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1 **Trace metal sorption on nanoplastics: an innovative analytical approach combining**
2 **surface analysis and mass spectrometry techniques.**

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10 **Abstract:** The mass and volume concentration of nanoplastics is extremely low, but incredibly high in
11 terms of surface area; this is expected to increase their toxicity through the ab/adsorption and transport
12 of chemical co-pollutants such as trace metals. In this context, we studied the interactions between
13 nanoplastics model materials functionalized with carboxylated groups, with either smooth or raspberry-
14 like surface morphologies, and copper as representative of trace metals. For this purpose, a new
15 methodologie, using two complementary surface analysis techniques: Time-of-Flight Secondary Ion Mass
16 Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) was developed. In addition,
17 inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the total mass of sorbed
18 metal on the nanoplastics.

19 This innovative analytical approach from the top surface to the core of nanoplastics demonstrated not
20 only the interactions with copper at the surface level, but also the ability of nanoplastics to absorb metal
21 at their core. Indeed, after 24 h of exposition, the copper concentration at the nanoplastic surface
22 remained constant due to saturation whereas the copper concentration inside the nanoplastic keeps

23 increasing with the time. The sorption kinetic was evaluated to increase with the density of charge of the
24 nanoplastic and the pH. This study confirmed the ability of nanoplastics to act as metal pollutant carriers
25 by both adsorption and absorption phenomena.

26 **Keywords:** Nanoplastics, metal sorption, XPS, ToF-SIMS, ICPMS.

27

28

29 **Introduction**

30 Plastics, due to their high demand in everyday usage, have been tremendously manufactured in the whole
31 world since the 1950's. The quantity produced increases year after year and results in an important
32 generation of waste. Around 10% of plastics are thrown away and hence found accumulated in the aquatic
33 systems (Koelmans and Kalčíková, 2019).

34 Characteristics such as low density, good mechanical properties, strong resistance to external stress and
35 low cost have contributed to the success of plastic materials in our daily lives. The problem with this type
36 of waste is that they tend to fragments into smaller pieces *i.e.* micro and nanoplastics (MPTs and NPTs)
37 through mechanical (Ekvall et al., 2019), photodegradation (Lambert and Wagner, 2016), chemical
38 degradation, or biodegradation (Dawson et al., 2018).

39 While microplastics represent particles with a diameter < 5 mm (Hartmann et al., 2019), NPTs are defined
40 as the smallest colloid plastic debris (1-1000 nm) of mixed shape and chemical composition (Gigault et al.,
41 2018). Although the breakdown of plastic waste is certainly the most common source of NPTs, material
42 wear such as synthetic fabrics or car tire abrasion can also lead to environmental NPTs.

43 NPTs represents an analytical challenge even up to this day due to their small size and low environmental
44 concentration (Mitrano et al., 2021). Currently, NPTs can be detected in several environmental
45 compartments, such as air (Masry et al., 2021), soil (Wahl et al., 2021), freshwater (Zhang et al., 2021),
46 oceans (Ter Halle et al., 2017) and biota (Kukkola et al., 2021) but not quantified. However, it is presumed
47 that due to their intrinsic properties, NPTs will have a greater impact onto biota. Indeed, unlike
48 microplastics, which may be stuck in living organisms, NPTs will pass biological barriers (e.g. the gut
49 epithelium) and enter the body of species (Grodzicki et al., 2021).

50 In addition, their small size implies a high surface-area-to-volume ratio, (Oriekhova and Stoll, 2018), which
51 is expected to increase their toxicity throughout the ab/adsorption and transport of chemical co-
52 pollutants such as trace metals or persistent organic pollutants (POPs) (Wagner and Lambert, 2018). The
53 interaction of different trace metals with environmental micro- or NPTs has already been demonstrated
54 mostly using metal in their higher oxidation states as Pb^{2+} (Davranche et al., 2019; Pessoni et al., 2019),
55 Cu^{2+} (Bellingeri et al., 2019), Ag^{2+} (Domenech et al., 2021) in different environmental conditions.
56 Furthermore, NPTs porosity, surface area, and polarity continue to grow due to aging, enabling a stronger
57 interaction with metals (Turner and Holmes, 2015). Indeed, the generation of oxygen containing groups
58 at NPT surface during weathering promotes the adsorption of hydrophilic pollutants such as metallic ions
59 (Mao et al., 2020). Finally, when studying the roles of NPTs as metal vectors, several environmental factors
60 influencing the rate and concentration of pollutant should be considered, including the surface chemistry
61 of NPTs, the pH of the medium and the exposure time (Zou et al., 2020).

62 Most of the aforementioned studies were focused on the evaluation of the kinetic of adsorption or the
63 adsorption capacity of MPTs or NPTs by the mean of classical isotherms theory. Nevertheless, to our
64 knowledge, the evaluation of the sorption of metallic ions both at the surface and the core of a NPTs has
65 not yet been studied. Such compartment could increase the preconcentration of pollutants by the NPTs
66 and thus accentuate their ability to act as a vector of pollutant.

67 The aim of the present study was to assess the interactions between NPTs and copper at both the surface
68 and core scale. The diffusion coefficient of metal species within plastic polymer bodies was evaluated to
69 be extremely slow in comparison with those applicable for metal ions in bulk aqueous media (Town et al.,
70 2018).

71 There has been an increasing concern over the combined toxic effects of microplastics, NPTs and metallic
72 pollutants on aquatic organisms due to their intrinsic interaction. Copper has often been chosen as target

73 analyte because as trace metal it is ubiquitous and persistent in the environment. It is found in all aquatic
74 compartments due to anthropogenic inputs as organic agriculture. If copper remains an essential trace
75 element for organisms, excessive doses can induce toxic effects (Hoang et al., 2009). Studies performed
76 on different species pointed out the negative influence of NPTs to environmental species through their
77 interaction with copper (Bellingeri et al., 2020; Gao et al., 2022; Machado et al., 2021; Wan et al., 2021).

78 In this work, NPT model materials of polystyrene have been elaborated free of surfactants and
79 preservatives to avoid any bias of interpretation (Pikuda et al., 2019) and with a functionalized surface
80 mimicking the oxidized environmental samples. The interaction mechanisms between these NPT model
81 materials and copper were studied at the surface scale using two surface analysis techniques: Time-of-
82 Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS). The
83 former was chosen to evaluate the elemental and molecular composition at the extreme surface (1-2nm)
84 of NPTs, while the latter was used to quantitatively characterize the chemical composition of the NPTs
85 surface (5-10nm). In addition, inductively coupled plasma mass spectrometry (ICP-MS) was used to
86 quantify the total mass of the sorbed metal on NPTs.

