# A biogenerated polymetallic catalyst from society's wastes

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## ABSTRACT

**Aims:** Preparation of the new metals-polymeric composite, $Met_x$-EPS (**I**), to be used as a green catalyst in water or in two-phase aqueous conditions.
**Study design:** Recovery and valorization of polymetallic wastes to obtain directly new catalysts using a microorganism to explore their application in removal of difficult and dangerous chemical pollutants present in aqueous environment.
**Place and Duration of Study:** Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Venezia Mestre, Italy; University of Nova Gorica, Nova Gorica, Slovenia, Institut Jozef Stefan, Ljubljana, Slovenia and Department of Biology, Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia, between February 2018 and January 2019.
**Methodology:** For the preparation of $Met_x$-EPS (**I**), the metals source was an exhausted catalytic converter that was grinded and treated with an acidic solution at room temperature. After filtration, the solution was concentrated, neutralized and added to a broth of *Klebsiella oxytoca* DSM 29614 to produce (**I**) where metals are embedded in a peculiar polysaccharide structure. The composite was easily recovered from the fermentation broth and purified. The process protocol was verified many times and was shown to be reproducible satisfactorily. The % recovery of metals, originally present in the converter, was good as determined by atomic absorption. The morphology and the chemical state of main metals in (**I**) were investigated by X-ray absorption spectroscopy methods (XANES and EXAFS). No metallic alloy seems to be evident.
**Results:** As first application of (**I**) as catalyst, the hydrodechlorination treatment of polychlorinated biphenyls (PCBs) was studied in water/methanol. A significant removal of higher chlorinated congeners was observed working at 1MPA of hydrogen and 60°C. This result improves significantly and surprisingly the methodology, previously studied by us using mono- or bi-metals embedded in the same polysaccharide moiety, indicating that positive synergies among the different metals were operating.
**Conclusion:** The preparation of this new polymetallic species embedded in a polysaccharide moiety starting from spent catalytic converters represents an alternative valorisation of metallic wastes. Moreover, a synergic effect was exerted by the different metals when the catalyst $Met_x$-EPS (**I**) was used in the hydrodechlorination treatment of polychlorinated biphenyls (PCBs) in water/methanol. Finally, a promising preliminary proof of concept for the removal of polychlorinated aromatic pollutants even in contaminated aqueous sites was carried out.



*Keywords: Metals-polymeric composite; biogenerated polymetallic exopolysaccharide; new catalyst from metallic wastes; hydrodechlorination of PCBs in water*


## 1. INTRODUCTION

As now requested by the circular economy, valuable metals have to be recovered from industrial scraps, such as for example exhausted catalytic converters. Current approaches to

treat relevant metallic waste categories are based on pyrometallurgical, hydrometallurgical or bio-hydrometallurgical methods, which present advantages and disadvantages in terms of energy consumption, use of special equipments and difficulty in the purification [1,2]. Then a following treatment is necessary to produce metallic catalysts. To overcome these drawbacks and to obtain directly a composite useful as catalyst, our protocol at first treats grinded exhausted catalytic converters at room temperature with a concentrated acidic solution, such as aqua regia or 80% nitric acid, to dissolve metals as ions and, after filtration of the solid residue, concentration and neutralization of the solution, takes advantage of the property of a plurimetal resistant microorganism *Klebsiella oxytoca* DSM 29614. This microorganism is able to generate, in the presence of heavy metal cations, a specific capsular exopolysaccharide (EPS) which may embed them and then be extruded from the cell so to be easily purifiable [3-4]. So a new metals-polymeric composite, $Met_x$-EPS (**I**) was obtained from exhausted catalytic converters and, after characterization with different methods, its catalytic activity and a possible synergic effect due to the presence of different metals embedded in EPS was verified in the hydrodechlorination treatment of a methanolic solution of polychlorinated biphenyls (PCBs) in distilled water and in a sample of polluted sea water (Mar Piccolo, Taranto, Italy). The results were compared with those recently obtained by us using Pd-EPS or Pd,Fe-EPS [5].

