Green biosynthesis of gold and silver nanoparticles obtained from the Antarctic algae *Palmaria decipiens* and *Desmarestia menziesii*

N. González-Ballesteros[1], M.C. Rodríguez-Argüelles[1], J.B. Rodríguez-González[2], M. Lastra[3,4], J. López[3,4], J. Troncoso[3,4]

1 Departamento de Química Inorgánica, Universidade de Vigo, 36310 Vigo, Spain
2 Scientific and Technological Research Assistance Center (CACTI), Universidade de Vigo, 36310 Vigo, Spain
3 Estación de Ciencias Marinas de Toralla (ECIMAT), University of Vigo, 36331 Vigo, Spain
4 Department of Ecology and Animal Biology, Marine Science, Faculty, University of Vigo, 36310 Vigo, Spain

INTRODUCTION

Over the last 30 years, the interest in nanotechnology has increased thanks to the wide number of applications of nanomaterials. Especially noble metal nanoparticles such as silver and gold are being studied to their application in nanomedicine. The remarkable strong broad-spectrum antimicrobial activity of silver nanoparticles allowed the development of products like textiles, food storage containers, antiseptic sprays, catheters, and bandages. On the other hand, gold nanoparticles display unique physico-chemical properties that have been investigated for biomedical applications including cancer imaging, drug delivery, gene therapy and thermotherapy. Over the last decades there has been a great surge of interest on the green synthesis of gold and silver nanoparticles, seaweeds have shown a huge potential in this field, having also been named as "bionanofactors".

MATERIALS AND METHODS

Aqueous extracts of The Rhodophyte *Palmaria decipiens* (Reinsch) Ricker 1987 (hereafter PD) and the Phaeophyta *Desmarestia menziesii* Agardh 1848 (hereafter DM) were obtained to the synthesis of gold and silver nanoparticles. The reducing power and the concentration in soluble phenols of the extracts were measured using the Oyaizu and the Folin and Ciocalteu method respectively.
The synthesis of gold nanoparticles was conducted through the reduction of $HAuCl_4$ at room temperature during 24 hours and the synthesis of silver nanoparticles took place with $AgNO_3$ at 100ºC during 8 hours.

Fig. 1. Photography of A) *D. menziessi* and B) *P. decipiens.*

RESULTS

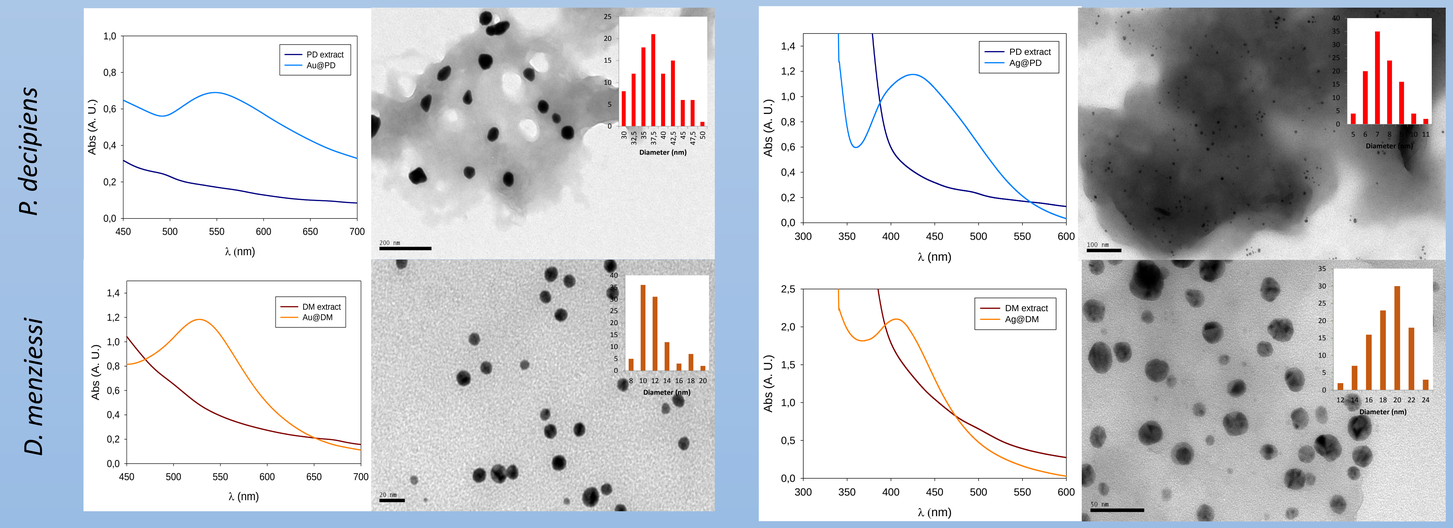
Characterization extracts
Total phenolic compound (TPC) and the reducing activity were determined. The results shown a direct relationship between the phenolic content and the reducing activity of the seaweeds. *D. menziessi* possess almost three times more reducing activity than *P. decipiens* and the double of phenolic content.