87 **Materials and Methods**

88 **Materials.** Acrylic Acid (AA \geq 99%), styrene (S \geq 99%), ammonium persulfate (APS \geq 99%), copper (II)
89 nitrate hydrate ($\text{Cu}(\text{NO}_3)_2$), nitric acid (HNO_3) (Sigma-Aldrich), sodium hydroxide pellets (NaOH) (ABCR)
90 were used as received without further purification unless noted. Deionized water, with a resistivity of 18.2
91 $\text{M}\Omega \text{ cm}^{-1}$ at 25°C, was filtered through a 0.22 μm Millipore filter prior to use.

92 **Synthesis of NPT material models.** Styrene / acrylic acid copolymer nanoparticles were elaborated by a
93 soap-free copolymerization process using APS as initiator. The detailed procedure of polymerization is
94 reported elsewhere (Pessoni et al., 2019).

95 All the reactions were performed at 70 °C under nitrogen atmosphere with a mechanical stirring at
96 350 rpm. The recipe for the copolymerization process is listed in Table S1. The NPT suspension was
97 purified by at least 5 cycles of centrifugation-dispersion in deionized water at 12 000 rotation per min
98 during 30 min until the supernatant conductivity is equal to that of deionized water.

99 **Microscopy.** The morphology of the NPT models were investigated by scanning electron microscopy
100 (SEM) using a Hirox SH-3000 with a 25 kV accelerated voltage. Atomic Force Microscope (AFM) images
101 were recorded using an AFM MultiMode8® from Bruker©, on peak force mode.

102 **Surface area.** The surface area was computed with the BET theory (Brunauer et al., 1938) applied on the
103 N₂ adsorption isotherm measured at 77 K on the Micromeritics® Tristar II 3020. Even if the surface area
104 computed are small, the criterion of Rouquerol *et al.* (Rouquerol et al., 2007) was used to accurately select
105 the range of relative pressures for the calculation of the specific surfaces. The surface area occupied by a
106 N₂ molecule at 77 K was taken as $\sigma = 16.2 \text{ \AA}^2$.

107 **Titration.** The titration measurements were performed on a Titrand 888 equipped with a stirrer 728 and
108 a combined pH glass electrode (pH: 0-14; 0-80°C; KCl: 3 M). All components were purchased from
109 Metrohm. The software used was Tiamo 2.5. The pH of the nanoparticle aqueous solution (1000 mg L⁻¹)
110 was increased to 10 with a 0.1M NaOH solution, then carboxylate functions were titrated using a 0.5x10⁻³
111 M HCl solution. The supernatant was titrated using a 0.1M NaOH solution.

112 **Copper and NPT exposure.** A stock solution of NPTs (80000 mg L⁻¹) and a stock solution of copper (40000
113 mg L⁻¹) prepared by solubilizing copper (II) nitrate crystals into ultrapure water were used to prepare
114 40000 mg L⁻¹ NPT dispersion with a copper concentration of 2000 mg L⁻¹. The pH was adjusted to 5 by
115 using a 1 M NaOH solution. The Cu/NPTs mixture was then left under stirring for 24 to 144 hours at room
116 temperature. The mixtures were then purified by centrifugation at 15000 rpm during 30 min, the
117 supernatant was collected to be analyzed by ICPMS whereas the pellet (NPTs with copper sorbed) was

118 redispersed in an equal volume of deionized water. This process of centrifugation, removal of the
119 supernatant and replacement by an equal volume of deionized water was reproduced two extra times.
120 After 3 cycles of centrifugation less than 3 % of residual copper was measured by ICPMS in the supernatant
121 (**Figure S6**). 50 μL of the washed mixture was deposited by drop casting onto a 10 mm^2 silica wafer cleaned
122 beforehand by UV/ozone exposition during 15 min to be analyzed by XPS and ToF-SIMS.

123 **XPS.** X-Ray Photoelectron Spectroscopy (XPS) measurements were performed on a Thermo K-alpha
124 spectrometer equipped with a focused monochromatized Al-K α radiation ($h\nu=1486.6$ eV). Core ionization
125 peaks were recorded with a 20 eV constant pass energy (PE) over an ellipsoidal area of 200 x 400 μm .
126 Charge effects were compensated by the use of a dual-beam charge neutralization system (low energy
127 electrons and ions). Data treatment was performed with CasaXPS software. Peak fitting was processed
128 with a non-linear Shirley-type background and mathematical components are obtained by a weighted
129 least-squares calculation method using 30 % Lorentzian and 70 % Gaussian line shapes. Spectral
130 calibration was done based on the C1s component at 285 eV binding energy, attributed to C-C/C-H
131 environment. Quantifications were calculated using Scofield's relative sensitivity factors corrected by -0.6
132 in intensity.

133 **ToF-SIMS.** ToF-SIMS analysis were carried out using a TRIFT V nanoToF II (Physical Electronics, Chanhassen
134 (MN), US) equipped with a 30 kV Bi-LMIG. All mass spectra were acquired at room temperature using the
135 same experimental conditions, so that to perform semi-quantitative analysis (comparing the ratio of peaks
136 intensities). For surface analysis ("bunched" mode, best mass resolution), the LMIG gun was tuned to
137 deliver Bi $_3^{++}$ bismuth clusters primary ions with a dc current of 12 nA over a 50 μm raster size; the mass
138 range was fixed between 0 and 2000 uma and the number of frames was set to 50 (dose: 5.4×10^{12}
139 ions/ cm^2) for both polarities. For 2D imaging ("unbunched" mode, best spatial resolution), a resolution of
140 256x256 image pixels, with a time per channel of 128, over 50x50 μm^2 field-of view was used and the

141 PIDD (primary ion dose density) never exceeded the static limit of 2.10^{13} ion.cm⁻². Dual beam (15 eV e⁻
142 /10eV Ar⁺) charge compensation system was used for all analyses. Data processing was performed using
143 ToF-DR software provided by Physical Electronics. All positive polarity mass spectra were calibrated using
144 CH⁺ (m/z = 13), CH₂⁺ (m/z = 15) and Na⁺ (m/z 23) peaks and all negative polarity mass spectra were
145 calibrated considering CH⁺(m/z = 13), C₂H⁺ (m/z = 15) and OH⁻ (m/z = 17) peaks.

