different methodology used in bioassays involving microalgae. These can range for up to EC50 data, in the case of AgNPs, representing five orders of magnitude. The importance of initial cellular density is also addressed in the text, as well as the need for keeping test conditions as close as possible to environmental conditions, in order to increase their environmental relevance. This review focuses on the fate and toxicity of silver, gold, and gold–silver alloy nanoparticles on microalgae, as key organisms in aquatic ecosystems. It is prompted by their increased production and use, and taking into account that oceans and estuaries are the final sink for those NPs. The design of bioassays and further research in the field of microalgae nanoecotoxicology is discussed, with a brief survey on newly developed technology of green (algae mediated) production of Ag, Au and Ag–Au bimetallic NPs, as well as some final considerations about future research on this field.

© 2015 Elsevier Ltd. All rights reserved.

### 1. Introduction

Ultra small particles have been present on the Earth from the beginning of its existence. Volcanic activity or hydrothermal processes naturally produce nanometre scale particles (Navarro et al., 2008a), but non-natural (engineered) very small particles have appeared in the environment as a result of human activity. The development of nanotechnology science has increased considerably since the beginning of the 21st Century. The term “nanotechnology” refers to “the creation, exploitation and synthesis of materials at a scale smaller than 1 μm” (Rai and Duran, 2011), but the modern term “nanomaterials” (NMs), more frequently cited in this revision as nanoparticles (NPs), refers to materials with one dimension under 100 nm (ASTM, 2006; Klaine et al., 2008). Current and frequent use for engineered NPs include catalysts (Hartmann, 2011), lubricants, paints and pigments (Kaegi et al., 2010),

cosmetics, sensor devices, bio-remediation (Boxall et al., 2007a; Gong et al., 2011), antibacterial and antifungal agents (El Nour et al., 2010; Tran et al., 2013; Devi and Bhimba, 2014), anti-fouling agents (Ren et al., 2014; Yee et al., 2014), anti-cancer drugs (Devi and Bhimba, 2013; Gerber et al., 2013; El-Kassas and El-Sheekh, 2014), aquaculture (Torkamani et al., 2010), various water treatments (Foldberg and Autrup, 2013), including drinking water (Zhang, 2013), air disinfection (Tran et al., 2013), food packaging, clothes (Foltynowicz et al., 2013; Kędziora et al., 2013), energy storage products (Mueller and Nowack, 2008), toothpaste (Klaine et al., 2008), plastics, weapons, (Boxall et al., 2007b), and protection of archaeological stones (Essa and Khallaf, 2014), etc.

Investment in nanotechnologies reached approximately 10 billion dollars in 2005 (Navarro et al., 2008a), and current estimates indicate that 66,000 metric tons of NPs are released into surface waters every year. A major part of the NPs in the air also finds its way into aquatic systems (Garner and Keller, 2014). According to Kędziora et al. (2013), 4% of general manufactured items, 16% of goods in healthcare and 50% of electronics and IT products contain emerging nanotechnology. It is expected that the average will

\* Corresponding author.

E-mail addresses: [ignacio.moreno@icman.csic.es](mailto:ignacio.moreno@icman.csic.es) (I. Moreno-Garrido), [sara.perez@icman.csic.es](mailto:sara.perez@icman.csic.es) (S. Pérez), [julian.blasco@icman.csic.es](mailto:julian.blasco@icman.csic.es) (J. Blasco).

increase in future decades (Savolainen et al., 2013).

The recent growth of the nanotechnology industry has raised concerns about the fate and potential hazards of the NPs (Klaine et al., 2008; Aschberger et al., 2011; Nowack et al., 2012; Whiteley et al., 2013), as the environment, and in particular the surface waters and, to a greater extent the oceans, will be the final receptors for all waste NPs (Fabrega et al., 2011a; Gong et al., 2011; Whiteley et al., 2013). In fact, many of the large scale chemical manufacturers producing NPs are located with a marine or estuarine discharge (Klaine et al., 2008). In spite of this, our knowledge of the effects and the mechanisms of toxicity of the various NPs on aquatic environments, mainly on the marine biota is far from being exhaustive (Boxall et al., 2007b; Baun et al., 2008; Chinnapongse et al., 2011; Walters et al., 2014).

Nanoparticles exhibit special characteristics which are related to their size (Klaine et al., 2012). It is estimated that 30–40% of the atoms of each NP is distributed on the surface (Auffan et al., 2009). This produces a high reactivity, even in substances that would remain non-reactive at other size scales, with potential and unexpected health or environmental hazards (Navarro et al., 2008a; Lapresta et al., 2012; Levard et al., 2012). This may also be valid for metallic NPs such as silver, gold and silver–gold alloy NPs (AgNPs, AuNPs, and Ag–AuNPs, respectively). These metallic NPs have been recently used in several fields, and the first results for toxicity tests on aquatic biota are beginning to appear in the scientific literature. In the SCOPUS list of scientific papers 460 publications can be found on AgNPs toxicity in marine environments, and 951 in aquatic environments, in general. There are 213 publications for toxicity of AuNPs in marine environments (301 in aquatic environments, in general); and 75 publications referring to the toxicity of Ag–AuNPs in marine environments (107 in aquatic environments, in general). Silver has been used since ancient times, and the use of colloidal silver has more than a century of history (Nowack et al., 2011). Nowadays, a very high number of nanotechnology applications for consumers involve nanoparticulated Ag. Products such as dressings, socks, air filters, toothpaste, healthcare and cosmetic products, vacuum cleaners, and washing machines usually contain AgNPs. These materials have been also used in catalysis, photocatalysis (Lee et al., 2011), pharmaceuticals, paints and pigments and archaeological protection (Boxall et al., 2007a; Klaine et al., 2008; Kaegi et al., 2010; Ji et al., 2011; Tran et al., 2013; Essa and Khallaf, 2014). Publications of articles on AgNPs have increased in the last decade, from 247 in 2001–3603 in 2011 (Tran et al., 2013), showing the growing interest in these nanomaterials. Although it is not easy to ascertain exactly the number of products containing AgNPs (Fabrega et al., 2011b), an estimation of AgNPs consumed appears to be 20 metric tons per year (SCENIHR, 2014).

