

# Carbohydrate Polymers

## Evaluation of adsorption ability of Cyclodextrin-Calixarene Nanosponges towards Pb<sup>2+</sup> ion in aqueous solution

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<b>Abstract:</b>	Highlights  - Some cyclodextrin-calixarene nanosponges were tested as sorbents for Pb <sup>2+</sup> ion species.  - The materials can simultaneously sequester both inorganic and organic pollutants.  - Functionalization of the materials has a critical outcome on their sorbent abilities.  - Their abilities were rationalized in terms of functional mobility of the solvent medium.
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To the Editor of Carbohydrate Polymers

Sir,

We are pleased to submit our manuscript entitled “Evaluation of adsorption ability of Cyclodextrin-Calixarene Nanosponges towards  $Pb^{2+}$  ion in aqueous solution”, by S. Cataldo, P. Lo Meo, P. Conte, A. Di Vincenzo, D. Milea and A. Pettignano, for publication on Carbohydrate polymers. The paper deals with an investigation on the possible use of nanoporous materials based on cyclodextrin and calixarene architectures (CyCaNSs), for the sorption of  $Pb(2+)$  species. The work is aimed at demonstrating that CyCaNSs, being able to sequestrate both inorganic and organic species, constitute valuable materials for designing pollutant removal devices. Therefore, the work may be of interest for researchers in the field of environmental remediation.

Sincerely yours

Prof. A. Pettignano

Prof. P. Lo Meo

***Highlights***

- Some cyclodextrin-calixarene nanosponges were tested as sorbents for  $\text{Pb}^{2+}$  ion species.
- The materials can simultaneously sequester both inorganic and organic pollutants.
- Functionalization of the materials has a critical outcome on their sorbent abilities.
- Their abilities were rationalized in terms of functional mobility of the solvent medium.

# 1 Evaluation of adsorption ability of Cyclodextrin- 2 Calixarene Nanosponges towards $Pb^{2+}$ ion in 3 aqueous solution

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18

## 19 **Highlights**

- 20 - Some cyclodextrin-calixarene nanosponges were tested as sorbents for  $Pb^{2+}$  ion species.
- 21 - The materials can simultaneously sequester both inorganic and organic pollutants.
- 22 - Functionalization of the materials has a critical outcome on their sorbent abilities.
- 23 - Their abilities were rationalized in terms of functional mobility of the solvent medium.

24 **ABSTRACT.** In this study, different pristine and chemically post-modified cyclodextrin-  
25 calixarene nanosponges (CyCaNSs) have been characterized by means of FFC-NMR relaxometric  
26 techniques, and used as adsorbent materials to remove  $Pb^{2+}$  from aqueous solutions. Considering  
27 that the removal treatments may involve polluted waters with different characteristics, the  
28 adsorption experiments were performed on solutions without and with the addition of background  
29 salts, under different operational conditions. In particular,  $NaNO_3$  and  $NaCl$  were used as salts to  
30 change the ionic strength in the range  $0.01 \sim 0.1 \text{ mol L}^{-1}$ ; the initial pH of the treated solutions was

31 fixed at the values of either 3.0 or 5.0, while the effect of temperature was studied in the range  
32 283.15~323.15 K. The adsorption abilities and affinities of the nanosponges towards  $Pb^{2+}$  were  
33 kinetically and thermodynamically investigated by measuring the metal ion concentration in the  
34 water samples of batch experiments by means of Inductively Coupled Plasma Emission  
35 Spectroscopy (ICP-OES) and Differential Pulse Anodic Stripping Voltammetry (DP-ASV). The  
36 acid-base properties of nanosponges and of metal ion as well as their interactions with the other  
37 interacting components of the systems have been considered in the evaluation of adsorption  
38 mechanism. Recycling and reuse experiments on the most efficient adsorbents were also  
39 performed. On the grounds of the results obtained, post-modified CyCaNSs appear promising  
40 materials for designing environmental remediation devices.