146 **ICPMS.** An Agilent 7900 ICPMS (Agilent, Tokyo, Japan) was used to determine the total copper content in
147 the supernatant by monitoring isotopes ⁶³Cu and ⁶⁵Cu. The system consists of an integrated auto-sampler,
148 a concentric nebulizer and a quartz cyclonic spray chamber as a sample introduction system. Each sample
149 was analyzed by triplicate. Results are expressed as the mean of three measurements.

150 **Copper sorption.** The equilibrium copper concentration in the supernatant was determined by ICPMS.
151 The sorbed amount of copper Q_{sorb} (mg g⁻¹) was determined according to the equation 1 where C_0 is the
152 initial copper concentration (mg L⁻¹), C_e is the residual copper concentration in the supernatant (mg L⁻¹) of
153 the first centrifugation step (see “Copper and NPT exposure” part), V is the total volume of the solution
154 (L) and m is the total NPT mass (g). The theoretical maximum of sorption $Q_{e,max}$ is obtained when $C_e = 0$.

$$155 \quad Q_{sorb} \text{ (mg g}^{-1}\text{)} = \frac{(C_0 - C_e)V}{m}$$

156 **Equation 1**

157 Environmental NPTs concentration is estimated to be at ppt range, however, without appropriate
158 sampling methods and sample treatment, underestimations of actual environmental concentrations
159 should not be excluded. Moreover, environmental concentration of both NPTs and pollutant vary over
160 time and spatiotemporal hotspots are more than probable. In our work, we decided to perform the
161 sorption experiment at relatively high NPTs concentrations considering the aforementioned remarks, i.e.
162 40000 mg L⁻¹ and the samples have been exposed to 2000 mg L⁻¹ of copper. Such experimental conditions

163 were necessary to favor sorption kinetics and being at a laboratory experiment time scale. Additionally,
164 these experimental concentrations were expected to allow both phenomena, *i.e.* adsorption and
165 absorption to occur while low concentration would very preferably to adsorption due to the stronger
166 interaction forces on the surface.

167 **Results and discussion**

168 **Nanoplastics material models synthesis and characterization.**

169 The soap-free process involves the copolymerization of a hydrophobic and a hydrophilic monomer. The
170 latter may be both polymerized and located either within the core or at the surface of the polymer
171 particles during their elaboration process. Only the part of it present at the latex particle surface provides
172 particle stability in water (Ceska, 1974).

173 Acrylic acid (AA) and styrene (S) were used in this work as hydrophilic and hydrophobic monomers
174 respectively. Beyond providing stability to the particles, the use of a carboxylic acid monomer as AA allows
175 to reproduce the surface oxidation occurring in environmental condition (Fotopoulou and Karapanagioti,
176 2012; ter Halle et al., 2017). Two batches have been synthesized and named PS9 and PS22; they differ
177 from the carboxylic content, *i.e.* the former was obtained with a monomer molar ratio $AA/S = 0.09$ while
178 the second latter corresponds to a molar ratio $AA/S = 0.22$. After polymerization in water dispersed
179 medium and purification, the NPTs were characterized in terms of size and size dispersity.

180 The polydispersity index (PDI) values of the samples were lower than 0.05 suggesting a narrow size
181 distribution *i.e.* monodisperse NPTs. The average particle size was measured in aqueous solution using
182 DLS; PS22 and PS9 exhibit a diameter size of 330 and 350 nm, respectively. This slight difference of particle
183 size can be explained by the initial acidic monomer content in the polymerization feed. Indeed, a higher
184 AA/S molar ratio results in the nucleation of more primary particles. As the concentration of monomer is

185 fixed in both synthesis, the number of monomer units per nanoparticle decreases and therefore the size
186 of latex particles is reduced (Polpanich et al., 2005)

187 The surface morphology has been characterized by SEM and AFM (Figure 1). PS9 and PS22 are spherical
188 particles differing from each other by their roughness as confirmed by AFM measurement. A smooth
189 surface with few defects was observed for the PS9 sample, while a rough surface assimilated to a
190 raspberry-like morphology was observed for the PS22.

191 Additionally, the specific surface of both samples was determined using the Brunauer-Emmett-Teller (BET)
192 method (**Figure S1**). As expected, the sample with a smooth surface (PS9) shows a lower specific surface,
193 with a value of $15 \text{ m}^2 \text{ g}^{-1}$ for PS9, while a specific surface of $29 \text{ m}^2 \text{ g}^{-1}$ was obtained for the sample PS22.
194 The higher surface area of PS22 sample in comparison to that of PS9 is in agreement with a difference of
195 roughness between the two samples as observed by AFM. The specific surface area for PS9 is close to the
196 one theoretically calculated considering a solid and smooth sphere ($16 \text{ m}^2 \text{ g}^{-1}$), while the experimental
197 result is twice as high as the theoretical one for the PS22 ($17 \text{ m}^2 \text{ g}^{-1}$).

198 The number of carboxylic functions by mean surface area (Equation 2) is obtained by dividing the amount
199 of acid groups by the surface area (measured by BET) of the titrated particles while the number of
200 carboxylic functions by grams of particles was obtained by dividing the number of titrated groups by the
201 mass of particles (Equation 3).

$$202 \quad [COOH](mol/nm^2) = \frac{n_{COOH}}{S_{Spec.} \times (\frac{m}{V \times \rho_{sty}})}$$

