Characterization of exopolysaccharides after sorption of silver ions in aqueous solution

M. Deschatre [a,b,c,d], B. Lescop [e], C. Simon Colin [b,c,d], F. Ghillebaert [f], J. Guezennec [g], S. Rioual [e,*]

[a] Mexel Industries SAS, Route de Compiègne, Verberie 60410, France
[b] Laboratoire de Microbiologie des Environnements Extrèmes, UMR 6197, Institut Français de Recherche pour l'Exploitation de la Mer, Centre de Brest, Plouzané, France
[c] Laboratoire de Microbiologie des Environnements Extrèmes, UMR 6197, Université de Bretagne Occidentale, UEB, IUEM, Plouzané, France
[d] Laboratoire de Microbiologie des Environnements Extrèmes, UMR 6197, CNRS, Plouzané, France
[e] Laboratoire de Magnétisme de Bretagne, Université de Brest, EA 4522, 6 Av. le Gorgeu, Brest Cedex 29285, France
[f] Ecotox, 11 Rue Principale, Affringues 62380, France
[g] AiMB : Advices in Marine Biotechnology, Plouzané 29280, France

ARTICLE INFO

ABSTRACT

Biosorption of silver ions by several exopolysaccharides (EPS) differing from each other in their chemical composition and functional groups was investigated. EPS were characterized before and after Ag(I) biosorption by comprehensively using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, transmission electron microscopy (TEM). The role of the different functional groups in the biosorption process was observed. In particular, sulfate groups were seen playing a major role. XPS and FTIR methods showed that the composition of lowest efficient EPS changed after Ag(I) biosorption with a relative increase of the carboxylate ions content. This change was accompanied by the formation of mainly silver oxide nanoparticles. As the consequence, the reducing character of the EPS is expected to influence the silver sorption capability of the EPS.

© 2014 Elsevier Ltd. All rights reserved.

Introduction

During the last decades, silver ions were extensively used in many industrial activities such as in electronics, jewellery, photography or electroplating domains, resulting in increasing contamination of waste water, especially in aquatic environment [1]. Actually, silver is one of the most toxic metal, in particular in its ionic form [2–4], and its absorption by humans can cause severe dysfunction of kidney, reproduction system, liver, brain and central nervous systems. Considering the serious environmental problems and the damage to human health caused by this toxic metal, great attention has been paid in its removal from water. Furthermore, recovery of silver is of economic interest due to its high commercial value. Different methods do exist to recover metal ions including conventional ones such as electrolysis [5], precipitation [6], flotation [7], ion-exchange [8] or adsorption [9,10]. Among these methods, biosorption of silver ions by biomaterials is becoming an emerging technique due to its simplicity, low cost and efficiency.

Recently, a number of biosorbents were developed and tested for removal and recovery of Ag^+, such as fungi *Cladosporium cladosporides* [11], bacteria *Myxococcus xanthus* [12], persimmon tannin [13] or chitosan resin [10].

Bacterial exopolysaccharides (EPS) are high molecular weight polymers excreted by numerous bacteria into the surrounding environment, and are considered as promising biosorbents because of their diversity of structures and properties along with the ease of production and biodegradability. Actually, EPS present ionizable functional groups such as carboxyl, acetate, hydroxyl, amine, phosphate or sulfate groups which may act as active sites for ionic biosorption [14]. They have been successfully used in the past for heavy metal ions removal from aqueous solutions [15–18]. However, only recently, Deschatre et al. [19] focused on sorption of silver ions by EPS. In this study, authors investigated sorption capacity of four EPS differing from each other in their chemical composition, and compared their efficiency for silver and copper ions capture. Metal biosorption experiments were conducted in batch process and showed the influence of factors such as initial metal concentration, EPS concentration or pH, on the retention capacity. Maximal metal sorption capacities were 333 mg Ag/g EPS M3 and 400 mg Cu/g EPS M1, thus highlighting differences in the

* Corresponding author. Tel.: +33 298016233; fax: +33 298016239.
E-mail address: rioual@univ-brest.fr (S. Rioual).

selectivity of each EPS. Such selectivity could be explained, at least partially, by the nature of functional groups within each EPS, as suggested by Fourier transform infrared spectroscopy (FTIR) analyses performed on EPS before and after metal sorption. However, mechanisms involved in the sorption mechanism of silver remain unclear. The aim of the present study was to identify EPS functional groups involved in silver sorption to better understand sorption mechanisms to predict and improve silver ions recovery. Thus, chemical structure of four EPS was studied before and after silver sorption, using X-ray photoelectrons (XPS), X-ray diffraction (XRD), FTIR and transmission electron microscope (TEM). Only the use of such complementary techniques enables one to get a good understanding of the sorption mechanism.

Material and methods

Chemicals

All chemicals used in this study were of analytical grade. Stock solutions of Ag(I) (500 mg L^{-1}) was prepared by dissolving (AgNO$_3$) from Sigma–Aldrich in ultrapure water. Bacterial production of exopolysaccharides along with the associated extraction and purification protocols have been previously described [20].