41  
42 *Keywords: Adsorption, FFC-NMR relaxometry, Lead, Nanosponges, Remediation, Speciation.*

43  
44 **1. Introduction**  
45 Sorbent materials able to sequester at the same time both inorganic and organic species  
46 constitute valuable tools for designing environmental remediation devices, aimed at the treatment  
47 of polluted soils and waters, and in particular at the detoxification of wastewaters. Systems based  
48 on chitosan (Sarode et al., 2019; Zhu & Zhou, 2018), alginate (Cataldo, Cavallaro, et al., 2013;  
49 Cataldo, Gianguzza, Pettignano, & Villaescusa, 2013), graphene (Siyal, Shamsuddin, Low, &  
50 Rabat, 2020; Zhang, Hou, Huang, & Fan, 2020), biochars (Cataldo, Chiodo, et al., 2018; M. A.  
51 Rao, Di Rauso Simeone, Scelza, & Conte, 2017; Ravindiran, Ganapathy, Josephraj, &  
52 Alagumalai, 2019; Wang & Wang, 2019), yeasts (Massoud, Hadiani, Hamzehlou, & Khosravi-  
53 Darani, 2019; Qin, Hu, Zhai, Lu, & Aliyeva, 2020), etc. have been widely tested for these

54 purposes. In particular, an increasing attention has been recently paid to composite materials  
55 based on cyclodextrins (CDs) (Julinová & Slavík, 2012; Karoyo & Wilson, 2015; Tong & Yuan,  
56 2012). In fact, these cyclic oligosaccharides gather several interesting and useful features  
57 (Szejtli, 1998). They can be considered as a sustainable material (being obtained via bacterial  
58 digestion of starch, and thereby constituting a renewable source). Moreover, they are highly  
59 functionalized molecules, containing plenty of primary and secondary hydroxyl groups liable to  
60 undergo chemical transformation by quite simple organic reaction routes (Khan, 1998).

61 Furthermore, CDs are probably the most accessible and studied class of supramolecular hosts,  
62 able to form inclusion complexes with a large variety of diversely structured organic guest  
63 species (Rekharsky & Inoue, 1998). They can also interact with inorganic cations (Bonomo,  
64 Pedotti, Vecchio, & Rizzarelli, 1996; Bose & Polavarapu, 1999; Oliveri, Pietropaolo, Sgarlata, &  
65 Vecchio, 2017; Rizzarelli & Vecchio, 1999; Tabushi, Kuroda, & Mizutani, 1984; Yoshihisa,  
66 Toyoaki, & Yoshio, 1972) via their hydroxyl groups and any other suitable donor groups that  
67 could have been inserted by chemical modification, and can even stabilize metal nanoparticles (J.  
68 Liu et al., 1999; J. Liu, Ong, Kaifer, & Peinador, 2002; J. Liu, Ong, Román, Lynn, & Kaifer,  
69 2000; M. Russo et al., 2015). The reaction between native or chemically modified CDs with  
70 suitable reticulating agents allows accessing to a further class of potential sorbent materials  
71 referred to as “Nanosponges” (NSs) (Caldera, Tannous, Cavalli, Zanetti, & Trotta, 2017;  
72 *Nanosponges: Synthesis and Applications*, 2019; Francesco Trotta, 2011; F. Trotta, Shende, &  
73 Biasizzo, 2012). Notwithstanding their insoluble hyper-cross-linked structure, NSs show an  
74 excellent permeability to aqueous media and a fair swellability (Paolo Lo Meo, Mundo,  
75 Terranova, Conte, & Chillura Martino, 2020), maintaining at the same time the inclusion abilities  
76 of the parent CDs. Therefore, NSs are excellent platforms to support nanosized catalysts (Noël et