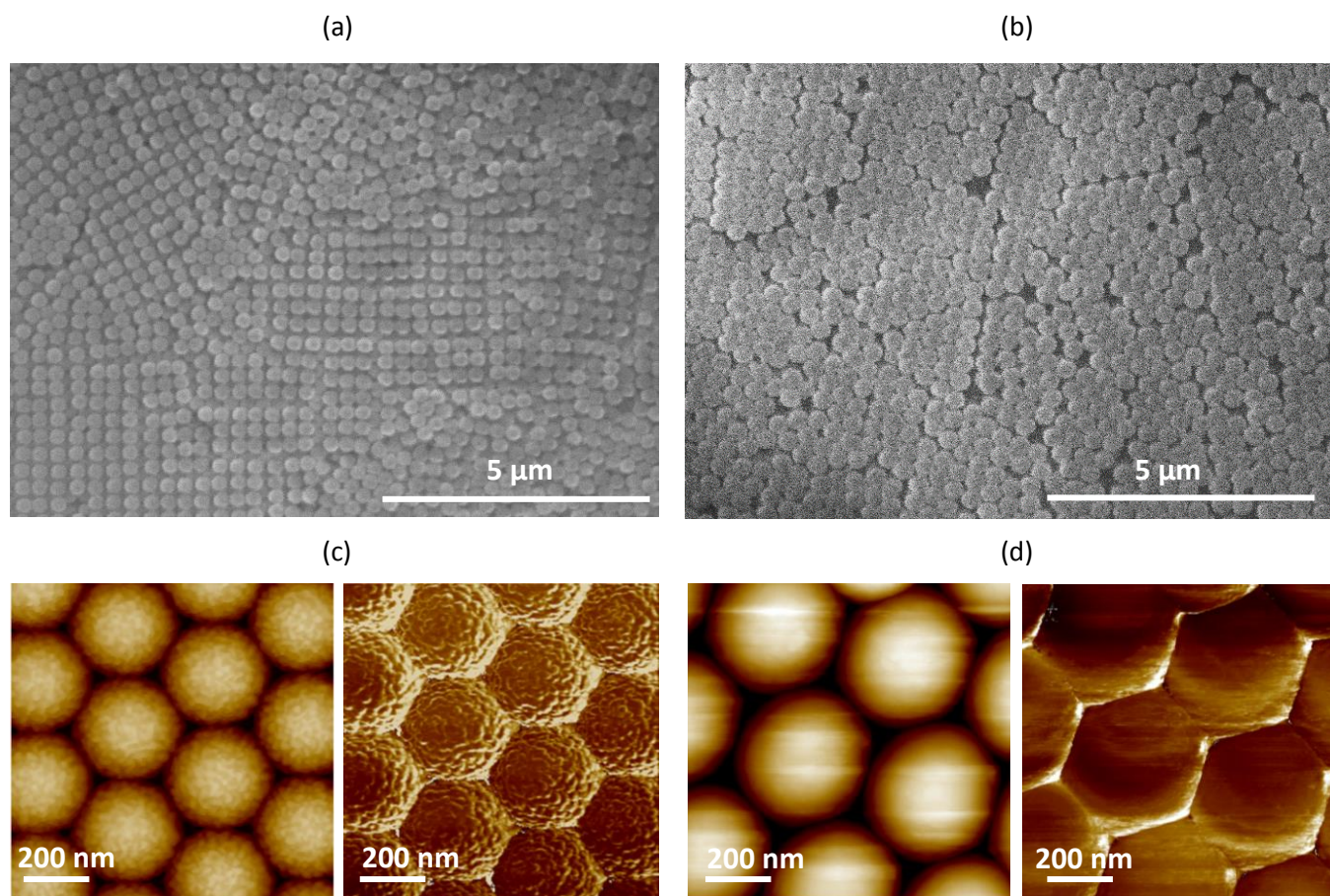
203 **Equation 2**

204

$$205 \quad [COOH](mol/g) = \frac{n_{COOH}}{m}$$

206 **Equation 3**

207 Where n_{COOH} (mol) is the number of carboxylic groups obtained by titration, S_{spec} ($\text{nm}^2 \text{g}^{-1}$) is the specific surface
208 determined by BET measurement, m (g) is the mass of NPTs, V is the volume of NPTs (cm^3), ρ_{sty} (g cm^{-3}) is the
209 density of polystyrene given at $1,04 \text{ g cm}^{-3}$.
210 PS22 and PS9 surface functionality reach respectively 24 COOH groups per nm^2 ($1.15 \text{ mmol}_{\text{COOH}} \text{ g}^{-1}$) and
211 $5 \text{ COOH}/\text{nm}^2$ ($0.11 \text{ mmol}_{\text{COOH}} \text{ g}^{-1}$).



212
213 **Figure 1.** First line: SEM images of a NPT film (a) PS22, (b) PS9 ; Second line Peak Force mode AFM images, height profile
214 (left), deformation profile (right) of the NPT film : (c) PS22 and (d) PS9.

215

216 **Exposure to copper.** The interaction between NPTs with a carboxylic functionalized-surface and copper
217 was investigated at pH of 3 and 5. If, a higher pH may appear to be more relevant to environmental
218 conditions, those conditions have been chosen to favor the NPTs/copper interaction. Indeed, the
219 literature reports pKa of 4.1 and 4.5 respectively for the acrylic acid monomer and the poly(acrylic acid),
220 respectively (Michaels and Morelos, 1955; Wiśniewska and Chibowski, 2005) and ionic copper is in

221 complexed form above pH 5 (Cuppett, 2006). Working from pH 3 to 5 ensures to keep copper under its
222 free ionic state and to have partially to predominantly negatively charged carboxylate groups at the NPTs
223 surface at the same time, thus favoring the interaction phenomena study. The effect of the surface
224 carboxylic group content is evaluated onto sorption mechanism as an image of the effect of the surface
225 oxidation *i.e.* aging of plastic debris. After an exposure time ranging from 24 to 144 hours, the samples
226 were analyzed by TOF SIMS and XPS to characterize the surface chemical composition from 1-2 nm up to
227 10 nm depth respectively, and by ICPMS to determine the copper content of the whole NPTs. Therefore,
228 the differences between surface and bulk analysis results allows us to determine the copper adsorbed at
229 the extreme surface and the copper absorbed by the whole NPTs.

230 **Surface analysis of NPTs before copper exposure.** In order to quantitatively characterize the surface of
231 NPTs, the two batches of NPT models (PS9 and PS22) were analyzed by XPS before exposition to copper.
232 The main elements detected at the surface of the two NPT models were carbon and oxygen as shown by
233 the full scan survey spectrum (**Figure S2**). The C1s spectra highlights the presence of 4 types of carbon at
234 a binding energies of 285 eV, 285.8 eV, 289.5 eV and 291.6 eV, respectively assigned to **C-C/C-H**, **C-C=O**,
235 **O-C=O** and π - π^* (Table. 1). Both the C-CO and COO bindings are characteristics of the AA units.

236 These data confirm the presence of acid groups at the surface of the NPT models. The proportions of **CO**,
237 **COO** and **O=C**, **O-C** are higher for PS22 (8.8 at.% and 7.9 at.%) compared to PS9 (1.9 at.% and 2.2 at.%),
238 which confirms a higher density of carboxylic groups at the surface of the former and highlights the
239 influence of the initial AA content in the feed during the synthesis. These results also confirm XPS as a
240 technique able to provide quantitative chemical information of NPT surface.

241 **Table 1.** XPS quantitative analysis for PS22 and PS9 samples.

Region	Be (eV)	FWHM (eV)	%at. Conc		Assignment
			PS22	PS9	
C1s	285.0	1.3	65.3	81.6	C-C / C-H
	285.8	1.3	8.8	1.9	CO
	289.5	1.5	8.8	1.9	COO
	291.6	1.3	1.3	5.6	π - π^*
O1s	533.5	1.8	7.9	2.2	O=C
	533.9	1.8	7.9	2.2	O-C

242

243 **Surface analysis of NPTs after copper exposure.** Quantitative and qualitative surface chemical
 244 composition of S/AA NPTs exposed to a copper solution was achieved by combining XPS and ToF-SIMS
 245 measurements.