## 2. MATERIAL AND METHODS / EXPERIMENTAL DETAILS / METHODOLOGY

### 2.1 Materials and Instrumentation

Nutrient broth (Difco), n-hexane (pesticide grade; Romil), PCB standards (AccuStandard) were utilised. Aroclor 1260 and the other reagents were Sigma-Aldrich products and used as received. The total amounts of elements were determined versus their relative standards solutions by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Optima 3100, Perkin Elmer). The FT-IR spectra (KBr pellets) of $Met_x$-EPS were recorded on an FT-IR Nicolet Magna 750 instrument. X-ray absorption spectra were measured on of $Met_x$-EPS sample in the energy range of K or L3 absorption edges of constituent metal cations (Pd K-edge (24350 eV), Rh K-edge (23220 eV), Zr K-edge (17998 eV), Pt L3 edge (11564 eV), Ce L3 edge (5724 eV)) to obtain corresponding XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) spectra of the investigated elements. The $Met_x$-EPS sample was prepared in the form of homogeneous self-standing pellets, each optimised to provide the total absorption thickness ($\mu$d) of about 1.5 above the investigated absorption edges. All absorption spectra were measured at room temperature in transmission detection mode at two different synchrotron radiation facilities (Zr, Pt and Ce at XAFS beamline at Elettra in Trieste, Italy; Pd and Rh at BL22 (Claess) beamline of ALBA in Barcelona, Spain); a Si (111) double crystal monochromator was used at the XAFS beamline of the Elettra and a Si(311) at BL22 of ALBA. The intensity of the monochromatic X-ray beam was measured by three consecutive ionization detectors. The samples were placed between the first pair of detectors. The exact energy calibration was established with simultaneous absorption measurement on the corresponding reference metal foil placed between the last pair of detectors. Absolute energy reproducibility of the measured spectra was ±0.03 eV. The absorption spectra were measured within the interval [-150 eV to 1000 eV] relative to the investigated absorption edge. In the XANES region, equidistant energy steps of 0.5 eV were used, while for the EXAFS region, equidistant k-steps ($\Delta k = 0.03$ Å$^{-1}$) were adopted, with an integration time of 1 s per step. The quantitative analysis of XANES and EXAFS spectra is performed with the IFEFFIT program package [6] in combination with FEFF6 program code [7] for ab initio calculation of photoelectron scattering paths. The determination of PCB congeners was performed in full scan mode on a fused silica capillary column (HP5-MS 30 m, 0.25 mm x 0.25 mm; Agilent Technologies) installed in a ThermoFinnigan (Trace GC 2000) coupled to a quadrupole mass spectrometer (ThermoFinnigan Trace MS), using the same conditions described in our previous work [5].

## 2.2 Recovery of acidic metallic solutions from grinded exhausted catalytic converters and preparation of a new metals-polymeric composite (I)

As typical procedure, grinding and pulverizing 20 g of exhausted catalytic converter was carried out using a mortar. The obtained powder was transferred to a 1 liter flask, into which 400 mL of 80% $HNO_3$ or of aqua regia [65% $HNO_3$ : 37% HCl (1:3)] was poured under stirring; after 24 h at room temperature the mixture was filtered and the residue solid washed with distilled water; the filtrate was then concentrated at reduced pressure up a volume of 80 mL. This solution was split in two parts, one was used for quantitative analyses of the extracted metals (**Table A**), the other (40 mL) was neutralized to pH 7.0 with a concentrated NaOH solution until a final volume of 50 mL and immediately added to a culture of *Klebsiella oxytoca*, DSM 29614 in 1 liter of NaC medium, which contained minimum minerals and sodium citrate as sole carbon and energy source, and had been prepared adapting the protocol already described in our previous works [3, 4]. The culture was grown under anaerobic conditions for 5 days and when a cell density upper than 1.0 Abs at 600 nm was reached, 50 ml of instantly buffered plurimetallic sample were added. After 48 h from this addition, the cell culture was put in a centrifuge to eliminate bacterial cells. The supernatant was treated with 800 ml of cooled 95% ethanol to precipitate $Met_x$-EPS. The purification procedure was repeated twice. After drying under vacuum, the material was finally grinded to powder to obtain 1-1.3g of polymetallic polysaccharide. The preparation of (**I**) using metals recovered by aqua regia treatment was repeated for three times verifying good reproducibility of the results.

## 2.3 Element determination in a new metals-polymeric composite (I)

Samples (1 mg) of dry pulverized polymetallic composites were digested with 2 ml of aqua regia, heating the mixture at 60°C until a complete dissolution for element determination. The recovery yield of the main metals is reported in **Table A**.

## 2.4 Optimized protocol of hydrodechlorination of Aroclor 1260 using the new catalyst (I)

A suitable amount of $Met_x$-EPS (**I**) to obtain a substrate/Pd ≈ 8/1 mol ratio (8.8 mg) was stirred in a Schlenk tube under nitrogen in 4 ml of distilled water or 4 ml of Mar Piccolo (Taranto, Italy) water for about 10 min. A solution of 7 mg of Aroclor 1260 (~0.0195 mmol assuming MW 358 as medium value) in 2 ml of methanol was then added to the aqueous phase as well as 1.7 mg (0.021 mmol) of ammonium acetate. The Schlenk tube was then transferred into a 150 ml stainless steel autoclave under nitrogen, pressurized with 1 MPa of $H_2$, instead of 3MPa used previously with Pd-EPS or Pd,Fe-EPS [5], and stirred at 60°C for 20 h. The reactor was then cooled to room temperature and opened under nitrogen. Then, the organic products were separated from the catalyst extracting them from the aqueous phase with 10 mL of n-hexane. The procedure of extraction was repeated three times. The organic phases were collected and dried on $Na_2SO_4$, then concentrated using a nitrogen flow (Turbovap 2, Caliper Science) and analyzed by GC-MS.