77 al., 2014; Marco Russo et al., 2019; Vasconcelos et al., 2016) or to provide smart/tailored  
78 materials for controlled drug delivery (Allahyari, Trotta, Valizadeh, Jelvehgari, & Zakeri-Milani,  
79 2019; Cavalli, Trotta, & Tumiatti, 2006; Chilajwar, Pednekar, Jadhav, Gupta, & Kadam, 2014;  
80 Swaminathan, Vavia, Trotta, & Torne, 2007; Francesco Trotta, Dianzani, Caldera, Mognetti, &  
81 Cavalli, 2014; Francesco Trotta, Zanetti, & Cavalli, 2012). Moreover, NSs are also ideal  
82 candidates as sorbent materials for environmental applications. The sequestration of metal  
83 cations, and the simultaneous adsorption of both inorganic and organic species by NS-based  
84 materials as well, has been occasionally explored (Morin-Crini & Crini, 2013; Sikder et al.,  
85 2019). For instance, promising results have been obtained in the simultaneous sequestration of  
86  $Pb^{2+}$  ions and a dye (Acid Red), using a composite material based on  $\beta$ CD and chitosan cross-  
87 linked with glutaraldehyde and EDTA dianhydride (Wu et al., 2018). The simultaneous  
88 sequestration of  $Pb^{2+}$  ions and Bisphenol A or Methylene Blue with a material obtained  
89 reticulating the  $\beta$ CD with hexachloro-cyclotriphosphazene has been reported (Yinli Liu et al.,  
90 2019).

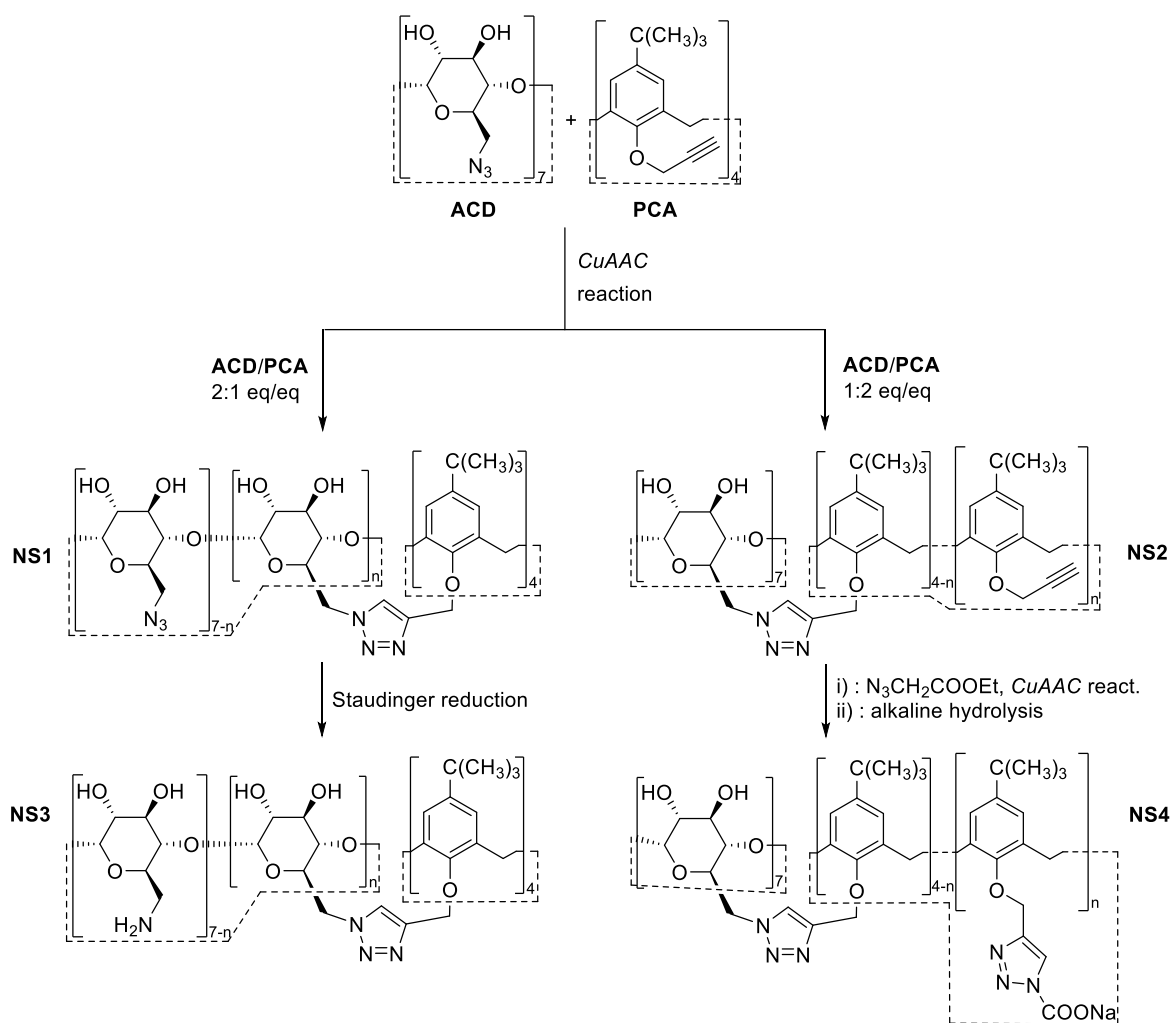
91 We have been recently interested in the synthesis and adsorption/release abilities of a new  
92 class of NSs obtained by co-polymerization of cyclodextrin and calixarene derivatives, which are  
93 joined together by means of 1,2,3-triazole linker units (Fontana et al., 2019; P. Lo Meo, Lazzara,  
94 Liotta, Riela, & Noto, 2014; Massaro et al., 2016). These materials (indicated hereinafter as  
95 CyCaNSs) benefit from the presence of two different co-monomers, having somehow  
96 complementary supramolecular host abilities, and from their viable chemical post-modification  
97 as well, which easily enables the introduction on the polymeric network of further functionalities  
98 such as amine or carboxyl groups (Cinà, Russo, Lazzara, Chillura Martino, & Lo Meo, 2017).  
99 Due to the presence of the aforementioned ionizable groups, these materials present pH-sensitive

