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Are nanoplastics able to bind significant amount of metals?

The lead example

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Main finding

Nanoplastics are able to sorb high amount of Pb(II) through sorption and intraparticle diffusion processes. They could be important vector of metallic pollutant in the environment.

Highlights

- Pb(II) binding experiments onto nanoplastics extracted from environmental micro-plastics were performed.
- Pb(II) was largely bound onto nanoplastics by specific adsorption and intraparticle diffusion.
- Nanoplastics could be significant vectors of metals in the environment

Abstract

The nanoscale size of plastic debris makes them potential efficient vectors of many pollutants and more especially of metals. In order to evaluate this ability, nanoplastics were produced from microplastics collected on a beach exposed to the North Atlantic Gyre. The nanoplastics were characterized using multi-dimensional methods: asymmetrical flow field flow fractionation and dynamic light scattering coupled to several detectors. Lead(II) adsorption kinetics, isotherm and pH-

37 edge were then carried out. The sorption reached a steady state after around 200 min. The
38 maximum sorption capacity varied between 97% and 78.5 % for both tested Pb concentrations.
39 Lead(II) adsorption kinetics is controlled by chemical reactions with the nanoplastics surface and to a
40 lesser extent by intraparticle diffusion. Adsorption isotherm modeling using Freundlich model
41 demonstrated that NPG are strong adsorbents equivalent to hydrous ferric oxides such as
42 ferrihydrite ($\log K_{ads}^{freundlich} = 8.36$ against 11.76 for NPG and ferrihydrite, respectively). The
43 adsorption is dependent upon pH, in response to the Pb(II) adsorption by the oxygenated binding
44 sites developed on account of the surface UV oxidation under environmental conditions. They could
45 be able to compete with Fe or humic colloids for Pb binding regards to their amount and specific
46 areas. Nanoplastics could therefore be efficient vectors of Pb and probably of many other metals as
47 well in the environment.

48 **Keywords.**

49 nanoplastics, Pb(II), adsorption, kinetics, DLS, A4F

51 **Main finding**

52 Nanoplastics are able to sorb high amount of Pb(II) through sorption and intraparticle diffusion
53 processes. They could be significant vectors of metallic pollutants in the environment.

55 **1. Introduction**

56 Due to the exceptional properties of plastics materials such as their low density and high
57 durability, the industrial production of plastics has intensely and exponentially grown since 1940s.
58 The reason of their success is explained by their multiples uses (e.g. food packaging, building,
59 transport, agriculture, etc.). However, these properties result also in their exceptional persistence in
60 the environment. Whereas marine pollution by plastics was the most highlighted (low et al., 2010;
61 Eriksen et al., 2014), microplastic contamination of freshwater, urban water, urban dust, flood plain

62 soil and atmosphere were also pointed out in several studies (Gaspary et al., 2014; Dris et al. 2016;
63 Dehghani et al., 2017; Scheurer and Bigalke, 2018; Dris et al. 2018).

64 Among plastic contaminants, microplastics have been the most studied (Andrady, 2011; Wright et
65 al., 2013). However, the existence of nanoplastics, was quite recently demonstrated by Ter Halle et
66 al. (2017) and Gigault et al. (2018). They defined nanoplastics as particles unintentionally produced,
67 whose size was varying from 1 to 1000 nm and displaying a colloidal behavior (Gigault et al., 2018).
68 They are produced from the use of manufactured objects but especially from aged-microplastics in
69 response to the photo-, chemical and physical degradation mechanisms that take place under
70 environmental conditions (Bouwmeester et al., 2015; Ter Halle et al., 2017). Their occurrence was
71 demonstrated under laboratory conditions from degradation of plastics items (Lambert and Wagner,
72 2016), environmental microplastics collected in seawater (Gigault et al., 2018) and under
73 environmental conditions in seawater samples (Ter Halle et al., 2017).

74 Nanoplastics display a nanoscale size. They are polydisperse with an open structure and a
75 heterogeneous and asymmetrical shape. They present an inhomogeneous charged surface and they
76 are able to aggregate relative to the environmental physico-chemical conditions (Gigault et al., 2018).
77 All these properties make them formidable potential adsorbents of contaminants and especially of
78 trace metals. However, regards to their extremely recent highlighting, no studies have ever been
79 interested in their ability to bind trace metals and the involved governing mechanisms. Nevertheless,
80 several studies demonstrated that both plastics pellets collected from beaches and micro-plastics
81 recovered from seawater of the North Atlantic gyre contain very variable amounts of trace metals
82 (e.g. Holmes et al., 2012; Turner and Holmes, 2015; Vedolin et al., 2018; Prunier et al., 2019). This
83 trace metal loading could result of the use of trace metals as additives in the plastics production and
84 also in sorption processes (Massos and Turner, 2017; Wang et al., 2017; Prunier et al. 2019). Wang et
85 al. (2017) suggested that the majority of metals carried by microplastics were derived from internal
86 load. However, Holmes et al. (2014) compared the sorption capacity of virgin pellets and pellets
87 collected from beaches. They provided evidence that trace metal adsorption was considerably

88 greater for the beach-sourced pellets. They attributed these results to the pellets weathering and to
89 the resulting specific adsorption onto charged mineral sites or to non-specific interaction between
90 the hydrophobic surface and the neutral or organic trace metal species. Adsorbed trace metals were
91 both cations and oxyanions. Ashton et al., (2010) suggested also that trace metals may co-precipitate
92 with or be sorbed onto hydrous oxides present onto the microplastic surface. Brennecke et al. (2016)
93 studied the sorption of Cu and Zn from antifouling paint onto virgin polystyrene (PS) pellets and
94 environmental aged polyvinyl chloride (PVC) fragments. They demonstrated that sorption of Cu was
95 higher onto aged PVC than virgin PS in response to the PVC higher surface area and polarity.

96 In such context, the nano size of the nanoplastics and their exceptional surface properties (charge
97 and asymmetrical shape) make them better vectors of trace metals than pellets and microplastics.
98 Their precise role in trace metal transfer and the involved mechanisms have therefore to be
99 elucidated.

100 For this purpose, we studied the sorption of Pb(II) onto 'model' nanoplastics obtained from
101 physical alteration of 'environmental' nanoplastics produced by sonication of microplastics collected
102 on a beach exposed to the North Atlantic gyre in Guadeloupe (France). Lead was chosen regards to
103 its high affinity for surface and to its toxicity. We developed an *in situ* polarography method allowing
104 performing adsorption kinetics, isotherm and pH-sorption edge experiments in a single reactor. The
105 evolution of the nanoplastic size and aggregation were monitored throughout the experiment using
106 dynamic light scattering (DLS).

107 2. Materials and methods

108 All used chemicals were of analytical grade. The solutions were prepared with ultrapure water
109 (Milli-Q system, Millipore). The containers used were (i) trace-metal cleaned with 10% (v/v) HNO₃ for
110 24 h at 45°C, (ii) soaked in and then rinsed with ultrapure water for 24 h at 45°C, and (iii) finally dried
111 at 30°C. All solutions were prepared with ultrapure water (18.2 Ω, MilliQ, Millipore). The Pb(II)
112 solutions were prepared using a 1000 mg L⁻¹ standard solution of Pb (NO₃)₂ (standard Metrohm

113 99.5% ion, VWR Chemicals). The analysis of Pb^{2+} in solution was carried out by polarography
114 (Metrohm 884 professional voltammetric meter).