# 3. RESULTS AND DISCUSSION

## 3.1 Catalyst characterization

The results of elemental determination are reported in **Table A**.

**Table A**. Main metals extracted from exhausted catalytic converters and present in $Met_x$-EPS[a].

| Analyzed Metals | C (mg/L) $HNO_3$ (n.a.) sol. (inc. ±10%) | C (mg/L) aqua regia (a.r.) sol. (inc. ±10%) | $(Met_xEPS)_{n.a.}$ Metal recovery yield% [b] | $(Met_xEPS)_{a.r.}$ Metal recovery yield% [b] |
|---|---|---|---|---|
| Pd | 428 | 748 | 89 | 99 |
| Pt | 31.9 | 479 | 81 | 83 |
| Rh | 2.07 | 111 | 84 | 85 |
| Al | 1623 | 2413 | 80 | >99 |
| Ce | nd | 2158 | nd | 99 |
| Zr | nd | nd | nd | nd |
| W | 121 | 174 | 29 | 10 |

[a] Experimental conditions: 20 g of exhausted catalytic converter; 400 ml of 80% $HNO_3$ or acqua regia; T = 20°C; t = 24 h; final volume of the acidic solution after distillation = 80 ml. [b] (Amount of metal encapsulated in EPS)/(amount of metal present in the starting acidic solution)%. nd = not determined

Even if the aqua regia treatment is, as expected, more efficient to extract metals from exhausted catalytic converters, the % of recovery of metals, bonded or encapsulated in the new composite, after the biological treatment, is not significantly affected and is very high (80->99%) with the exception of tungsten (**Table A**).

As already described in more detail [S. Paganelli et al., Ca' Foscari University, Venice, Italy, paper submitted to ChemistrySelect], $Met_x$-EPS (**I**) was characterized by FT-IR and by the x-ray absorption spectroscopy methods XANES and EXAFS. The IR spectrum (**Appendix, Fig. 1**) confirmed the presence of metals bound to capsular EPS. It looks quite similar to the spectrum of a previous prepared Pd-EPS [4] but with a very intense sharp band at 1384 $cm^{-1}$. The intense symmetric stretching of $COO^-$ vibration to 1384 $cm^{-1}$, on the basis of literature, should demonstrate, in our opinion, that carboxyl group was a contributor in the sorption of metals [8, 9]. In the region between 1550-1650 $cm^{-1}$ it is possible to observe two peaks, one of them or both could be due to the asymmetric stretching of $COO^-$ vibration bounded to metals [8]. Indeed the EPS is formed by an eptameric structure with two D-glucuronic acids, four L-rhamnose, and one D-galactose [10]. However it is not possible to exclude also contribution of nitrogen species such as any nitrogen heterocyclic compounds eventually formed during the fermentation or membrane protein amide bonds [9]. Finally, the other intense peak at 1065 $cm^{-1}$, as it was already observed for other similar metal EPS, is to attribute to phosphate groups [4, 9] .

The presence of metals bounded to capsular EPS and valence and structural information of metal cations in the $Met_x$-EPS complex at the atomic scale were confirmed by x-ray absorption spectroscopy methods XANES and EXAFS [S. Paganelli et al., Ca' Foscari University, Venice, Italy, paper submitted to ChemistrySelect]. It is known that, in the XANES spectrum, an increase of oxidation state results in a shift of each absorption feature to higher energies [4,11]. The Pd K-edge profile of the Pd in the $Met_x$-EPS complex are identical to the Pd XANES spectrum of the Pd metal foil with fcc crystalline structure and also to FePd-EPS(A), FePd-EPS(B) and Pd-EPS samples, previously reported by us [4]. It clearly indicates that palladium also in (**I**) is predominantly as Pd (0) (**Appendix, Fig. 2a.**).

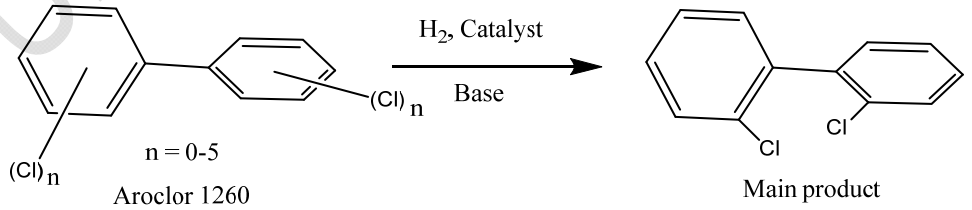
Results of Pd K-edge EXAFS analysis (**Appendix, Fig. 2b**) suggested that Pd in (**I**) is in the form of Pd(0) metallic nano-particles with fcc crystalline structure, similar to that found in mono- and bi-metallic (Pd-EPS and FePd-EPS) samples from previous investigations [4]. However smaller nano-clusters of Pd metal are formed and the average size of Pd metal nanoparticles is less than 1 nm (**Appendix, Table 1**). Furthermore, in EXAFS analysis of Pd neighborhood, we found that part of Pd atoms is coordinated to oxygen atoms at about 1.97 Å which is characteristic for Pd oxides (**Appendix, Table 1**). So it is possible that about 10% of Pd atoms is in the form of PdOx nanoparticles simply encapsulated in the polysaccharide moiety or that Pd atoms located on the surface of the Pd metallic nanoparticles may be bonded to the OH or COOH groups of EPS. The results (**Appendix, Fig. 2b**) are similar, but not identic, to those observed on mono- and bi-metallic samples [4].