246 *X-ray Photoelectron Spectroscopy (XPS)*

247 In addition to carbon and oxygen, after exposure copper was clearly identified as one of the main
 248 elements present at the surface of the NPT model materials on the XPS survey spectra (**Figure S3**).

249 The XPS C1s, O1s and Cu2p high-resolution spectra of NPTs exposed to copper for 24 h are presented in
 250 Erreur ! Source du renvoi introuvable.. The C1s core peak shows no difference in chemical environment
 251 with the results obtained before exposition.

252 The 4 types of carbon, C-C/C-H at 285eV, C-CO at 285.8 eV, COO at 289.5 eV and π - π^* at 291.6 eV, are
 253 still present with similar proportions. Also, no difference in the C1s chemical environment was noted as a
 254 function of either the incubation time within the copper solution (Erreur ! Source du renvoi introuvable.
 255 **and Figure S4**) or the pH of the solution (pH= 3 or 5) (Erreur ! Source du renvoi introuvable.). Such results
 256 confirm the absence of any bond between copper and carbon atoms that would have modified the carbon
 257 spectra.

258 Contrary to the C1s core peak, the O1s core peak shows a new component at a higher binding energy
259 (532.0 eV) after copper exposition, which is assigned to the oxygen bound to copper metal O-Cu. This
260 component is observed whatever the exposition time or the pH of the solution, but its atomic percentage
261 (presented in the **Table 2**) is clearly different depending on the type of NPTs and the pH with the following
262 tendency $PS22_{(pH5)} > PS9_{(pH5)} > PS22_{(pH3)} > PS9_{(pH3)}$. Indeed, the atomic percent of O-Cu for the PS22 sample
263 is measured at 4.5 and 0.8 % at pH 5 and 3 respectively while it is only 1.1 and 0.5 % for the PS9 at pH 5
264 and 3 respectively which proves the influence first of the pH and second of the carboxylic groups
265 proportion on the interaction with copper.

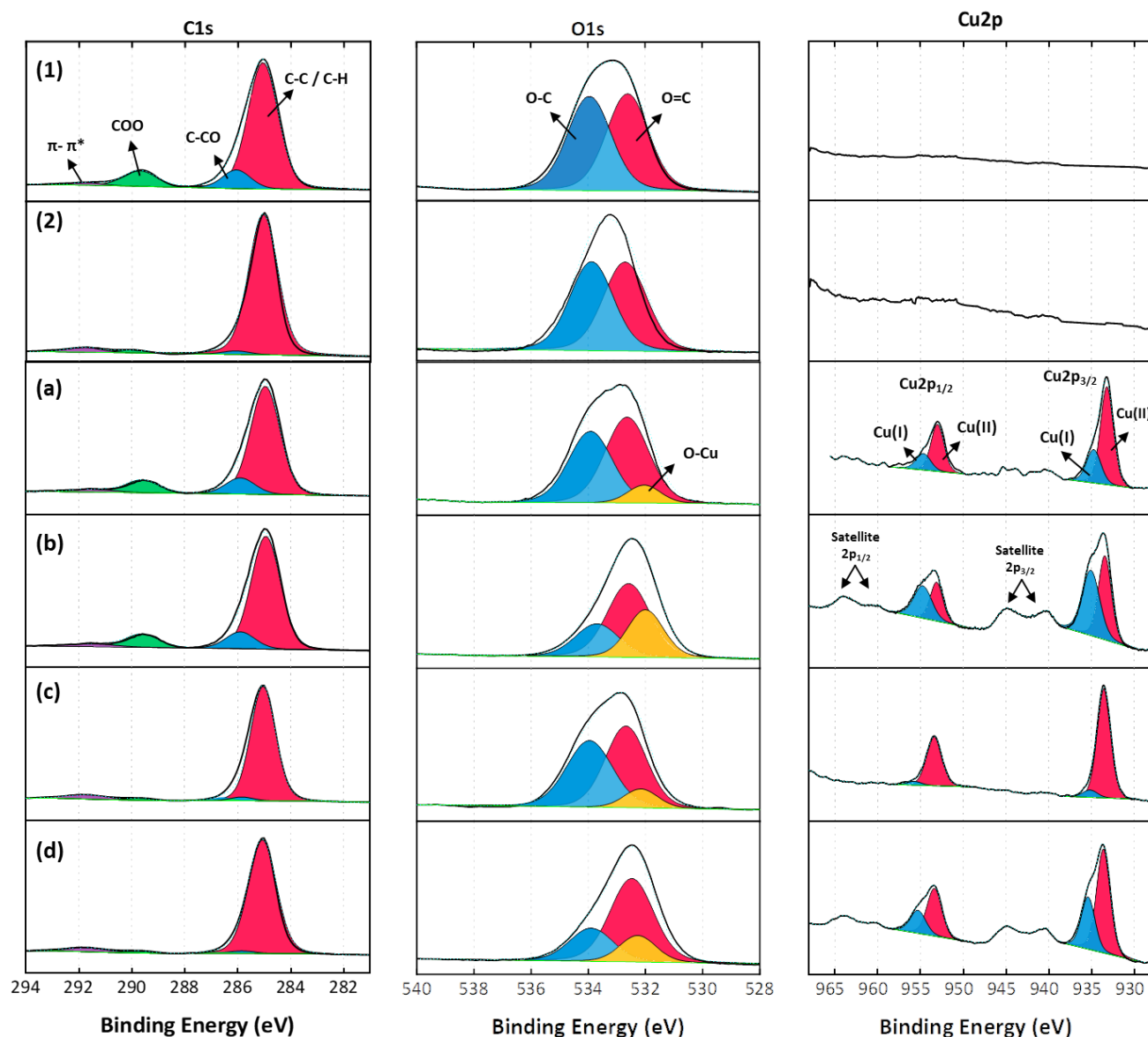
266 The Cu 2p core peak shows two main peaks assigned to Cu 2p_{3/2} and Cu 2p_{1/2} components due to the spin-
267 orbit coupling. Each peak can be deconvoluted into two components at 933.5 / 935.0 eV and 953.1 / 954.7
268 eV respectively, which are characteristics of a mixture of Cu(I) and Cu(II) species. In addition, the presence
269 of a shake-up satellite specific to the presence of Cu(II) species is also observed (Pauly et al., 2014), more
270 predominantly for pH 5. It is noted that the atomic percentage of Cu is more important at pH 5 compared
271 to pH 3 and for PS22 compared to PS9, which is in agreement with the results obtained for O1s.