115 2.1. Nanoplastics production

116 Environmental nanoplastics were produced by the sonication of 58 g of microplastics (5 mm to 2
117 cm) in 300 mL of ultrapure water. Sonication was performed during 5 days. The suspension was
118 filtrated at 0.8 μm (Sartorius). Microplastics were collected in 2017 on the beach of Baie Sainte-Marie
119 in Guadeloupe (France), which is exposed to the North Atlantic gyre. This sample corresponding to
120 Guadeloupean nanoplastics was called NPG. Microplastics were isolated from the sand by a sea
121 water extraction method relative to their density. Dynamic light scattering (DLS) displayed that both
122 samples were poly-dispersed with an average hydrodynamic diameter 150-450 nm. Zeta-potential
123 analysis demonstrated that they are negatively charged on the 2-to-14 pH range. At pH 6, zeta-
124 potential was equal to -30.2 mV. Their final concentration in the suspension was determined by
125 measuring the dissolved organic carbon (DOC). The NPG sample displayed a DOC concentration of 50
126 mg L^{-1} . Note that it cannot be excluded that a few amount of the measured DOC corresponds to
127 organic matter.

128 2.2. Adsorption experiments

129 **Kinetic experiments.** Kinetic experiments of $\text{Pb}(\text{II})$ adsorption onto NPG were performed *in situ*,
130 namely directly in a polarographic cell. This *in situ* methodology avoids any external treatment of the
131 sample, Pb^{2+} concentration being continuously measured in the cell. Ten ml of the NPG solution were
132 introduced in a polarographic cell. The pH of the NPG suspensions was fixed at 7 using HNO_3 and/or
133 NaOH at 0.1 M and their ionic strength was fixed at $10^{-2} \text{ mol L}^{-1}$ using KCl . Before adding $\text{Pb}(\text{II})$, a first
134 polarographic measurement was performed to check (if any) the Pb^{2+} concentration release by NPG.
135 Then, $\text{Pb}(\text{II})$ was added to obtain a concentration of 2 and 6 mg g^{-1} (g of dissolved organic carbon,
136 DOC). The concentration of Pb^{2+} in the suspension was measured every 2 min during 5 h.

137 **Adsorption isotherms.** They were carried out *in situ* directly in a polarographic cell. Ten ml of
138 the NPG solution was introduced in a polarographic cell. The pH of the NPG suspensions was fixed at
139 7 using HNO₃ and/or NaOH at 0.1 M. The ionic strength was fixed at 10⁻² mol L⁻¹ using KCl. Before
140 adding Pb(II), a first polarographic measurement was performed to check (if any) the initial Pb²⁺
141 concentration. Then, Pb(II) was added every 4h (as assessed by the steady state) in order to obtain
142 Pb(II) total concentration of 4, 8, 12, 16, 20 and 24 mg g⁻¹ (g of DOC). The Pb²⁺ concentration was
143 measured by polarography.

144 **pH-adsorption edge experiment.** This experiment was carried out *in situ* directly in a
145 polarographic cell and not as classically performed in distinct batches. Fifteen mL of NPG solution
146 were introduced in a polarographic cell. Its initial pH was fixed at 2 using HNO₃ at 0.1 M. The ionic
147 strength was fixed at 10⁻² mol L⁻¹ using KCl. Lead(II) was added in order to obtain a concentration of 6
148 mg g⁻¹ (g of DOC). After 4h, the Pb²⁺ concentration was measured by polarography. Then, every 4 h,
149 the pH was increased using an automatic titrator in SET mode (Titrino 719, Metrohm). The pH was
150 successively fixed at 3, 4, 5, 6 and 9. The Pb²⁺ concentration was measured at steady state for each
151 pH.

152 2.3. Chemical Analysis

153 **Dissolved organic carbon (DOC).** DOC concentrations were determined using a Total Carbon
154 Analyzer (Shimadzu TOC-V CSH) by a standard solution of potassium hydrogen phthalate (Sigma
155 Aldrich). The uncertainty of the measurement was 5%.

156 **Pb(II) measurement.** Pb(II) concentrations were determined as Pb²⁺ species concentrations
157 using polarography directly in the NPG suspensions. They were determined using a Methrohm
158 polarograph (Methrom 884 professional ASV) under Anodic Stripping Voltammetry (ASV) mode using
159 a hanging dropping mercury electrode (HDME). The analytical conditions are summarized in Table S1
160 (supplementary file). Deoxygenation of the medium was carried out using a continuous N₂ bubbling.
161 The analyses were carried out under stirring at 3000 rpm.

162 All experiments being performed directly in a polarographic cell, the metered addition method
163 could not be carried out. A calibration curve was therefore performed for a Pb^{2+} concentration
164 ranging in between 0 and $400 \mu\text{g L}^{-1}$. To evaluate the impact of the NPG presence on the
165 measurement, calibration curve were carried out with and without NPG. Moreover, to avoid any
166 Pb(II) sorption onto NPG and ensure that all the Pb(II) was under Pb^{2+} species, the pH was fixed at 2.
167 None influence of the NPG presence was observed. The calibration curve realized with NPG at pH 2
168 was therefore used to determine the experimental Pb^{2+} concentration (supplementary file Fig. S1).
169 The detection limit of the method was $0.05 \mu\text{g L}^{-1}$ for Pb.

170 2.4. Nanoplastics size measurement.

171 **Dynamic Light Scattering (DLS).** DLS was used to determine the size of the nanoplastics both in
172 the initial suspension and during the adsorption experiments. The *in situ* DLS measurements were
173 performed using a Vasco Flex model of nanoparticle size analyzer (Cordouan Technology, Pessac,
174 France). The probe was placed in front of the polarographic cell and measured directly in the
175 solution. The detection limit of the DLS instrument was investigated with PSL 100 nm standards
176 within the range of $2 \times 10^{-5} \text{g L}^{-1}$ to $2 \times 10^{-1} \text{g L}^{-1}$. Although detection remains possible over the entire
177 concentration range, an average size analysis is only possible over the concentration range of 2×10^{-2}
178 to $2 \times 10^{-4} \text{g L}^{-1}$ using the Pade-Laplace algorithm. Each measurement corresponds to a statistical
179 average of six measurements. In addition, each of the six measurements is composed of six
180 acquisitions of light scattered for 80 s.

181 **Asymmetrical Flow Field Flow Fractionation (A4F) coupled to static light scattering (SLS) and**
182 **inductively coupled plasma-mass spectrometry (ICP-MS).** A4F-SLS-ICP-MS was used to fractionate
183 and size sort nanoplastics with metallic composition associated to. The A4F fractionation running
184 conditions are summarized in table S2 (supplementary file).