100 adsorption/release abilities towards various probe guests such as *p*-nitroaniline derivatives, dyes  
101 and bioactive molecules (Di Vincenzo et al., 2019). Their acid-base properties have been  
102 recently assessed. Interestingly, it has been positively shown that the insertion in the polymeric  
103 network largely enhances (up to several order of magnitude) the basic strength of the triazole  
104 linker units (Di Vincenzo et al., 2019). In view of a possible utilization of CyCaNSs as materials  
105 for environment remediation purposes, an investigation of their possible sequestration abilities  
106 towards metal cations was needed. In particular, we paid attention to the Pb<sup>2+</sup> ion for several  
107 reasons. Among toxic metal ions, indeed, lead is one of the most extensively used in several  
108 fields like, e.g., PVC production, ammunition, paints, vehicle batteries, etc. Moreover, lead is  
109 considered one of the most toxic metal. Exposure of plants, animals and humans to lead causes  
110 well known negative effects (Crompton, 2007). In particular, the long term exposure of humans  
111 can cause learning and behavioral difficulties in children, damage to liver and kidneys, reduction  
112 of bone growth and disease to immune system (Gidlow, 2015; Mason, Harp, & Han, 2014).

113 In the present study we investigated the adsorption abilities towards the Pb<sup>2+</sup> ion of four  
114 selected CyCaNSs NS1-NS4 (Figure 1). More in detail, materials NS1 and NS2 are obtained by  
115 reacting, under the typical conditions of the well-known *CuAAC* coupling reaction (Meldal &  
116 Tornøe, 2008), the heptakis-(6-azido)-(6-deoxy)-βCD (**ACD**) and the tetrakis-propargyloxy-  
117 calix[4]arene (**PCA**) in two different equivalent ratios (2:1 and 1:2) respectively. These ratios  
118 were chosen in such a way that the resulting products possess either azide or alkyne unreacted  
119 functional groups, able to undergo further transformation (Cinà et al., 2017). Hence, material  
120 NS3 is obtained from NS1 by Staudinger reduction, whereas NS4 is obtained from NS2 by  
121 *CuAAC* reaction with ethyl azidoacetate and subsequent alkaline hydrolysis. All these materials  
122 have already undergone full structural and morphological characterization (FT-IR, <sup>13</sup>C[<sup>1</sup>H] CP-