The Pt L3-edge XANES analysis would suggest that there are two forms of Pt in (**I**), one is metallic Pt(0) nanoparticles (about 36 %), as expected, the other in the form of a Pt(II) complex bound to two Cl atoms and two nitrogen atoms like in $PtCl_2(pyridine)_2$ (**Appendix, Fig 3a**) [12]. Pt L3-edge EXAFS results strongly support this finding (**Appendix, Fig 3b**, **Table 2**). The results clearly suggest that microorganism *Klebsiella oxytoca* encapsulates Pt species in EPS partly in the form of metallic Pt(0) nanoparticles and partly in the form of complexes structurally similar to $PtCl_2(pyridine)_2$. It is difficult to have a clear-cut explanation for the latter form. Maybe $PtCl_2$, originally added to the fermentation broth, can bind to nitrogen heterocyclic species, e.g. piperazine derivatives, probably formed during the fermentation process [13].

The Ce L3-edge XANES analysis (**Appendix, Fig. 4**) and the comparison with $CeVO_4$ and $CeO_2$ XANES spectra showed that all Ce in the $Met_x$-EPS sample is in the form of three valent Ce cations, most probably in the form of $Ce^{3+}$oxide nanoparticles [14]. Finally the results of Zr and Rh EXAFS analysis of $Met_x$-EPS sample (**Appendix, Figs. 5 and 6**) suggested that both elements, Zr and Rh, are in oxidized form, as a mixture of different Zr and Rh nano-oxides. Zr-Zr distances are characteristic for Zr oxides [15] while Rh-Rh distances are characteristic for crystalline $Rh_2O_3$ [16] . Also Ce, Zr or Rh cations coordination to OH and COOH groups cannot be excluded.

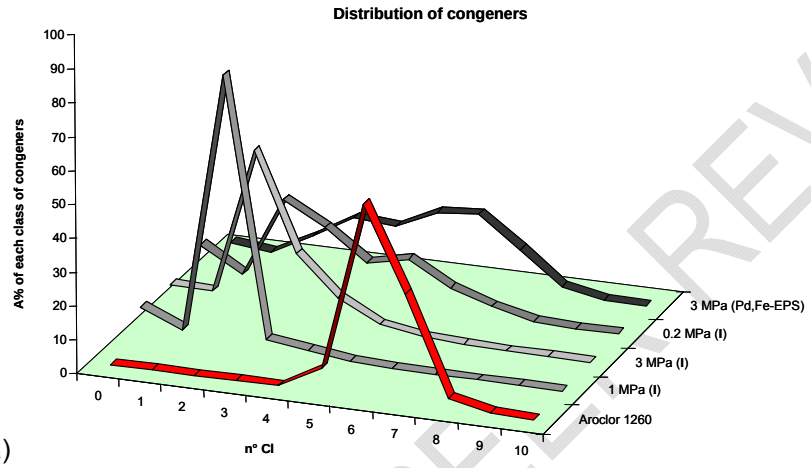
## 3.2 Catalyst activity

Removal of polychlorinated pollutants present in water by catalysed hydrodechlorination is still a challenging target due to the presence of different catalyst poisons. As part of our research activity in environmental remediation and in finding potential sustainable protocols using heterogeneous water compatible catalysts we had recently studied the hydrodechlorination of a methanolic solution of Aroclor 1260 (a reference PCB mixture) with Pd-EPS and Fe,Pd-EPS in pure distilled water in the presence of ammonium acetate [5] (**Scheme 1**).