185 The detection consisted in a static light scattering (SLS, Multi Angle Light Scattering - MALS, Dawn
186 Heleos 2, Wyatt Technology) to characterize the particles size. The incident laser wavelength of the
187 SLS is $\lambda=658\text{nm}$. A Berry formalism that allows giving the more suitable fit of the light scattered

188 according to the angle was used. UV detector was fixed at 254 nm, which corresponds to the
189 absorption peak of the colloidal materials. Finally, an inductively coupled plasma-mass spectrometer
190 (ICP-MS 7700x, Agilent technologies) was directly coupled at the end of the detection chain without
191 using the nebulizer pump. No online quantification was performed. Here ICP-MS was used to localize
192 the Pb(II) on the colloidal size range. The ICP-MS was operated without the collision cell, because of
193 the lack of interferences for the mass isotope of interest (^{207}Pb). The sample and skimmer cones were
194 in nickel. The RF power and the plasma gas flow rate were fixed at 1500 W and 15 L min $^{-1}$,
195 respectively.

196 3. Results

197 3.1. Adsorption kinetics

198 Lead concentration decreased extremely rapidly (Fig. 1a). After 2 min, the concentration
199 decreased from 2 to 0.43 mg g $^{-1}$ (78.5 % of binding) and 6 to 0.17 mg g $^{-1}$ (97.2 % of binding) for both
200 concentrations, respectively. Lead was therefore significantly adsorbed to NPG. The kinetic profile
201 consisted of a rapid adsorption following by a subsequent approach to steady state, which was
202 reached after around 200 min (Fig. 1a).

203 The kinetics was modeled using a pseudo-first-order. However, the Lagergreen pseudo-first-
204 order equation was not applicable to our Pb(II)-NPG system, no linearization of the experimental
205 data was obtained. The pseudo-second order was then tested. In this model, the rate-limiting step is
206 the surface adsorption that involves chemisorption. The model is based on the solid phase
207 adsorption capacity (Ho et al. 1996 a-b) and predicts the behavior over the whole range of
208 adsorption (Ahsu et al. 1991). The corresponding equation is:

$$209 \quad \frac{dQ_t}{dt} = K (Q_e - Q_t)^2 \quad (\text{eq.1})$$

210 With Q_t , the adsorbed Pb(II) concentration at time t (mg g $^{-1}$ of DOC), Q_e the adsorbed Pb(II)
211 concentration at steady state (mg g $^{-1}$ of DOC), and K the rate constant of adsorption for the pseudo-
212 second-order (g mg $^{-1}$ min $^{-1}$).

213 The integrated equation is:

$$214 \quad \frac{1}{Q_t} = \left(\frac{1}{Q_e}\right) \cdot t + \frac{1}{K \cdot Q_e^2} \quad \text{or} \quad \frac{1}{Q_t} = \frac{h}{1 + K \cdot Q_e \cdot t} \quad (\text{eq.2})$$

215 Where h can be considered as the initial sorption rate. When t tends to 0, $h = KQ_e^2$

216 The linearity of the plots, the R^2 and the coherence between the theoretical and the
 217 experimental Q_e indicated that chemical reaction is the main rate-controlling step of the binding
 218 process (Fig. 1b and Table 1). The rate constant (K) decreased with the increasing Pb(II) initial
 219 concentration as previously observed and discussed by Ho and Ofomaja (2006) and Ho et al. (2006)
 220 for Pb(II) adsorption onto palm fiber and peat.

221 Since the pseudo-second-order kinetic model did not allow identifying potential diffusion
 222 mechanism, the kinetic results were then analyzed using an intraparticle diffusion model. The
 223 following equation was used (El-Ashtoukhy et al., 2008):

$$224 \quad Q_t = K_i \cdot t^{0.5} + C \quad (\text{eq. 3})$$

225 K_i is the rate constant of the intraparticle diffusion, whereas C corresponds to the intercept and
 226 provides information on the thickness of the boundary layer.

227 The Q_t was plotted relative to the \sqrt{t} in Fig. 1c and the kinetics parameters in Table 3. If the
 228 intraparticle diffusion model is involved the plot of Q_t relative to \sqrt{t} should be linear and if the
 229 intraparticle diffusion model is the rate-controlling step, the plot should pass through the origin ($C =$
 230 0). However, if $C \neq 0$, it indicates some degree of boundary layer control. The intraparticle diffusion
 231 model is therefore not the rate-controlling step, but it could operate simultaneously with other
 232 processes. The diffusion gradient can be linearized into four regions representing the external mass
 233 transfer, and the intraparticle diffusion in the macro, meso and micropore structure of the adsorbent
 234 (Allen et al., 1989; Tan et al. 2007; Ho and McKay, 1998). Multilinear lines were obtained for both
 235 initial concentrations of Pb(II) (Fig. 1c). Moreover, any of them passed through the origin indicating
 236 that the intraparticle diffusion process was not the rate-controlling step. However, the first linearity
 237 can be considered as a first step of an instantaneous adsorption or adsorption on the outer surface
 238 which was produced during the first 25 min of the sorption and corresponded to 83% and 89 % of

239 total bound Pb(II) for 6 and 2 mg g⁻¹ initial concentration, respectively. The second part represented a
240 more slow and progressive part of the adsorption that could be driven by an intraparticle diffusion
241 process that limited the adsorption process and corresponded to 4% and 5 % of total bound Pb(II) for
242 6 and 2 mg g⁻¹ initial concentration, respectively.

243 Therefore, Pb(II) seemed to be rapidly sorbed by a chemisorption processes which was
244 confirmed by the pseudo-second order model parameter, that may be followed by an intraparticle
245 diffusion process lasting up to 25 min.

246 3.2. Adsorption isotherm

247 Experimental data of the adsorption isotherm are reported in Fig. 2. The adsorbed Pb(II)
248 concentration increased with the increasing initial Pb(II) concentration. However, the proportion of
249 adsorbed Pb(II) was higher for the low concentration than for the high concentration, suggesting a
250 progressive saturation of the surface.

251 The isotherm was fitted using the non-linear Langmuir and Freundlich models. Since no linearity
252 was obtained for Langmuir model, Freundlich model was therefore the only model described in this
253 work. The Freundlich isotherm assumes a multilayer sorption onto a heterogeneous surface. The
254 Freundlich isotherm corresponds to:

$$255 \quad Q_e = K_{ads} C_e^n \quad (\text{eq. 3})$$

256 Where Q_e is the adsorbed Pb(II) concentration (mg g⁻¹), K_{ads} is the Freundlich adsorption constant, C_e
257 is the concentration of Pb(II) in solution (mg g⁻¹) and n is the non-linearity coefficient.

258 In Fig. 2 were plotted the linearized data. Values for the Freundlich constant and coefficient are
259 derived from the linear regression analysis of the log Q_e versus log C_e . The obtained values are $n=$
260 0.34, $K_{ads} = 4.89$. The correlation coefficient R^2 equal to 0.98 indicates that the Freundlich model is
261 suitable to describe the sorption processes between Pb(II) and NPG. The coefficient n , ranging
262 between 0 and 1, is indicative of a cooperative adsorption (here $n=0.38$).