Metal biosorption experiments

Biosorption experiments were performed in a flask by dissolving 50 mg of dry EPS in 100 mL of silver solution at initial concentration of 500 mg L^{-1}. Experiments were performed in the dark due to the photosensitivity of silver nitrate. Solutions were prepared in triplicate and were gently shaken during 3 h. During experiments, pH was regularly checked. At the end of the experiment, solutions were ultra filtered using Pellicon tangential flow filtration cassettes with a nominal molecular weight cutoff of 100 kDa to eliminate all free silver ions remaining in the solution. Permeates were analysed by inductive coupled plasma atomic emission spectroscopy (ICP AES; Horiba Jobin Yvon ULTIMA 2) to determine silver ions concentration, while retentates were freeze-dried prior to further analyses by XRD, XPS FTIR and TEM.

Analytical techniques

Crystalline structure of four EPS (M1–M4) was analysed by X-ray diffraction (XRD) with an Empyrean PANalytical apparatus using the CuKα radiation. Composition of EPS polymers was determined by X-ray photoelectron spectroscopy (XPS) before and after sorption. Briefly, the experimental apparatus consisted of an Mg-Kα X-ray source (Thermo VG) and a cylindrical mirror analyzer from RIBER. The fitting procedure was made by CasaXPS software and by considering linear and Shirley backgrounds [21]. FTIR spectra of dried EPS were recorded on Thermo Scientific Nicolet iS10 FTIR spectrometer, equipped with a universal attenuated total reflectance sampling device containing diamond Zn/Se crystal. Spectra were scanned at room temperature in transmission mode over the wave number range of 4000–600 cm^{-1}, with a resolution of 4 cm^{-1}. The TEM microscope used for the observation of silver nanoparticles created by precipitation was a JEOL JEM 1400.

Results and discussion

X-ray photoelectron spectroscopy

It is well admitted that biosorption of metals ions by biosorbents is due to the presence of ionizable functional groups such as carboxyl, acetate, hydroxyl, amine, phosphate, and sulfate groups [14], which are considered as potential binding sites for metal ions sequestration [22]. Metal biosorption occurs by interactions between metallic cations and EPS functional groups through complex mechanisms such as ion exchange, precipitation, adsorption or complexation [22]. To investigate the influence of functional groups involved in silver biosorption mechanism by EPS, XPS analyses were carried out on EPS before and after silver biosorption experiment. As shown by Table 1, neutral sugars and uronic acids appeared in the four studied EPS. XPS C(1s) and O(1s) spectra were thus systematically recorded. One should note that EPS M2 differs from other EPS since it is mainly composed of neutral sugar and shows a high polydispersity index (I_p = 4.2) and a relatively low (870 kDa) molecular mass [19]. Since EPS M1 and M4 contain sulfate and hexosamine content, respectively, N(1s) and S(2p) spectra are also considered in the following.

XPS characterization of EPS before biosorption

C(1s) spectra presented in Fig. 1(a) displays an important structure at 284.8 eV due to the presence of C—C and C—H bonds and an asymmetric tails at high binding energy due to the presence of carbon based functional groups. Generally, observed feature can be reproduced by considering the four possible C_i (i = 0–3) contributions indicated by arrows in Fig. 1(a) which corresponds to non-functionalized carbon (C—C, C—H), carbon singly bounded (i.e., C—O or C—N for M4), carbon doubly bounded to oxygen (i.e., acetal carbon O—C—O or C=O) and carbon bounds to two oxygen (O=C—O). The relative energies of the three last contributions with respect to the first one are 1.7 ± 0.1, 3.1 ± 0.1 and 4.4 ± 0.2 eV [23,24], respectively. To decompose the spectra, only the three first components (C_i, i = 0–2) were considered here due to the weakness of the fourth component. The binding energies and intensities of these components derived from the fitting procedure are given in Table 2. As observed, the binding energy of C_1 is very close to the predicted value of 286.5 eV and indicates the presence of alcohol groups C—OH for EPS M1–M4 and C—N for EPS M4. In contrast, the C_2 contribution is clearly shifted toward high energy with respect to the expected nominal value of 287.9 eV. This reveals the importance of carboxylate ions which lead to contribution at 288.3 eV [25]. However, O—C—O or C=O bonds may also be present, in agreement with the expected structure of polysaccharides. Table 2 displays the total intensity of the carbon based functional groups ($C_1 + C_2$) and the C_1/C_2 ratio for each EPS. It appears then clearly that there is an important difference in the total quantities of available functional groups in the four EPS. Furthermore, the ratio between the amount of carboxylate and alcohol groups differs in the EPS leading to a relative enrichment of alcohol for EPS M2 and carboxylate for EPS M4.

The O(1s) spectra are presented in Fig. 1(b). Spectra were deconvoluted by considering only one contribution. Positions and intensities of this contribution are reported in Table 2. By

Table 1
Characteristics and chemical composition of the four studied exopolysaccharides.

EPS	Strains	Mw (kDa)	I_p	Proteins (%)	Neutral sugars (%)	Uronic acids (%)	Hexosa mines (%)	Sulphates (%)	Substituents
M1	*Paracoccus* sp.	4300	1.3	3	48	8	–	29	Acetate
M2	Unidentified	870	4.2	5	90	Traces	–	–	–
M3	*Alteromonas* sp.	1800	2.6	4	46	20	–	–	–
M4	Vibrio sp.	1300	2.2	2	11	27	30	–	Acetate