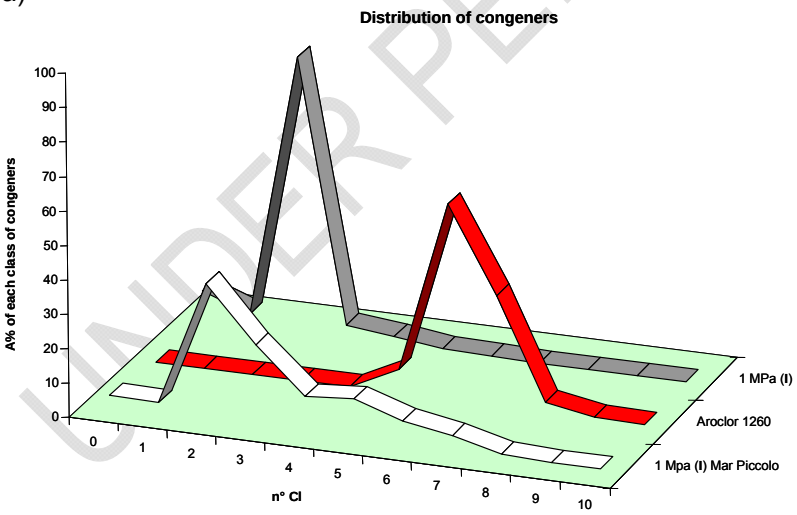



**Scheme 1**. Hydrodechlorination of Aroclor 1260.

An improvement in the dehalogenation reaction using the bimetallic catalyst had been observed working at a pressure of 3MPa of hydrogen with a substrate/catalyst 8/1 molar ratio (referred to Pd amount), at 60°C in 20 h, but a relevant amount of $Cl_5$-$Cl_7$ congeners was still present. Therefore we were encouraged to test this new polymetallic ($Met_x$-EPS) (**I**) on the same substrate to try to improve our previous results, working either in pure distilled water or diluting this PCBs mixture in a sample of polluted sea water taken from Mar Piccolo (Taranto, Italy) which contained also other pollutants such as PAHs and heavy metals. Quite surprising, very stimulating and promising results were achieved working under much milder reaction conditions. As shown in Fig. 1a it was possible to obtain a complete removal of congeners having a content of chlorine atoms >3 working at a pressure of 1MPa of hydrogen with the same substrate/catalyst 8/1 molar ratio (referred to Pd amount). Quite satisfactory results were also obtained using a real polluted water spiked with Aroclor 1260 as depicted in Fig. 1b.




a)




b)

**Fig. 1**. Hydrodechlorination of Aroclor 1260 results compared with previous best results [5]: a) in pure water; b) diluting Aroclor 1260 in polluted sea water of Mar Piccolo

It indicates that this new catalyst is quite robust and is able of working in water and of resisting to the poisoning. Synergic positive effects due to the presence of polymetals were clearly demonstrated either in the hydrodechorination reaction or in the ability to break down/reduce the amounts of palladium poisons present in the polluted sea water. Furthermore PCBs concentrations of some very toxic dioxin–like PCBs congeners: BZ 118, 156, 157, 167, 170, 180, 189 in Aroclor 1260 were reduced to nearly zero (A%) (**Table B**) using this new catalyst and it is a significant improvement in the used protocol.

**Table B.** PCBs concentrations of some dioxin–like PCBs congeners: BZ 118, 156, 157, 167, 170, 180, 189 in Aroclor 1260 and in the product obtained after hydrogenation in the presence of Pd, Fe-EPS or $Met_x$-EPS(**I**)

| BZ Number of some dangerous PCBs congeners [a] | Aroclor 1260 A % | Pd,Fe-EPS A % (3 MPa of $H_2$)[b] | $Met_x$-EPS(**I**) A % (1 MPa of $H_2$) |
|---|---|---|---|
| **118** (+149) | 10.18 | 5.16 | 0.04 |
| **156** (+173) | 1.84 | 0.39 | nd |
| **157** (+197) | 0.31 | 0.07 | nd |
| **167** | 0.72 | 0.29 | nd |
| **170** (+190) | 4.25 | 1.33 | nd |
| **180** | 8.88 | 3.27 | nd |
| **189** | 0.13 | 0.02 | nd |

[a] congeners number according to Ballschmiter K, Zell M(1980) Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography. Fresenius Z Anal Chem 302: 20-31; [b] see ref. [5]; nd = not detected

## 4. CONCLUSION

The idea to prepare new polymetallic species embedded in a polysaccharide moiety starting from spent catalytic converters was realized as a contribution of alternative valorisation of metallic wastes and direct preparation of new metallic catalysts. Even if no metallic alloy seems to be evident, nevertheless positive synergies among the different metals were found when(**I**) was used as a catalyst in the removal of PCBs by hydrodechlorination reaction, permitting to work under milder conditions with a better efficacy than previous studies [5]. Finally, a promising preliminary application for the removal of these pollutants even in contaminated aqueous sites has been carried out, showing that the catalyst is quite robust and potentially useful for a continuous process.

## COMPETING INTERESTS

The authors declare no conflict of interest.

## REFERENCES


[1] Jadhav UU, Hocheng H, Achiev J. A review of recovery of metals from industrial waste. Mat. Manufacturer Eng. 2012; 54: 159-167.

[2] Izatt RM, Izatt SR, Bruening RL, Izatt NE, Moyer BA. Challenges to achievement of metal sustainability in our high-tech society. Chem. Soc. Rev. 2014; 43: 2451-2475.

[3] Baldi F, Marchetto D, Paganelli S, Piccolo O. Bio-generated metal binding polysaccharides as catalysts for synthetic applications and organic pollutant transformations. New Biotechnology 2011; 29: 74-78.

[4] Arčon I, Paganelli S, Piccolo O, Gallo M, Vogel-Mikuš K, Baldi F. XAS analysis of iron and palladium bonded to a polysaccharide produced anaerobically by a strain of *Klebsiella oxytoca*. J. Synchrotron Rad. 2015; 22: 1215-1226.