263 These results showed that Pb(II) adsorption onto NPG was expected to be non-linear, namely
264 produced through the formation of multilayer or through the formation of heterogeneous surface
265 complexes. The surface complexes heterogeneity is the result of the variability of the binding sites
266 (carboxylic, phenolic, hydroxyl, etc.) or of the denticity of the complexes (monodentates, bidentate,
267 etc.).

268 3.3. pH adsorption-edge

269 The evolution of the Pb(II) adsorption relative to pH was non-conventionally plotted (Fig. 3).
270 Since the experiments were both *in situ* and non-sequentially performed, it was not possible to
271 evaluate, as done with the previous experiment, the Pb(II) concentration released by NPG at each
272 pH. We therefore chose to present the evolution of the Pb^{2+} concentration (Fig. 3).

273 A Pb^{2+} concentration decrease following the increasing pH is displayed in Fig. 3. Several
274 mechanisms could explain such result and notably the complexation of Pb(II) by the OH^- ligand,
275 whose concentration increased with the increasing pH up to the precipitation of Pb(II) as hydroxide
276 at $pH > 7$. The Pb(II) speciation was calculated through VisualMinteq 3.1 considering the
277 experimental conditions but, without NPG (Fig. 4). To allow a better comparison between the
278 experimental and the modeled data, the Pb(II) concentration was presented in $mg\ g^{-1}$ (g of DOC even
279 if no DOC was input in the calculation, namely to convert $mol\ L^{-1}$ as $mg\ g^{-1}$). Without any NPG, the
280 modeling demonstrated that Pb^{2+} decreased from pH 6 in response to its complexation as $PbOH^+$ and
281 from pH 7.5 to the precipitation of $Pb(OH)_2$. By contrast, with NPG, Pb^{2+} decreased from $pH > 2$, the
282 largest decrease proceeding from pH 4. These results clearly demonstrated that the Pb^{2+} decrease
283 was provided in response to the NPG occurrence, namely in response to the Pb^{2+} adsorption onto
284 NPG.

285 3.4. Size and elemental composition characterization

286 DLS analysis was performed on NPG associated to Pb(II) on the studied pH range, concentrations
287 and contact-time(kinetics) (Fig. S2, supplementary file). No significant changes were observed in the
288

289 auto-correlation function (ACF) and in the d_{zH} according to the different conditions. Nevertheless,
290 some difference on the polydispersity could have occurred and could not be identified by DLS. The
291 structural and physical changes of environmental nanoparticles are usually difficult to identify with
292 DLS due to their high polydispersity in size and composition (Gigault et al., 2018). To isolate,
293 fractionate and characterize, free-Pb(II) and Pb(II)-doped NPGs, A4F-SLS-ICPMS was further used (Fig.
294 5). The fractograms displayed a signal with a retention time covering the size range from 50 nm up to
295 400 nm (in diameter) based on A4F calibration (Gigault et al., 2017) (Fig. 5.a). The intensity of the UV
296 signal was slightly higher for Pb(II)-doped NPG than for free-Pb(II) NPG. Such results might be
297 produced in response to the Pb(II) adsorbed onto the NPG surface or to the NPG dispersion in
298 presence of Pb(II). The retention time was not modified indicating no modification of the size
299 distribution range. However, the UV signals showed a large colloidal fraction (from 10kDa to 60kDa)
300 at a retention time $t_R=2$ min. Residues of polymers, additives and organic matter remaining on the
301 microplastics surface, possibly released during the sonication. The SLS analysis validated these
302 observations. They displayed that NPG have a gyration radius ranging from 70 to 250 nm using Berry
303 formalism for both Pb(II)-doped and free-Pb(II) NPG. Angular dependence of the light scattered did
304 not fit using the spherical formalism indicating an indirect shape deviating from the ideal sphere (SI,
305 Fig. S2). The on-line coupling of ICPMS and A4F-UV-SLS allow obtaining the elemental composition
306 associated to the UV and SLS signals (Fig. 5b). The m/z 207 trace, corresponding to Pb(II) increased
307 from $t_R=5$ min to $t_R=17$ min for Pb(II)-doped NPG (black trace) as compared to free-Pb(II) NPG (blue
308 trace) indicating that Pb(II) was associated to NPG. Noted that for free-Pb(II) NPG, the m/z 207 trace
309 presented some spikes, starting especially at $t_R=12$ min, namely at approximately 100 nm size. Such
310 spiked signal corresponds to the signal generally observed with ICP-MS in single particle mode. When
311 a significant amount is localized in a nanometer resolved surface, the quantity of ionized metal is
312 significantly higher, which corresponds to either metal nanoparticles trapped inside colloids or metal
313 accumulation within a cavity of a porous material. Nevertheless, for the Pb(II)-doped NPG, the spiked

314 signal was attenuated suggesting either, a Pb(II) surface adsorption or ,that the equilibrium time was
315 long enough to allow a significant Pb(II) accumulation in the porosity.

316 4. Discussion

317 4.1. NPG is a significant Pb(II) adsorbent

318 Adsorption kinetic experiments displayed that 78.5 and 97 % of Pb(II) were sorbed onto the
319 nanoplastics at pH 7. These proportions are high and suggest that nanoplastics are strong Pb(II)
320 adsorbent. The Freundlich K_{ads} defined for Pb(II)-NPG in the present study was compared to the
321 Freundlich K_{ads} of various adsorbents. For the comparison, it was necessary to recalculate our
322 constants using the same calculation units than those of the literature. They are reported in Table 2.
323 Since in the literature, no data exist for the Pb(II) binding to nanoplastics, our results were therefore
324 compared to those obtained for plastics pellets collected on beaches on which Pb(II) was
325 experimentally adsorbed using sea and river water samples (Holmes et al., 2012; 2014). Note that the
326 beached pellets are micrometric and that they were submitted to sonication during 5 min before
327 being used. Although pH values were close to each other, the present Freundlich K_{ads} is 3 to 4 order
328 of magnitude higher than those of beached pellets (Table 2). The environmental nanoplastics (NPG)
329 are therefore stronger Pb(II) adsorbent than environmental micrometric plastics. Note however,
330 that the sonication step submitted to the beached pellets could have released many nanometric
331 parts decreasing thus their binding capacity. Regards to these results, the present Freundlich K_{ads} was
332 compared to the K_{ads} calculated for Pb(II) binding to minerals known to be strong metals adsorbents,
333 namely the Fe oxyhydroxides. First, K_{ads} was compared to those calculated for Pb(II)-goethite
334 sorption. Goethite is a well-crystallized Fe oxyhydroxides with a low specific surface around 45 g m^{-2} .
335 The present Freundlich K_{ads} was 1 or 2 orders of magnitude higher than those of goethite (Table 2).
336 However, the binding experiments of Pb(II) to goethite were performed at lower pH. The metal
337 sorption onto Fe oxyhydroxides being strongly dependent to pH, the difference noted in between the
338 Freundlich K_{ads} could be involved by this pH difference, see notably the Olu-Owolabi and Ajayi (2011)

339 study where pH was 4.2. By contrast, Freundlich K_{ads} of Pb(II)-ferrihydrite sorption is in the same
340 order of magnitude than the present K_{ads} . Ferrihydrite is a Fe oxyhydroxide with a high specific
341 surface varying between 250 to 600 g m^{-2} and is considered to be the strongest metal sorbent
342 amongst various particulate Fe oxyhydroxides. The similarity of the ferrihydrite and the present
343 Freundlich K_{ads} therefore suggests that NPG are strong adsorbent of Pb(II). Finally, the Freundlich K_{ads}
344 was compared to that obtained for nano-goethite, to eventually identify the role of the nano-size on
345 the sorption. Both Freundlich K_{ads} are in the same order of magnitude although they were highly
346 different for particulate goethite. Finally, our data were compared to that obtained for a purified
347 humic acid (PPHA). The Freundlich K_{ads} was calculated from data extracted from the Pb-humic acid
348 data compilation performed by Milne et al., (2001). Freundlich isotherm was not able to model Pb-
349 humic acid binding data except that of Pinheiro et al. (1994), the Langmuir isotherm providing better
350 modeling. Regarding the pH conditions, we can consider that both Freundlich K_{ads} are in the same
351 order of magnitude.