123 MAS SS-NMR, SEM, BET/BJH porosimetry) (Cinà et al., 2017; P. Lo Meo et al., 2014). Their  
 124 average compositions are summarized in Table 1. Moreover, they have been tested for their pH-  
 125 dependent adsorption abilities towards a set of diverse model pollutants, such as *p*-nitroaniline  
 126 derivatives and commercial dyes (Bromocresol green, Toluidine blue, Methylorange), suitably  
 127 selected according to their different size, shape, hydrophobic/hydrophilic character and possible  
 128 presence of charged or ionizable groups.  
 129



130  
 131 **Figure 1.** Nanosponges NS1-NS4.

132

133 **Table 1.** Average composition (mmol g<sup>-1</sup>) of CyCaNSs.<sup>a</sup>

	co-monomers		from NMR			from potentiometric titration		
	PCA	ACD	Triazole groups	Amine groups	Carboxyl groups	Triazole groups	Amine groups	Carboxyl groups
NS1	0.495	0.461	1.66	-	-	0.49	-	-
NS2	0.847	0.246	1.46	-	-	0.42	-	-
NS3	0.518	0.481	1.66	1.71	-	0.40	0.68	-
NS4	0.677	0.196	2.71	-	1.64	0.69	-	0.75

134 <sup>a</sup> from ref. (Di Vincenzo et al., 2019).

135

## 136 **2. Materials and Methods**

137

### 138 *2.1. Materials*

139 The CyCaNSs NS1-NS4 had been already prepared for previous works (Cinà et al., 2017; Di  
 140 Vincenzo et al., 2019). Sodium nitrate and sodium chloride pure salts (Fluka) were used, after  
 141 drying at 383.15 K for 2 h, to adjust the ionic strength of solutions. Nitric acid, hydrochloric acid  
 142 and sodium hydroxide used to adjust the pH of the metal ion solutions were prepared by diluting  
 143 concentrated Fluka solutions. Pb<sup>2+</sup> ion solutions were prepared by weighing the Pb(NO<sub>3</sub>)<sub>2</sub>  
 144 (Aldrich, analytical grade) salt. Standard solutions of the metal ion used for calibration curves  
 145 were prepared by diluting 1000 mg L<sup>-1</sup> standard solution in 2% HNO<sub>3</sub> (CertiPUR, Merck). All  
 146 the solutions were prepared using freshly, CO<sub>2</sub>-free ultrapure water ( $\rho \geq 18 \text{ M}\Omega \text{ cm}$ ) and grade A  
 147 glassware.

148

### 149 *2.2. Procedures for kinetic, thermodynamic and recycling experiments*

150 Preliminary adsorption tests towards Pb<sup>2+</sup> ion on the four CyCaNSs were performed by placing  
 151 ca. 8 mg of each adsorbent material in an Erlenmeyer flask containing 20 mL of Pb(NO<sub>3</sub>)<sub>2</sub>,

152 solution ( $c_{\text{Pb}^{2+}} = 42.3 \text{ mg L}^{-1}$ ), at pH = 5.0, in  $\text{NaNO}_3$   $0.1 \text{ mol L}^{-1}$  and at  $T = 298.15 \text{ K}$ . The  
153 solutions were stirred at 180 rpm for 24 hours using an orbital mixer (model M201-OR, MPM  
154 Instruments) before measuring the metal ion concentration by means of DP-ASV technique.  
155 Batch kinetic and thermodynamic adsorption experiments were carried out only with NS3 and  
156 NS4 materials.