[5] Baldi F, Gallo M, Paganelli S, Tassini R, Sperni L, Piccolo O, et al. Hydrodechlorination of Aroclor 1260 in Aqueous Two-phase Mixture Catalyzed by Biogenerated Bimetallic Catalysts. Int. Res. J. Pure & Appl.Chem. 2016; 11: 1-9 and loc. ref.

[6] Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Rad. 2005;12: 537-541.

[7] Rehr JJ, Albers RC, Zabinsky SI. High-order multiple-scattering calculations of x-ray-absorption fine structure. Phys. Rev. Lett. 1992; 69: 3397-3400.

[8] Papageorgiou SK, Kouvelos EP, Favvas EP, Sapalidis AA, Romanos GE, Katsaros FK. Metal–carboxylate interactions in metal–alginate complexes studied with FTIR spectroscopy. Carbohydr. Res. 2010; 345: 469-473.

[9] Tan L, Dong H, Liu X, He J, Xu H , Xie J. Mechanism of palladium(II) biosorption by *Providencia vermicola*. RSC Adv. 2017; 7: 7060-7072.

[10] Leone S, De Castro C, Parrilli M, Baldi F, Lanzetta R. Structure of the Iron-Binding Exopolysaccharide Produced Anaerobically by the Gram-Negative Bacterium *Klebsiella oxytoca* BAS-10. Eur.J.Org. Chem 2007; 5183-5189.

[11] Wong J, Lytle FW, Messmer RP, Maylotte DH. K-edge absorption spectra of selected vanadium compounds. Phys. Rev. B 1984; 30: 5596-5610.

[12] Arčon I, Kodre A, Abra RM, Huang A, Vallne JJ, Lasič DD, Colloids and Surfaces B: Biointerfaces , 2004, 33, 199-204.

[13] Meng W, Xiao D, Wang R. Enhanced production of tetramethylpyrazine in *Bacillus licheniformis* BL1 by *bdhA* disruption and 2,3-butanediol supplementation. World J. Microbiol. Biotechnol. 2016; 32: 32-46.

[14] Kozjek Škofic I, Padežnik Gomilšek J, Kodre A, Bukovec N, Solar Energy Materials & Solar Cells , 2010, 94 , 554-559.

[15] Bouvier P, Djurado E, Ritter C, Dianoux AJ, Lucazeau G. Low temperature phase transformation of nanocrystalline tetragonal ZrO2 by neutron and Raman scattering studies. Int. J. Inorg. Mater. 2001; 3: 647-654.

[16] Coey JMD. The crystal structure of $Rh_2O_3$. Acta Cryst. 1970; B 26: 1876-1877.