352 All these comparisons demonstrated that NPG are strong adsorbent of Pb(II), much stronger
353 than beached micrometric plastics pellets. Their sorption capacity seems to be similar to strong metal
354 sorbent such as ferrihydrite, nano-goethite and humic acid. Their sorption properties can thus be
355 attributed to their nano-size and subsequent high specific surface area such as those of ferrihydrite,
356 nano-goethite and humic acid.

357 4.2. Mechanisms involved in Pb(II) adsorption

358 We demonstrated that NPG is a strong adsorbent of Pb(II). Let us go further to elucidate which
359 are the mechanisms involved in the Pb(II) binding to NPG.

360 The first interesting results are provided by the adsorption kinetic study. The kinetic rate could
361 not be modeled using the pseudo first-order model demonstrating that the adsorption kinetics was
362 not controlled by the diffusion. By contrast, the pseudo-second order model allowed with success to
363 model the kinetic data, indicating that the major rate limiting step was the surface adsorption
364 involved by chemical interactions in between Pb(II) and NPG. Although this process dominates the

365 adsorption, intraparticle diffusion seems also to partly control the mechanism of Pb(II) adsorption
366 onto NPG.

367 Lead(II) sorption onto NPG was strongly dependent to pH as shown by the pH-adsorption-edge
368 experiment (Fig. 3). With the increasing pH, the surface electronegativity increased in response to
369 the surface functional groups deprotonation. In such conditions, Pb(II) affinity for the surface
370 increased, Pb(II) being able to be bound through electrostatic interactions (outer sphere complex)
371 and/or covalent binding (inner sphere complex). The formation of inner spheres supposes the
372 presence of surface sites able to exchange electron such as, hydroxyl, carboxylic and phenolic
373 functional sites. Figure 3 shows that Pb^{2+} concentration strongly decreased from $pH > 4$ (i.e. Pb(II)
374 adsorption strongly increased). This pH corresponds to pH from which carboxylic groups generally
375 become significantly deprotonated ($pK_{a\ R-COOH} \approx 4.8$). If no data are available for nanoplastics, several
376 studies showed that plastics debris collected on beach or seawater displayed a higher oxidation state
377 than the reference sample (Ter Halle et al., 2017). Fourier Transform Infra-red Spectroscopy (FTIR) of
378 weathered plastics showed that oxygenated moieties such as, aldehydes, ketones, alcohol,
379 hydroperoxides and carboxylic acids groups increase in the plastics with the duration exposure
380 (Andrady, 2017). The increase of the oxygen moieties and oxygenated function is involved by the UV
381 irradiations weathering. The modeling of the adsorption isotherm data with the Freundlich model
382 demonstrated that the adsorption was not only favorable but, heterogeneous in response to either a
383 multilayer sorption or the formation of heterogeneous surface complexes (surface sites and complex
384 denticity heterogeneity). Since Pb(II) is a transition metal whose potential to form covalent binding is
385 high, the multilayer binding is therefore unlikely. However, regarding the oxidation state of the NPG
386 surface, the formation of heterogeneous complexes with various sites such as, carboxylic, hydroxyl or
387 phenolic sites is more than expected. Note, however, that Pb(II) sorption onto NPG surface does not
388 affect the aggregation/dispersion of the NPG, since no difference in their size and R_g variation was
389 observed with or without Pb(II).

390 As previously explained, fractograms of free Pb(II) and Pb(II)-doped NPG obtained with A4F-
391 ICPMS, exhibited spikes in the R_g range over 100 nm. Passing 100 nm in R_g , the frequency of high-
392 intensity spikes increases. Nevertheless, the present A4F-ICPMS set up is not optimized to
393 characterize nanoparticle size using the single particle-ICPMS mode (Schwertfeger et al., 2016;
394 Bustos and Winchester, 2016). Dwell and settling times are not indeed sufficient to obtain a robust
395 correlation between the intensity of the spike and the exact size distribution. These spikes and
396 single-particle event in the fractograms could be explained by the absorption and accumulation of
397 Pb(II) in the NPG structure/porosity, confirming the intraparticle diffusion of Pb(II). Note that the
398 Pb(II) occurring in the porosity and in the residual structure of the free-Pb(II) NPG are strongly
399 trapped since very few were released at acidic pH as shown by the polarographic measurements. The
400 number and intensity of spikes was higher for free-Pb(II) than for Pb(II)-doped NPG in response to
401 the Pb(II) adsorption in high proportion onto the NPG surface that partly hid the spike signal. Such
402 result confirms the large surface adsorption of Pb(II) to NPG as previously evidenced by experimental
403 data and modeling.

404 All these results demonstrated that Pb(II) is adsorbed on the NPG in high amount through its
405 binding as surface complexes with the oxygenated binding sites produced by the UV irradiation
406 under environmental conditions. This major process is, however, coupled to a physical
407 trapping/concentration of Pb(II) in the structure/porosity of the largest NPG in response to an
408 intraparticle diffusion mechanism.

409 *4.3. Is this sorption mechanism environmentally significant?*

410 The present results clearly demonstrate that nanoplastics have strong affinity for metals. The
411 question becomes then to identify whether this affinity could impact significantly the metal
412 environmental fate. The answer depends on two major parameters: (i) the nanoplastics
413 environmental amount and (ii) their ability to compete with the other significant metal ligands such
414 as, Fe(III) nano-oxides and/or organic matter.