Colloidal elemental gold has been used for years as vectors in tumour therapy. Recently, AuNPs have also been used for flexible conducting inks and as catalysts (Klaine et al., 2008), components for anti-ageing creams (Boxall et al., 2007a), paints (Renault et al., 2008), solar cell engineering and memory devices (Yah, 2013). Other uses include water purification, catalysis, pollution control (Yah, 2013), cancer treatment and diagnosis (Gerber et al., 2013). As for AgNPs, it is difficult to identify the total amount of AuNPs produced, consumed and wasted every year, but an approximate estimation for AuNPs consumed seems to be 3 metric tons per year (<http://www.grandviewresearch.com/industry-analysis/gold-nanoparticles-industry>).

Ag–AuNPs have been studied for their catalytic properties (Link et al., 1999). These bi-metallic NPs can be obtained by co-reduction of chloroauric acid and silver nitrate, and with sodium citrate in aqueous solution (Link et al., 1999).

In this review, we carry out a survey on the fate, behaviour and

toxicity of AgNPs, AuNPs, and Ag–AuNPs on photosynthetic marine microbiota, including also a comparison with fresh water species. Some recent techniques used in the green (plant mediated, including algae and microalgae) biosynthesis of AgNPs and AuNPs are analysed, together with some final considerations on gaps in our knowledge and proposed future research in this field.

## 2. Fate and behaviour of silver and gold NPs in the environment

Surface waters receive considerable quantities of waste or released metallic NPs. Silver and gold NPs concentrations in the environment are expected to increase in the next decades (Tiede et al., 2009b). For instance, Kaegi et al. (2010) estimated that 30% of the AgNPs from an outdoor façade, with an AgNP-containing paint, is released into the environment. Ultimately, a major part of the NPs which is not directly released into estuaries or oceans will sink as sewage sludge. In some countries, a large proportion of this sewage is used as fertilizer, while in others it is incinerated. It is not easy to determinate what percentage of NPs remains in every environmental compartment (Fabrega et al., 2011b), but the possibility of metallic NP contamination via sewage sludge cannot be dismissed (Schlich et al., 2013).

As with all NPs, agglomeration/aggregation processes are key issues for the understanding of the behaviour and fate of Ag or AuNPs in the environment (Navarro et al., 2008b; He et al., 2013). In order to clarify terms, it is necessary to understand the difference between *agglomeration* (weakly binding of particles, with the total external surface area of the agglomerated particles being similar to the sum of the surface areas of the individual particles) and *aggregation* (strongly binding of particles, with the external surface area of the aggregated particles being significantly smaller than the sum of the surface areas of the individual particles). It is assumed that the forces holding an agglomerate are weak forces (van der Waals forces or simple physical entanglement), while those holding the aggregates are stronger (such as covalent forces or complex physical entanglement) (OECD, 2012). In aquatic environments, agglomeration/aggregation and settling into the sediment seems to be the common fate for most of the NPs (García Alonso et al., 2014; Buffet et al., 2014). Homo-aggregation is frequent in bioassays involving high NPs concentrations, but although this does not happen in bioassays involving low NPs concentrations (García-Negrete et al., 2013), hetero-aggregation of NPs with almost any other particle present in media also occurs (Egorova, 2011). Some authors suggest that the settling of NPs in aquatic media must be very slow (Matranga and Corsi, 2012), while others maintain that settling could be fast, due to the aggregation with suspended matter (Quik et al., 2014; Velzeboer et al., 2014). However, aggregation of NPs does not always suppose a decrease in the toxicity of those nanomaterials in aquatic organisms. Wei et al. (2010) report higher toxicity of carbonate nanotubes large aggregates to *Dunaliella tertiolecta*. On the other hand, aggregation could facilitate ingestion by grazers: Arulvasu et al. (2014) reported high toxicity of AgNPs to *Artemia* (brine shrimp) at near  $1 \mu\text{g}\cdot\text{L}^{-1}$  AgNPs (LD50 after 24 h). Other authors suggest that grazing of NPs aggregates is highly related to toxicity in those organisms.

The detection of size and distribution of AgNPs or AuNPs, and related ions, in bioassays has been traditionally performed by diffusive gradients in thin films (DGT), ion-selective electrodes or ultra-filtration, often combining those techniques with ICP-MS, spectroscopy, dynamic light scattering, X-Ray spectroscopy or cyclic voltammetry (Gray et al., 2013; Teo and Pumera, 2014). Some studies have used flow-field flow fractionation (FFFF) (F4) in order to separate and analyse NPs (Kennedy et al., 2010). Scanning Electron Microscopy, (SEM), Transmission Electron Microscopy (TEM),

Download English Version:

<https://daneshyari.com/en/article/4550672>

Download Persian Version:

<https://daneshyari.com/article/4550672>

[Daneshyari.com](https://daneshyari.com)