272 Regarding the XPS quantitative analysis at different exposure times : 24 h (**Table 2**) ; 48 h (**Table S2**) and
273 144 h (**Table S3**), two results can be highlighted:

274 1) At the same exposure time, the adsorbed copper concentration increases both with the carboxylic acid
275 surface density and the pH ($PS22_{(pH5)} > PS9_{(pH5)} > PS22_{(pH3)} > PS9_{(pH3)}$). Indeed, PS22 sample exposed to
276 copper for 24 h exhibits anatomic % of Cu 2p component of 4.6 at pH 5 while it is only 0.9 at pH 3. Similarly,
277 for PS9 sample the measured atomic % is 2.1 at the highest pH and 0.4 at the lowest. Considering
278 carboxylic acid surface groups as the main adsorption sites for copper ions, an increase in carboxylic acid
279 implies the adsorption of more copper. Therefore, the increase of copper concentration for the highest
280 functionalized sample (PS22) is consistent. Considering the pH of exposure, the pKa of PAA is close to 4,

281 therefore at pH 5 the acid groups are predominantly on their basic COO^- form (Michaels and Morelos,
 282 1955; Wiśniewska and Chibowski, 2005) and the adsorption of the positively charged Cu^{2+} copper ions is
 283 hence favored.. 2) There is no significant variation of copper concentration throughout the different
 284 exposure times (24, 48 or 144 hours) whatever the pH value, indicating that the sorption kinetic is high
 285 enough to obtain a maximum of adsorption before the first measurement occurring after 24 h of
 286 exposure. It can be assumed that in less than a day the NPT surface is saturated with copper.

287

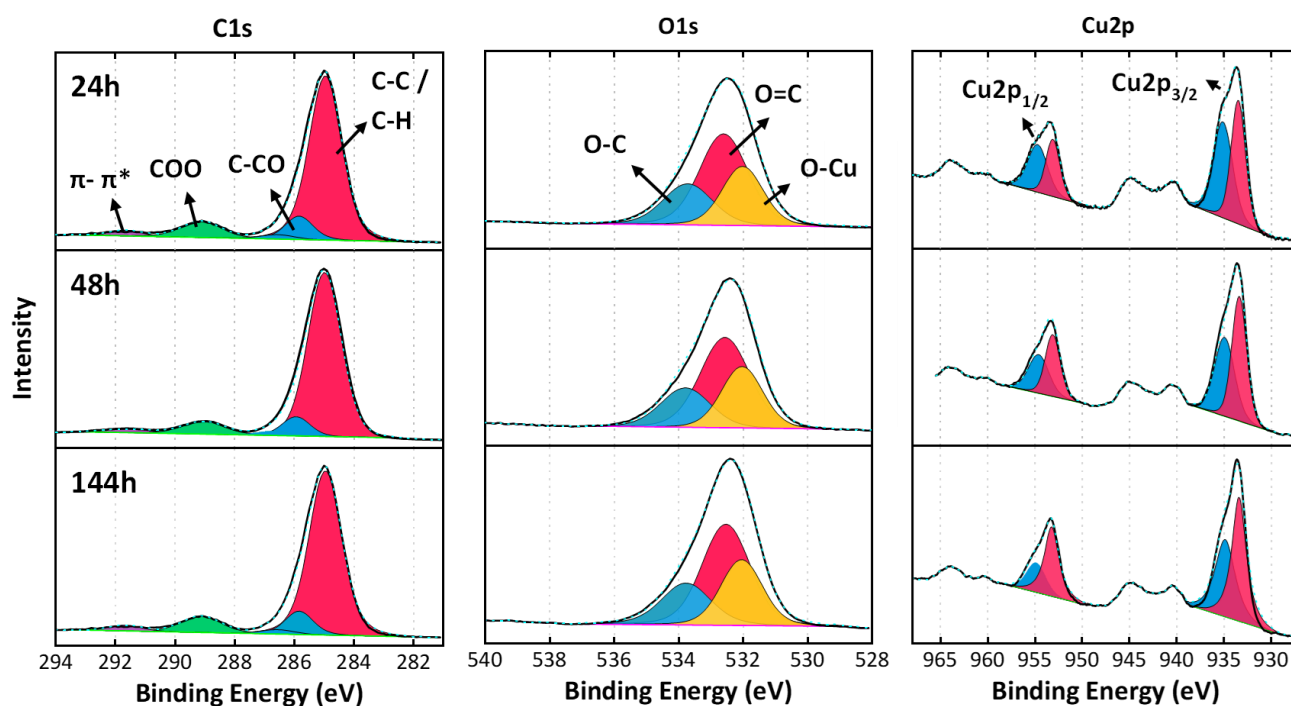


288

289 **Figure 2.** C 1s, O 1s and Cu 2p high resolution XPS spectra of (1) PS22 and (2) PS9 without copper exposure; and of PS22 at (a)
 290 pH3, (b) pH5 and PS9 at (c) pH3, (d) pH5 after copper exposure for 24 h, the quantification data can be found in the table 2.