415 No thorough quantitative information exists on the true amount of nanoplastics occurring in the
416 environment. However, hypotheses regarding their presence within environment allow some
417 estimations to be performed as follows. Although across the oceans, the total mass of microplastics
418 was estimated, using circulation models, to vary in between 9.3 to 23.6 10^3 tons, only 1% of this
419 estimated amount is actually found in the ocean (Jambeck et al., 2015). Several authors suggested
420 that this difference could be explained by the alteration of the micro-plastics as nanoplastics in
421 response to the ultraviolet radiation, physical wave forces and hydrolysis in ocean (Andrady et al.,
422 2011; Gigault et al., 2016; Ter Halle et al. 2017). If nanoplastics would be equally distributed in the
423 whole ocean water (liquid water), their hypothetical concentration would vary from 7 to 18 $\mu\text{g L}^{-1}$,
424 which is rather low. However, accumulation zones of microplastics have been identified in several
425 regions such as, Arctic water or oceanic gyres where microplastics can exceed 6×10^5 pieces km^{-2} ,
426 which represent for the average depth of oceans 2.3×10^{18} pieces L^{-1} (Law et al., 2010; Bergman et
427 al., 2016, Peeken et al. 2018). Considering that these microplastics represent 1% of the plastics
428 present in ocean, the nanoplastics amount in such samples can potentially reach 2.3×10^{20} pieces L^{-1}
429 which is rather high. In soils, the quantitative occurrence of microplastics and nanoplastics are
430 considered as scarce and inexistant, respectively (Rillig et al., 2012). However, the plastic particle
431 loading in agroecosystems should be high due to inputs of both recycled organic wastes and plastic
432 film mulching (Ng et al., 2018). Therefore, in some specific worldwide microplastic accumulation
433 areas, nanoplastics concentrations could be significant making them alternative actors to be
434 considered in the metal cycles and accumulation.

435 Concerning their ability to compete with strong soluble or solid ligands for metal binding a first
436 answer can be found in Table 1. The Freundlich K_{ads} compilation indeed demonstrates that for
437 equivalent mass, the Freundlich K_{ads} being in the same order of magnitude, nanoplastics could be
438 potential competitors for Fe nano-oxides and humic substances. However, this competition will
439 depend on the specific area and the binding sites density between the competitive ligands and the
440 nanoplastics. Finally, the key points to be considered before starting regarding such competition are

441 the interactions that could be performed between these ligands and the nanoplastics (aggregation,
442 coating, repulsion, etc.). These interactions could, indeed, increase the potential of nanoplastics to
443 bind metals (through additive effects) or by contrast limit their sorption capacities by recovering their
444 surface limiting as a consequence their binding sites availability.

445 **5. Conclusion**

446 Nanoplastics, recently identified and characterized, are emerging pollutants. Their size makes
447 them potential vectors of other pollutants such as metals. This study provided evidence that
448 nanoplastics, formed in natural conditions under which they are mechanically degraded and
449 especially oxidized by UV irradiations, are able to adsorb Pb(II). Lead(II) adsorption seems to be
450 controlled by chemical and physical interactions with NPG. Adsorption is strongly dependent to pH.
451 A large increase in the adsorption was evidenced for $\text{pH} > 4$ that corresponds to the carboxylic sites
452 deprotonation. This observation suggests that Pb(II) could be bound to the surface oxygenated
453 binding sites through inner sphere complexes, which result in an heterogeneous adsorption process.
454 To a lesser extent, sorption seems to depend on a Pb(II) intraparticle diffusion as evidenced by
455 modeling and analytical results.

456 The sorption capacity of nanoplastics are high, with Pb(II) Freundlich binding constants close to
457 those of ferrihydrite, nano-goethite and humic acid, known to be strong adsorbents of metals. If no
458 evidence were provided that microplastics are able to load high amount of metals, by contrast the
459 present study demonstrated that the nanometric size and surface properties of nanoplastics
460 produced under environmental conditions, can allow nanoplastics to be efficient vectors of Pb(II) and
461 probably of many other metals. Moreover, both modalities of Pb binding to NPG raise the question
462 of the subsequent bioavailability of the bound metals. Are adsorbed Pb(II) more available than
463 porosity trapped Pb(II) or inversely?

464

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468

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Table 1: Kinetic parameters calculated using the pseudo second order model and the intraparticle diffusion model for the kinetic adsorption experiment at $[\text{Pb(II)}] = 2 \text{ mg g}^{-1}$ and $[\text{Pb(II)}] = 6 \text{ mg g}^{-1}$.

Kinetic parameters	Kinetic experiment at $[\text{Pb(II)}] = 2 \text{ mg g}^{-1}$	Kinetic experiment at $[\text{Pb(II)}] = 6 \text{ mg g}^{-1}$
Pseudo-second order model		
Q_e theoretical (mg g^{-1})	1.89	5.44
K ($\text{g mg}^{-1} \text{ min}^{-1}$)	0.24	0.072
h ($\text{mg g}^{-1} \text{ min}^{-1}$)	0.88	2.14
R^2	1	0.999
Q_e experimental (mg g^{-1})	1.89	5.46
Intra-particle diffusion		
Ki_1 ($\text{mg g}^{-1} \text{ min}^{-1/2}$)	0.07	0.16
C_1 ($\text{g mg}^{-1} \text{ min}^{-1}$)	1.5	4.2
R^2_1 ($\text{mg g}^{-1} \text{ min}^{-1}$)	0.98	0.98
Ki_2 ($\text{mg g}^{-1} \text{ min}^{-1/2}$)	0.008	0.023
C_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	1.76	5.06
R^2_2 ($\text{mg g}^{-1} \text{ min}^{-1}$)	0.87	0.78

Table 2: Comparison of the present calculated Freundlich K_{ads} and the Freundlich K_{ads} of Pb(II) binding to various adsorbents.

Sample	K_{ads}	K_{ads} (present study)	Calculation units	References
Beached pellet in sea water pH= 7.8	2.1×10^{-1}	4.6×10^2	y: $\mu\text{g g}^{-1}$ x: $\mu\text{g L}^{-1}$	Holmes et al. (2012)
Beached pellets in sea water pH= 7.8	6.5×10^{-1}	3.5×10^3	y: nmol g^{-1} x: nmol L^{-1}	Holmes et al. (2014)
Beached pellets in river water pH= 6.3	3.7×10^{-1}	3.5×10^3	y: nmol g^{-1} x: nmol L^{-1}	Holmes et al. (2014)
Goethite pH= 6, IS = 10^{-3} M	3×10^{-4}	4.5×10^{-3}	y: mol g^{-1} x: mol L^{-1}	Christophi and Axe (2000)
Goethite pH = 4.2	1.710^{-1}	1.4×10^1	y: mmol kg^{-1} x: $\mu\text{mol L}^{-1}$	Olu-Owolabi and Ajayi (2011)
Ferrihydrite pH = 5.5	11.76	8.31	y: mg g^{-1} x: mg L^{-1}	Rout et al. (2012)
Nano-goethite pH = 5.5	10.33	8.31	y: mg g^{-1} x: mg L^{-1}	Mohapatra et al. (2010)
Purified Humic Acid (PPHA) pH = 5	1.40	8.31	y: mg g^{-1} x: mg L^{-1}	Pinheiro et al. (1994)