157 The kinetic experiments were carried out in  $\text{NaNO}_3$ , at  $I = 0.10 \text{ mol L}^{-1}$  and  $T = 295.15 \text{ K}$ . The  
158 initial pH of the solution was adjusted at 5 and was monitored during the experiments. The  
159 adsorbent material (15.0 mg) of was added to the solution containing the metal ion ( $c_{\text{Pb}^{2+}} \approx 35 \text{ mg}$   
160  $\text{L}^{-1}$ , 20 mL) in a voltammetric cell under constant and regular stirring. The metal ion  
161 concentration in solution was measured at various adsorbent/solution contact times in the interval  
162 0~400 minutes.

163 The voltammetric apparatus was constituted by a Metrohm 663 VA stand combined with the  
164 Autolab potentiostat in conjunction with the IME663 interface. The voltammetric apparatus was  
165 controlled by NOVA v. 1.10 software. The VA stand was equipped with a three electrode system  
166 consisting of: *i*) a MultiMode Electrode Pro (Metrohm, code 6.1246.120) working in the Static  
167 Mercury Drop Electrode (SMDE) mode; *ii*) a glassy carbon auxiliary electrode (code  
168 6.1247.000); *iii*) a double junction Ag/AgCl/ KCl ( $3 \text{ mol} \cdot \text{L}^{-1}$ ) reference electrode (code  
169 6.0728.030). The DP-ASV measurements were performed after bubbling purified  $\text{N}_2$  gas into the  
170 solutions for 150 s. The experimental electrochemical conditions were chosen in order to  
171 optimize the quality parameters, as signal/noise ratio, repeatability and accuracy (deposition  
172 potential  $-0.55 \text{ V}$ ; deposition time 1 s; equilibration time 10 s; potential interval  $-0.55$  to  $-0.20 \text{ V}$ ;  
173 scan rate  $0.01 \text{ V s}^{-1}$ ; step potential 3 mV; modulation amplitude 50 mV; modulation time 0.01 s;  
174 interval time 0.2 s).

175 Isotherm experiments were carried out at pH 3 and 5, without ionic medium, in  $\text{NaNO}_3$  0.1  
176  $\text{mol L}^{-1}$  and in  $\text{NaCl}$  0.01, 0.05 and 0.1  $\text{mol L}^{-1}$ , in the temperature range 283.15 – 323.15 K. In  
177 each isotherm experiment, nine samples of either NS3 or NS4 (ca. 5 mg each) were placed in  
178 different Erlenmeyer flasks containing 10~15 mL of a  $\text{Pb}(\text{NO}_3)_2$  solution ( $5 \leq c_{\text{Pb}^{2+}} / \text{mg L}^{-1} \leq$   
179 70). The solutions were stirred at 180 rpm for 12 hours using an orbital mixer (model M201-OR,  
180 MPM Instruments) and then were separated from the adsorbent before measuring the pH and the  
181 metal ion concentration.

182 The reuse and recycling of NS3 and NS4 were studied packing ~10 mg of each nanosponge  
183 into a glass column (diameter = 2 cm, length = 5 cm). 20 mL of  $\text{Pb}(\text{NO}_3)_2$  solution ( $c_{\text{Pb}^{2+}} = 35$   
184  $\text{mg L}^{-1}$ , pH = 5.0,  $T = 298.15$  K) were flowed at reflux into the column with a flow rate of 6 mL  
185  $\text{min}^{-1}$  for 12 h (the reaching of adsorption equilibrium was verified) by using a peristaltic pump  
186 (Gilson, Minipuls 3). The sorbent material was then washed with 100 mL of distilled water  
187 before the  $\text{Pb}^{2+}$  desorption carried out with 20 mL of  $\text{HNO}_3$  0.1  $\text{mol L}^{-1}$  solution for 6 h. After a  
188 further washing with 100 mL of distilled water, the next test cycle began. The water samples  
189 derived from each adsorption and desorption step were collected in 50 mL test tubes. Four  
190 adsorption / desorption cycles were carried out for each adsorbent.