	P. decipiens	*D. menziessi*
TPC (mg galic acid/g seaweed))	0.34±0.03	0.84±0.02
Reducing Activity (mg ascorbic acid/g seaweed)	43.7±0.6	126.3±0.9

Band assignment for FTIR Wavenumber (cm^{-1})

Assignment	*P. decipiens*	Au@PD	Ag@PD	*D. menziesii*	Au@DM	Ag@DM
ν N-H, O-H	3406	3421	3420	3392	3422	3421
ν C-H	2929	2933	2929	2926	2930	2927
ν_a C=O	1652	1648	1648	1649	1636	1636
ν_s C=O	1415	1413	1413	1409	1410	1410
ν -SO3	1248	1245	1243	1255	1239	1226
ν C-OH	1075	1077	1078	1082	1085	1087

The synthesis of nanoparticles was conducted through the reduction of $HAuCl_4$ and $AgNO_3$ led by the seaweed extracts with different reaction conditions. Their formation was confirmed by UV-Vis spectroscopy by the presence of the characteristic surface plasmon resonance band. In the case of Au@PD the maximum appears at 548 nm whereas in Au@DM show up at lower wavelength at 527 nm. Silver nanoparticles appeared at lower wavelength, 425 nm for Ag@PD and 405 nm for Ag@DM. Transmission Electron Microscopy was used for a better featuring of the size and shape spectra. Au@PD and Au@DM present mean diameters of 36.8 ± 5.3 and 11.5 ± 3.3 nm respectively. Ag@PD were the smallest particles synthesized, with a mean diameter of 7.0 ± 1.2 nm, compared with Ag@DM, with mean diameter of 17.8 ± 2.6 nm.



In order to study further the formation and stabilization process of gold and silver nanoparticles in PD and DM extracts FTIR spectroscopy analysis were conducted. When comparing each extract with their corresponding gold and silver nanoparticles, it has been observed the same pattern in the shifts in bands. This changes in wavenumber and intensity allow to identified the principals groups involved on the reduction of gold(III) and silver(I) and the capping of the nanoparticles. The principal groups involved on the synthesis and stabilization process are amino, hydroxyl and carbonyl groups from proteins, polysaccharides and polyphenols.

CONCLUSIONS

The present study is the first dealt with an eco-friendly synthetic route that uses aqueous extracts from the red Rhodophyte *Palmaria* decipiens and the Phaeophyta *Desmarestia menziesii* in obtaining gold and silver nanoparticles. The extracts acts as reduction and stabilising agents, avoiding the aggregation of the nanoparticles. Even though the mechanism of reaction led by seaweeds is not fully known and more studies should be conducted, our results suggest that hydroxyl and sulfonic groups from polysaccharides and amino and carbonyl groups from proteins could be involved in the metal reduction and in the nanoparticle formation.

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