291

292



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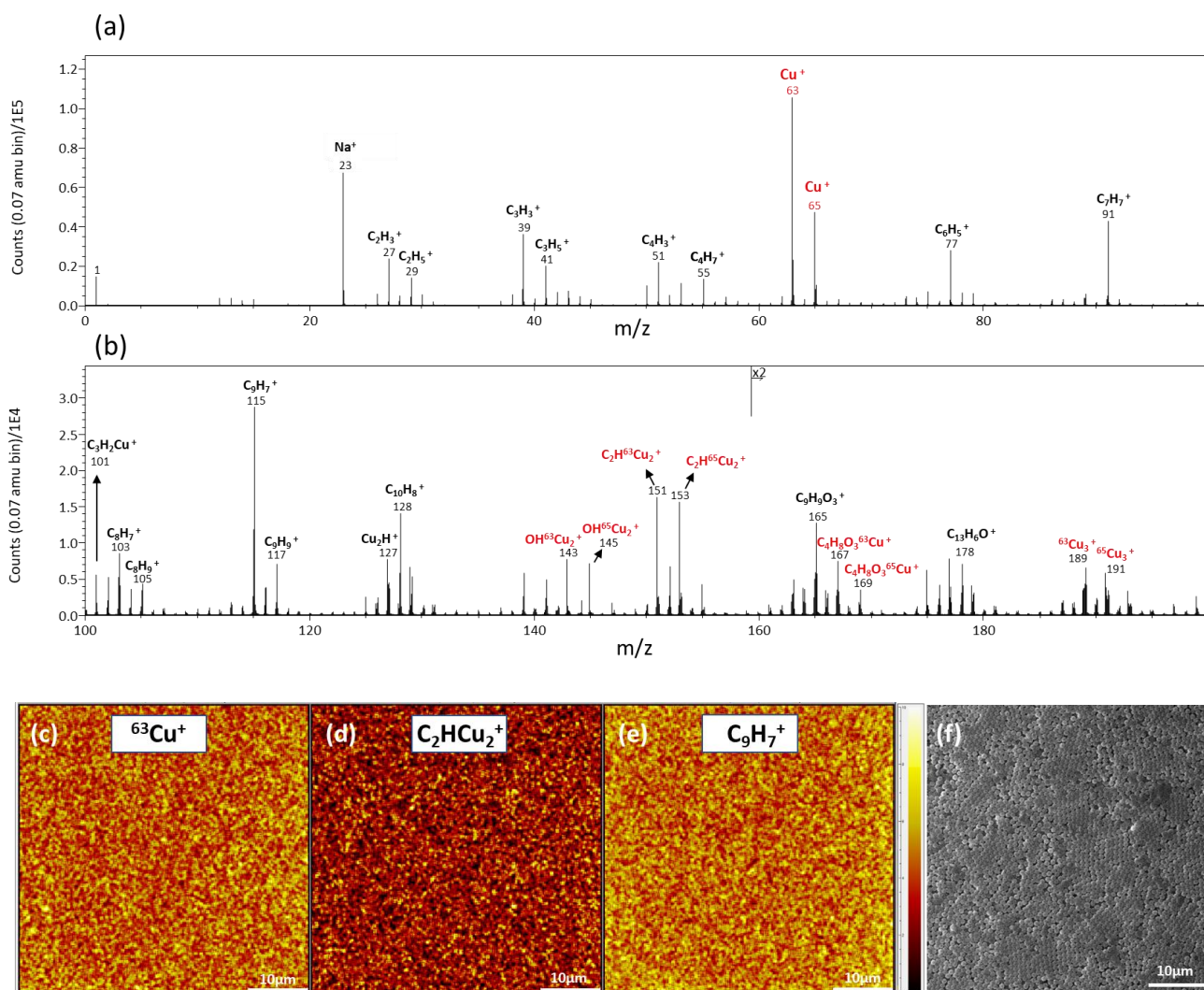
294 **Figure 3.** XPS C 1s, O 1s and Cu 2p core peaks of PS22 sample incubated with copper at pH 5 for 24 h (first line), 48 h (second
 295 line) and 144 h (third line), the quantification data can be found in the table 2.

296

297 **Table 2.** XPS quantitative analysis of PS22 and PS9 samples exposed for 24h with copper at either pH 5 or 3.

Region	Be (eV)	FWHM (eV)	Assignment	%at. Conc			
				pH = 3		pH = 5	
				PS22	PS9	PS22	PS9
C1s	285.0	1.3	C-C / C-H	61,2	85.0	59.2	84.1
	285.8	1.3	C-CO	9.0	2.2	8.5	2.1
	289.5	1.5	COO	9.0	2.2	8.5	2.3
	291.6	1.3	π - π^*	2.5	5.7	2.3	4.1
O1s	533.5	1.8	O=C	8.8	1.8	8.1	2.7
	533.9	1.8	O-C	7.8	2.2	3.5	1.5
	532.0	1.5	O-Cu	0.8	0.5	4.5	1.1
Cu2p	933.5	1.8	Cu2p _{3/2}	0.4	0.3	1.4	0.7
	935.0	2		0.2	0.02	1.1	0.5
	953.1	1.8	Cu2p _{1/2}	0.2	0.2	1.3	0.6
	954.7	2		0.1	0.02	0.8	0.3

300 **Figure 4** presents the ToF-SIMS mass spectra obtained in positive polarity for PS22 sample after 24h
301 exposure time with copper. Two main peaks at m/z 63 and 65 characteristics of the two copper isotopes
302 $^{63}\text{Cu}^+$ and $^{65}\text{Cu}^+$ are clearly detected with the expected isotopic ratio. The same result is obtained with the
303 PS9 sample (**Figure S5**). These results confirm the presence of copper at the extreme surface (1-2 nm) of
304 the NPTs after 24h exposure time whatever the surface carboxylic group content. Organic fragments
305 specific of the polymer structure of the NPTs are also observed, such as C_2H_3^+ , C_3H_3^+ , C_6H_5^+ , C_7H_7^+ or C_9H_7^+ .
306 More interestingly, oxidized copper molecular fragments like $\text{Cu}_2(\text{OH})^+$ and $\text{C}_4\text{H}_8\text{O}_3\text{Cu}^+$, as well as C_2HCu^+
307 fragment which comes from the fragmentation of a bigger polymeric molecule associated with Cu, can be
308 identified, confirming the interactions between the NPTs containing carboxylic groups and copper.
309 Moreover, ToF-SIMS 2D chemical imaging of the NPTs surface highlights the spatial distribution of species
310 of interest like Cu^+ , C_2HCu_2^+ or C_9H_7^+ as shown in **Figure 4**. (c), (d) and (e) respectively; the color scale
311 indicated on the side represents the signal intensity, the yellow/white color corresponds to the highest
312 and black one to the lowest. Copper is relatively well dispersed at the surface over the analyzed area at
313 the ToF-SIMS resolution and by comparison with the SEM image (**Figure 4.f**).



314

315 **Figure 4.** ToF-SIMS surface analysis of PS22 sample after 24h exposure time with copper: positive polarity spectra over m/z
 316 range 0 to 100 (a) and 100 to 200 (b); 2D chemical imaging (10 μm scale bar, the color scale represents the signal intensity,
 317 yellow/white for the highest and black for the lowest) of : c) $^{63}\text{Cu}^+$; d) C_2HCu_2^+ and e) C_9H_7^+ fragments. f) SEM image (10
 318 μm scale bar).

319

320 **Total copper determination (ICPMS).** The free copper fraction (*i.e.* the amount of copper not
 321 absorbed/adsorbed onto the NPTs and hence remaining free in the aqueous solution) was quantified by
 322 ICPMS. This fraction was collected in the supernatant after centrifugation of the NPT suspension exposed
 323 to copper. The fraction of copper sorbed by the NPTs was deduced by subtracting the free copper from
 324 the initial concentration of copper in the mixture and is expressed as sorption capacity Q_{sorb} (mg of copper
 325 per g of NPT) (**Figure 5** (right)).