191 The  $\text{Pb}^{2+}$  concentration in the solutions collected in isotherm and recycling experiments was  
192 measured by Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) technique by using  
193 a PerkinElmer Model Optima 2100, equipped with an auto sampler model AS-90. The  $\text{Pb}^{2+}$   
194 emission intensities were measured at two wavelengths (194.168 and 253.652 nm) and each  
195 measurement was repeated three times. Calibration curves were done in the same experimental  
196 conditions and covering the metal ion concentration range of adsorption experiments. The pH of  
197 the metal ion solutions before and after kinetic or isotherm experiments was measured with a

198 combined ISE-H<sup>+</sup> glass electrode (Ross type 8102). The ISE-H<sup>+</sup> electrode was previously  
199 calibrated at the same experimental conditions of the adsorption experiments. To this end, 25 mL  
200 of standardized HNO<sub>3</sub> or HCl solution was titrated with NaOH by using a potentiometric titration  
201 system (Metrohm, Model 888 Titrando) controlled by the TIAMO software.

202

### 203 *2.3. Models for kinetic and isotherm studies of Pb<sup>2+</sup> adsorption*

204 Kinetic data were first fitted with the pseudo-first order equation (PFO) of Lagergren (Yuh-  
205 Shan, 2004) (eq. 1) and the pseudo-second order equation (Blanchard, Maunaye, & Martin,  
206 1984) (PSO, eq. 2):

$$207 \quad \frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$208 \quad \frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

209 where  $q_t$  and  $q_e$  are the adsorption capacity of the adsorbent material (mg g<sup>-1</sup>) at time  $t$  and at  
210 the equilibrium, respectively,  $k_1$  (s<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> s<sup>-1</sup>) are the rate constants of adsorption. The  
211 relevant integrated forms of equations (1) and (2) are, respectively:

$$212 \quad q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

$$213 \quad q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

214 However, as we will explain hereinafter, kinetic data were also subjected to a double  
215 exponential (DEM) regression analysis model according to the equation (5):

$$216 \quad q_t = q_e [1 - \alpha \cdot e^{-k_1 t} - (1 - \alpha) \cdot e^{-k_2 t}] \quad (5)$$

217 where the parameter  $\alpha$  accounts for the relative contribution of each exponential term to the  
218 overall adsorption amount ( $0 < \alpha < 1$ ).

219 The adsorption equilibrium data have been processed according to the well-known Langmuir  
220 (Langmuir, 1918) (L, eq. 6) and Freundlich (Freundlich, 1907) (F, eq. 7) models:

$$221 \quad q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (6)$$

$$222 \quad q_e = K_F c_e^{1/n} \quad (7)$$

223 where  $q_m$  (mg g<sup>-1</sup>) is the maximum adsorption ability of the adsorbent,  $c_e$  (mg L<sup>-1</sup>) is the Pb<sup>2+</sup>  
224 concentration in solution at equilibrium;  $K_F$  (L<sup>1/n</sup> g<sup>-1</sup> mg<sup>1-1/n</sup>) and  $K_L$  (L·mg<sup>-1</sup>) are the constants of  
225 Freundlich and Langmuir models, respectively.

226 The Pb<sup>2+</sup> ion adsorption capacity at different contact times  $t$  ( $q_t$ , mg g<sup>-1</sup>) or at different Pb<sup>2+</sup> /  
227 adsorbent ratios ( $q_e$ , mg g<sup>-1</sup>) were calculated by the eq. 8:

$$228 \quad q_t \text{ or } q_e = \frac{V (c_0 - c_t)}{m} \quad (8)$$

229 where  $V$  (L) is the volume of the metal ion solution and  $m$  is the mass of CyCaNS (g);  $c_0$  and  $c_t$   
230 are the Pb<sup>2+</sup> ion concentrations in the solutions (mg L<sup>-1</sup>) at  $t = 0$  and  $t = t$ , respectively. At the  
231 equilibrium condition, eq. 7 was used by replacing  $c_t$  with  $c_e$  to calculate  $q_e$ .