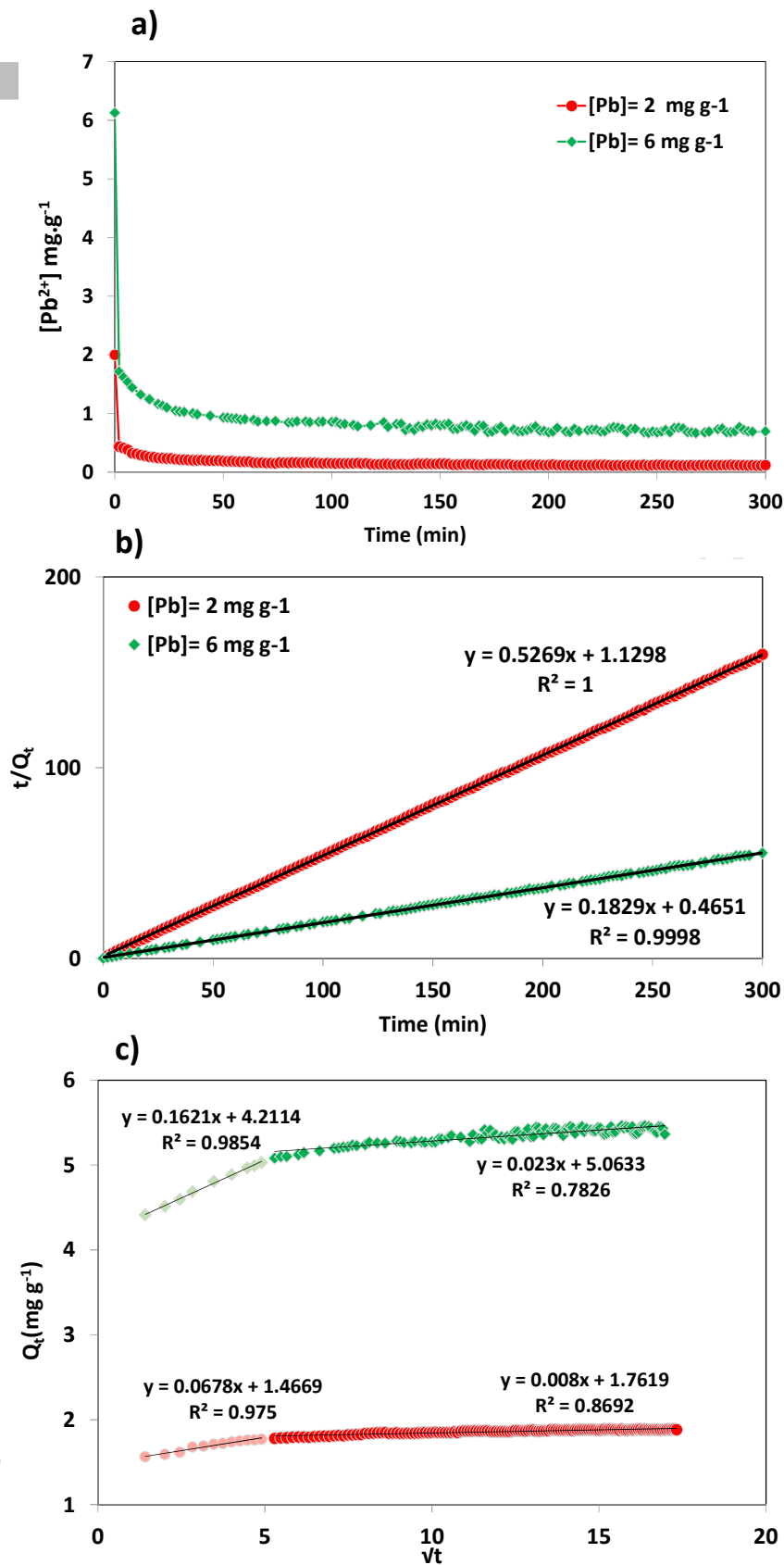


Figure 1: a) Time-dependent Pb(II) sorption onto NPG for b) Pseudo second order kinetics modelling, c) Intraparticle diffusion kinetic model for $[Pb(II)]_{initial} = 0.3$ mg L⁻¹ and $[Pb(II)]_{initial} = 0.1$ mg L⁻¹, corresponding to red and green symbols, respectively

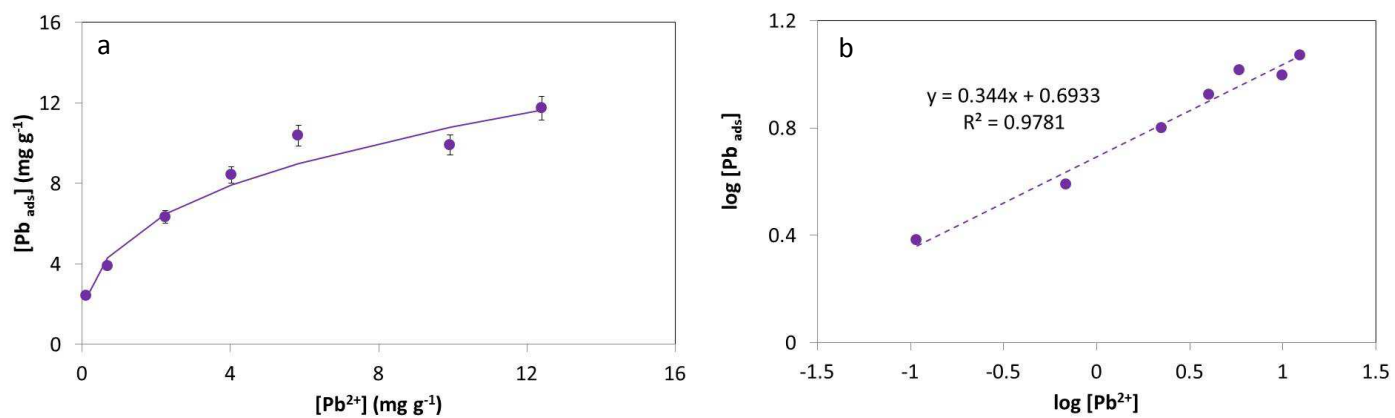


Figure 2: Adsorption isotherm of Pb(II) onto NPG at pH 7: a) experimental and modeled data and b) linearization of the experimental data using the Freundlich model.

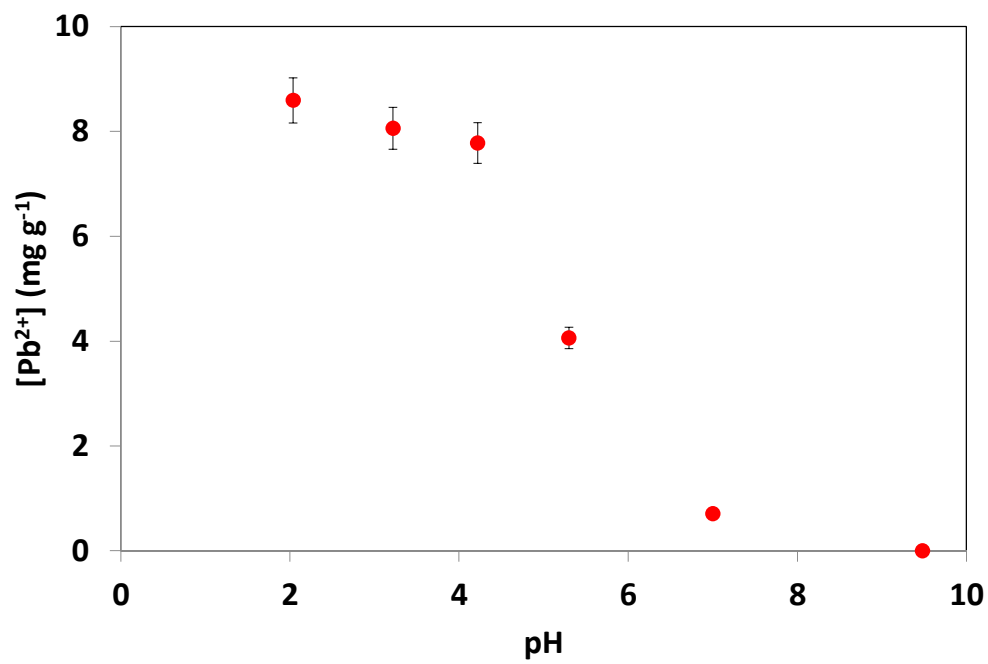


Figure 3: Evolution of the Pb^{2+} concentration relative to pH in presence of NPG at $50\ mg\ g^{-1}$.