326 It stands out that, for a similar exposition time, the copper concentration sorbed by the NPTs increases
327 both with the pH and the density of carboxylic sites at the surface. For instance, after 24 h of exposure a
328 sorption capacity of 14.4 and 52.8 mg g⁻¹ were obtained for the PS22 sample at pH 3 and 5 respectively,
329 while it's evaluated at 8.8 and 25.1 mg g⁻¹ for the PS9 sample at pH 3 and 5 respectively. These results
330 confirm the sorption of copper by NPTs and the role of the carboxylic sites present at the NPTs surface:
331 the more carboxylic groups the more sorbed copper.

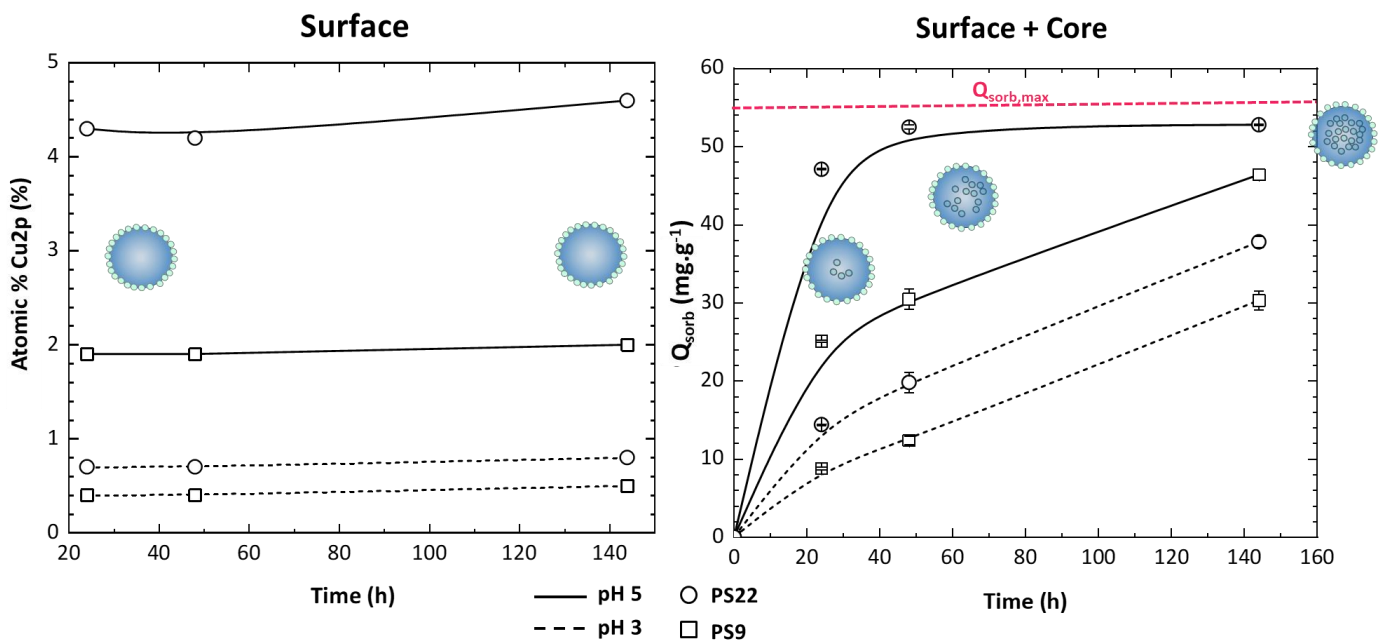
332 **Highlighting the diffusion of copper**

333 To evaluate the ability of copper to diffuse in the core of the NPTs, we compared the evolution of the
334 trend (**Figure 5**) between the surface analysis (by XPS: left) and total analysis (surface + core: by ICPMS,
335 right)

336 Unlike the surface analysis, the total copper concentration in the particle increases with the copper
337 exposure time. This is particularly clear for all samples at pH 3 while for PS22 sample at pH 5 the
338 concentration reaches a plateau at 48 h. It is assumed that the latter is due to the fast kinetic of sorption
339 as almost all the copper in the solution was sorbed by the PS22 NPTs after only 24 h of exposure (the
340 theoretical maximum of sorption $Q_{\text{sorb,max}}$ is represented by the red line).

341 This trend could not be observed by surface analysis; indeed, the atomic percent of copper at the surface
342 measured by XPS remained quite constant between 24 to 144 h of exposure time regardless of the
343 conditions. Such results suggest that the extreme surface (5-10 nm) of the NPT model materials is quickly
344 saturated in copper, but copper still diffuse inside the NPT with time.

345



346

347 **Figure 5.** Evolution of the copper atomic percent (left, obtained by XPS) and the masse sorption capacity (right, obtained by
 348 ICPMS) of PS22 and PS9 samples at pH3 and 5; the red line represents the theoretical maximum of sorption.

349

350 **Conclusion and perspectives** In this work, for the first time, two complementary surface techniques

351 (XPS and ToF-SIMS) has been used to study the interactions between copper and NPTs model materials

352 at the extreme surface. XPS has proved to provide both elemental and quantitative information, showing,

353 on the one hand, a significant amount of copper at the NPT surface after 24 h of incubation and, on the

354 other hand, an increase of this amount in direct correlation with the increasing of the functionalization of

355 the NPT surface. In addition, the complementary molecular information obtained by ToF-SIMS confirmed

356 the direct interaction of copper with the carboxylic groups. Finally, the diffusion of copper within the core

357 of a NPT was reported for the first time, by comparing the evolution of the copper concentration at the

358 surface, obtained by XPS, and in the whole NPT materials, obtained by ICPMS. Indeed, the atomic percent

359 of copper measures at the surface of the NPTs remained unchanged regardless of the exposure time

360 whereas the concentration of copper sorbed keeps increasing with the time. In addition, copper sorption

361 rate seems to increase with the carboxylic group content at the NPT surface.

362 This study confirmed the ability of nanoplastics to act as metal pollutant carriers by both adsorption and
363 absorption phenomena and the phenomenon is more rapid with aged (more oxydized) plastic debris. It
364 should be noted that, the formation of biofilm at the nanoplastics surface in addition to the desorption of
365 the metallic pollutant from the NPTs represents additional parameters that must be taken into account in
366 perspective works.

367 **Conflicts of interest**

368 There are no conflicts of interest to declare.

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374

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