## APPENDIX

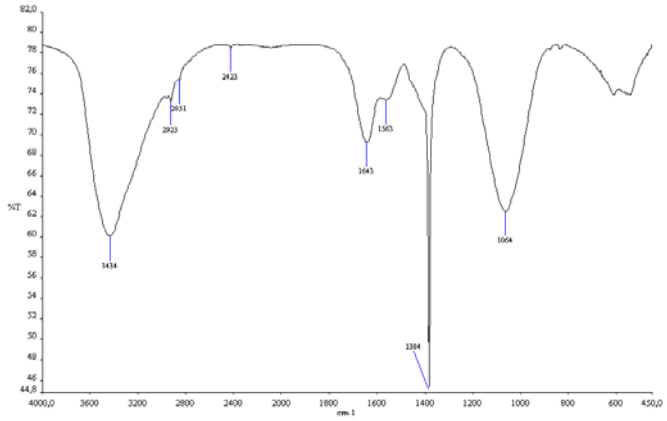


**Fig. 1.** FT-IR spectrum of $Met_x$-EPS

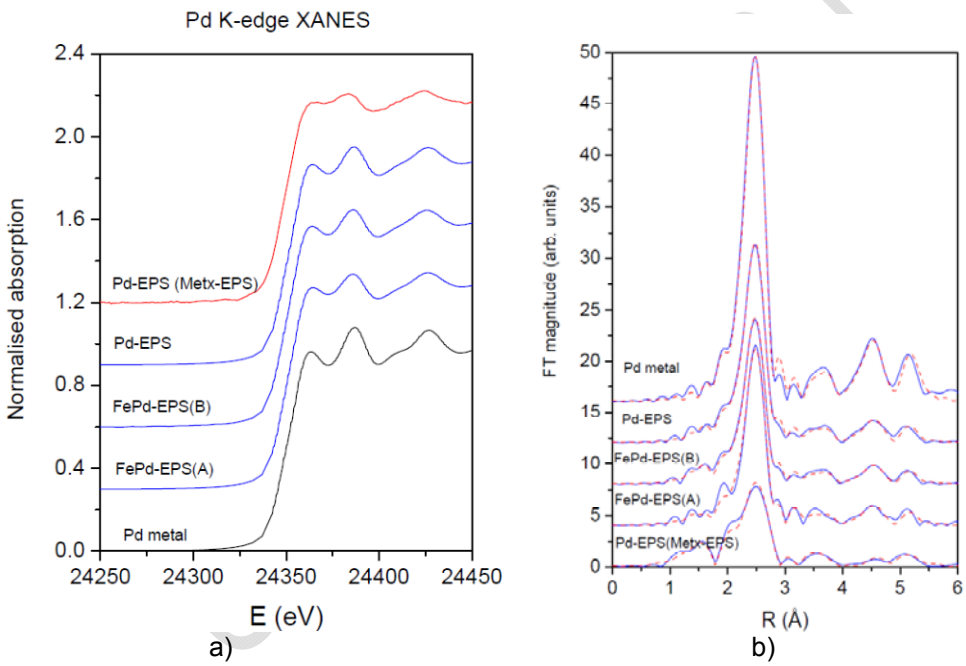



**Fig. 2. a**)Pd K-edge XANES spectra of the Pd-species in $Met_x$-EPS sample compared to Pd-EPS, FePd-EPS(A), FePd-EPS(B) samples and reference Pd metal foil with f-c.c. crystal structure; **b**) Pd EXAFS Fourier transform magnitude of k3-weighted Pd EXAFS spectra of Pd-EPS, FePd-EPS(A), FePd-EPS(B), Pd-species in $Met_x$-EPS samples and Pd metal foil, calculated in the k range 3–16 $Å^{-1}$ and R range 1–5.5 Å . Experiment: solid line; best-fit EXAFS model of the nearest coordination shells: dashed line.

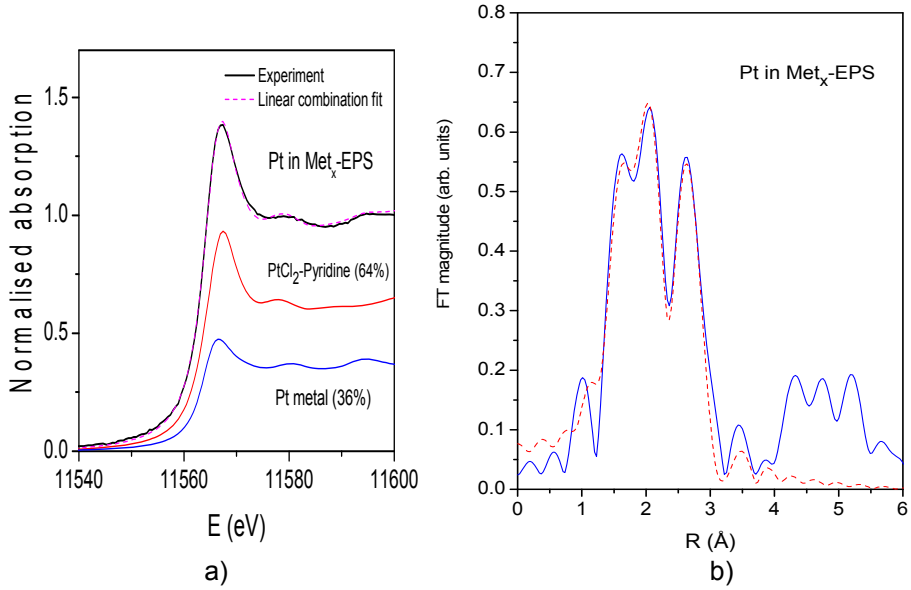



**Fig. 3**. **a**) Pt L3-edge XANES spectrum measured on the Pt in Metx-EPS sample: Black solid line: experiment; magenta dashed line: best-fit linear combination of XANES profiles of Pt fcc metal (36%), and cis-dichlorobis pyridine platinum reference compound (64%); **b**) Fourier transform magnitude of k2-weighted Pt L3-edge EXAFS spectra of Pt in Metx-EPS sample, calculated in the k range 3–12 Å$^{-1}$ and R range 1–3.8 Å. Experiment: solid line; best-fit EXAFS model of the nearest coordination shells: dashed line.

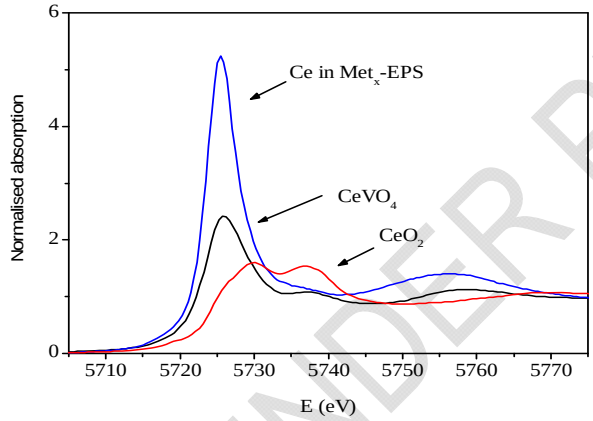



**Fig. 4**. Ce L3-edge XANES spectra of the Ce species in Met$_x$-EPS sample compared to $CeVO_4$ and $CeO_2$ spectra as references for $Ce^{3+}$ and $Ce^{4+}$, respectively.