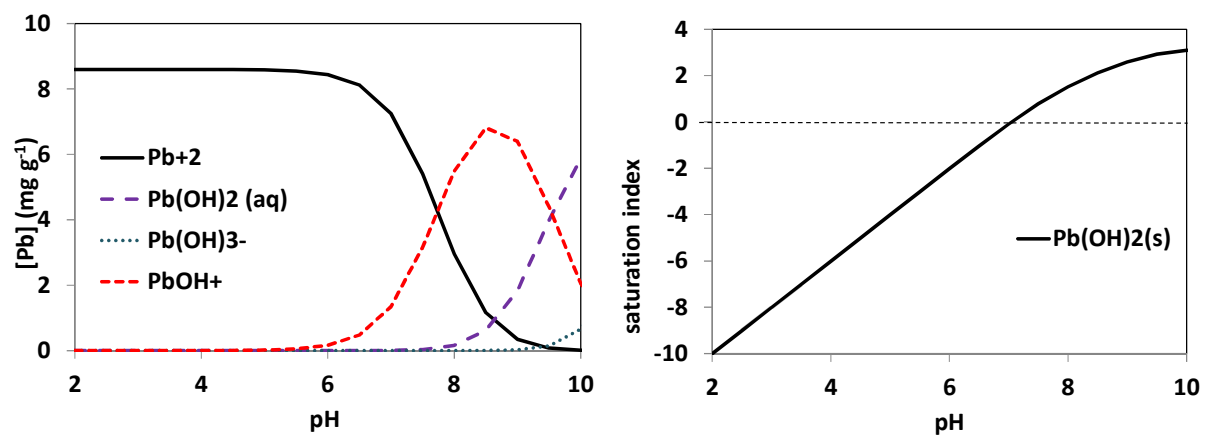


Figure 4: Pb(II) speciation under pH-adsorption-edge experimental condition but without NPG: a) corresponds to the Pb^{2+} speciation in solution and b) the evolution of the saturation index of $\text{Pb}(\text{OH})_2(\text{s})$, the unique species that was identified to precipitate.

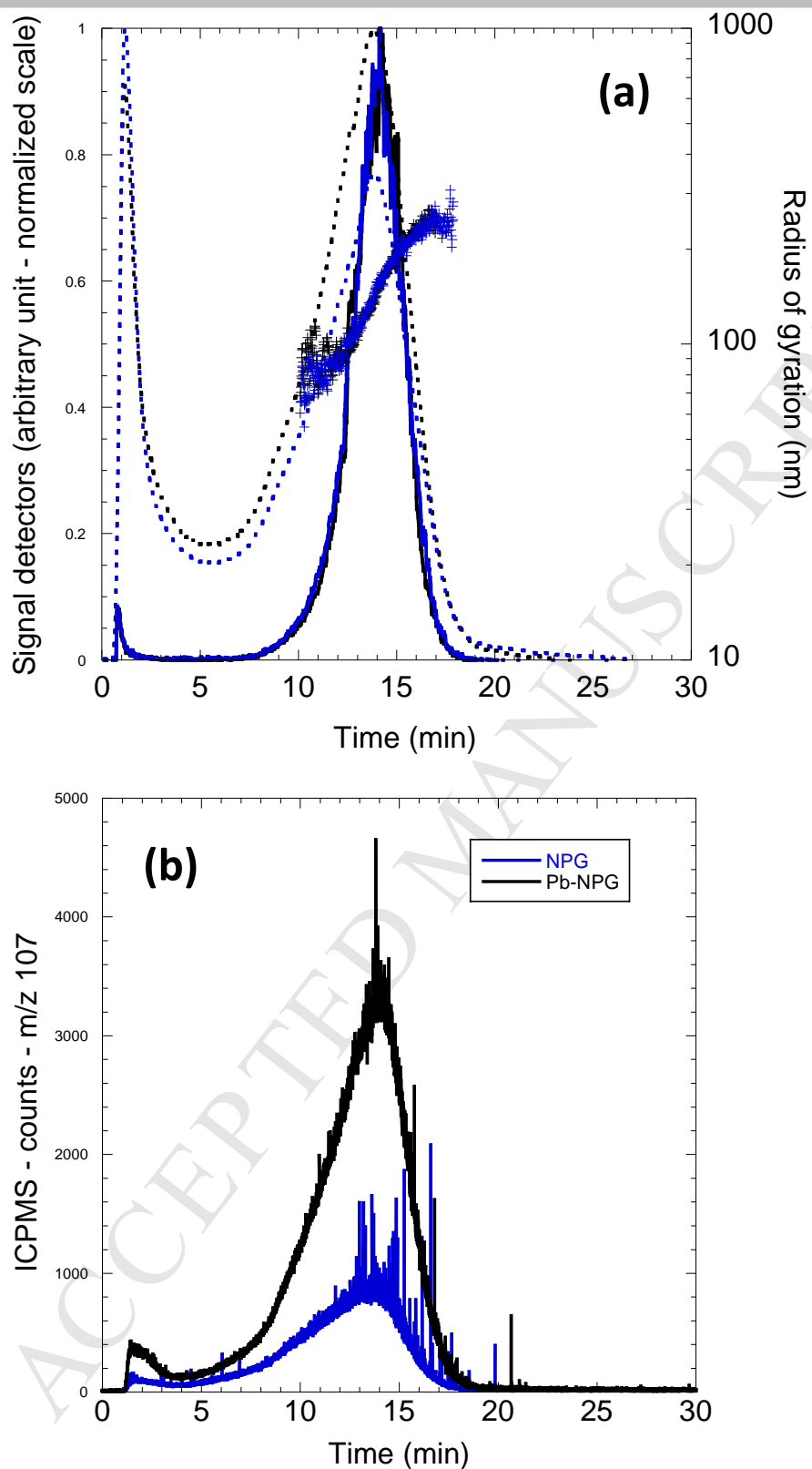


Figure 5: A4F fractograms of free Pb(II) and Pb(II)-doped NPG (a) the UV and SLS detection with the R_g variation (blue cross), (b) the ICP-MS detection with m/z 207 (Pb(II)).

Highlights

- Pb(II) binding experiments onto nanoplastics extracted from environmental microplastics were performed.
- Pb(II) was largely bound onto nanoplastics by specific adsorption and intra-particle diffusion.
- Nanoplastics could be significant vectors of metals in the environment