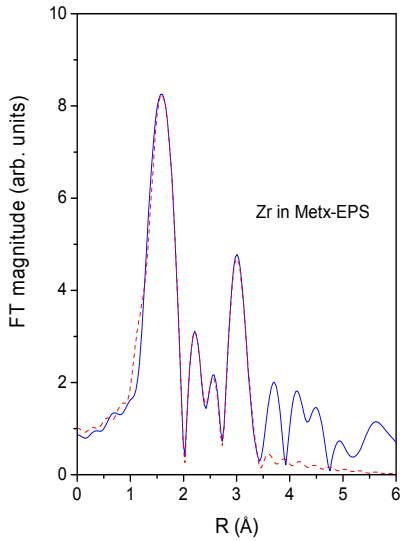



**Fig. 5**. Fourier transform magnitude of k3-weighted Zr K-edge EXAFS spectra of Zr in $Met_x$-EPS sample, calculated in the k range 3–11 $Å^{-1}$ and R range 1–3.4 Å. Experiment: solid line; best-fit EXAFS model of the nearest coordination shells: dashed line.

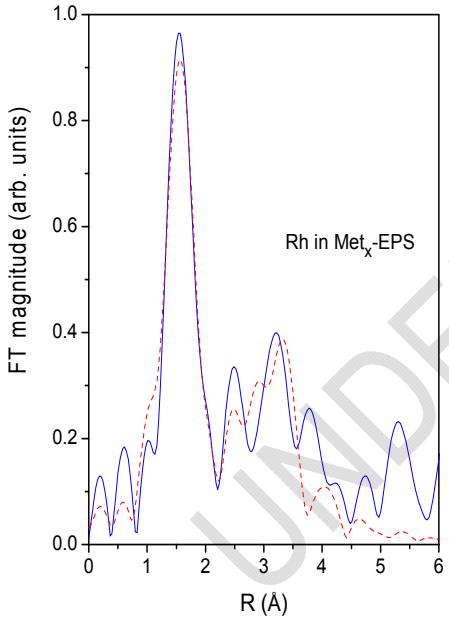



**Fig. 6**. Fourier transform magnitude of k2-weighted Rh K-edge EXAFS spectra of Rh in $Met_x$-EPS sample, calculated in the k range 3–11 $Å^{-1}$ and R range 1–3.4 Å. Experiment: solid line; best-fit EXAFS model of the nearest coordination shells: dashed line.

**Table 1.** Parameters of the nearest coordination shells around Pd atoms in $Met_x$-EPS sample and in reference Pd metal foil with fcc crystal structure (a=3.8900 Å): average number of neighbour atoms (*N*), distance (*R*), and Debye-Waller factor ($\sigma^2$). Uncertainty of the last digit is given in parentheses. A best fit is obtained with the amplitude reduction factor $S_0^2$ = 0.87. The goodness-of-fit parameter, *R*-factor, is given in the last column.

| Pd neigh. | *N* | *R* [Å] | $\sigma^2$ [Å$^2$] | *R*-factor |
|---|---|---|---|---|
| | | Pd in the $Met_x$-EPS sample | | |
| O | 1.4(2) | 1.97(1) | 0.005(2) | |
| Pd | 0.6(3) | 3.50(4) | 0.008(4) | |
| Pd | 5.3(6) | 2.749(4) | 0.0075(6) | 0.014 |
| Pd | 4(2) | 3.91(1) | 0.013(1) | |
| Pd | 7(2) | 4.77(1) | 0.013(1) | |
| Pd | 7(3) | 5.53(1) | 0.013(1) | |
| | | **Reference Pd metal foil** | | |
| Pd | 12 | 2.745(2) | 0.0058(2) | |
| Pd | 6 | 3.896(2) | 0.0086(5) | 0.003 |
| Pd | 24 | 4.772(2) | 0.0088(5) | |
| Pd | 12 | 5.510(2) | 0.0090(5) | |

**Table 2.** Parameters of the nearest coordination shells around Pt atoms in $Met_x$-EPS sample: average number of neighbour atoms (*N*), distance (*R*), and Debye-Waller factor ($\sigma^2$). Uncertainty of the last digit is given in parentheses. A best fit is obtained with the amplitude reduction factor $S_0^2$ = 0.91. The goodness-of-fit parameter, *R*-factor, is given in the last column.

| Pt neigh. | *N* | *R* [Å] | $\sigma^2$ [Å$^2$] | *R*-factor |
|---|---|---|---|---|
| N | 1.2(3) | 2.04(3) | 0.002(1) | |
| Cl | 1.2(3) | 2.37(4) | 0.003(4) | 0.02 |
| Pt | 7(3) | 2.71(1) | 0.013(1) | |
| C | 4.6(8) | 2.97(7) | 0.003(2) | |