232 The conditional Langmuir constant values (in NaNO<sub>3</sub> 0.1 mol L<sup>-1</sup>, pH = 5.0;  $c_{Pb^{2+}}$  in mol L<sup>-1</sup>)  
233 (Yu Liu, 2009) in the temperature range 283.15 - 323.15 were used to calculate the  
234 thermodynamic parameters  $\Delta G$  (kJ mol<sup>-1</sup>),  $\Delta H$  (kJ mol<sup>-1</sup>) and  $\Delta S$  (kJ mol<sup>-1</sup> K<sup>-1</sup>) by using Gibbs  
235 and van't Hoff equations (eqs 9 and 10). The following assumptions were done: *i*) the adsorption  
236 is reversible, *ii*) the stoichiometry of adsorption doesn't change; *iii*) equilibrium condition is  
237 established during adsorption experiments (Crini & Badot, 2008; Tran, You, & Chao, 2016).

$$238 \quad \Delta G = -RT \ln K_L \quad (9)$$

$$239 \quad \ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

240 The LIANA, Kaleidagraph 4.0 and OriginLab suite software packages were used to perform  
241 fitting analyses of adsorption isotherms and kinetic data.

242

#### 243 2.4. FFC-NMR relaxometry

244 Relaxometric experiments (Pellegrino Conte, 2019; Pellegrino Conte & Lo Meo, 2020; Paolo  
245 Lo Meo et al., 2020) were performed with a STELAR SmarTracer apparatus at 3.0, 1.0 and 0.3  
246 MHz, by applying a pre-polarized sequence. Samples of the nanosponges NS3 and NS4 (400 mg  
247 each) were placed in a NMR tube (9 mm inner diameter) and equilibrated with a NaNO<sub>3</sub> 0.1 mol  
248 L<sup>-1</sup> solution adjusted at pH 5.0 by adding a small amount of HNO<sub>3</sub>. Excess solution was carefully  
249 pipetted out before relaxometric determinations. Analysis of relaxometric data was performed  
250 as described elsewhere (Paolo Lo Meo et al., 2020). In details, the  $T_1$  relaxation kinetic data  
251 recorded were first subjected to regression analysis according to equation (11):

$$252 \quad I_t = I_0 + I_1 \cdot e^{-R_{fast}t} + I_2 \cdot e^{-R_{slow}t} \quad (11)$$

253 where  $R_{fast}$  and  $R_{slow}$  account for the relaxation of water molecules residing at the solid-liquid  
254 interface and flowing in the pores, respectively. Hence, the surface water fraction  $f_s$  can be  
255 calculated according to the relationship (12):

$$256 \quad f_s = (R_{slow} - R_w)/(R_{fast} - R_w) \quad (12)$$

257 where  $R_w$  is the relaxation rate of bulk water. Relaxation kinetics were also subjected to  
258 Inverse-Laplace transform analysis by means of the UPEN algorithm. The distributions obtained  
259 were in turn decomposed as a sum of two Log-normal distributions,  $F_{fast}(T_1)$  and  $F_{slow}(T_1)$ , from  
260 which the PCI indexes were calculated according to equation (13):

$$261 \quad PCI = \frac{\left( \int_{T_{A,fast}}^{T_{B,fast}} F_{fast}(T_1) T_1 dT_1 \right)^{-1} - R_w}{\left( \int_{T_{A,slow}}^{T_{B,slow}} F_{slow}(T_1) T_1 dT_1 \right)^{-1} - R_w} \quad (13)$$

262 where the integration limits are defined as discussed in the reference work.

263

## 264 **3. Results and Discussion**

### 265 *3.1. Speciation analysis*

266 As a general rule, the percentages of protonated/unprotonated functional groups of the  
267 adsorbent material, and the percentages of all the species formed by the metal ion to be adsorbed  
268 at the experimental conditions of the treated aqueous solution as well, play an important role on  
269 the efficiency of adsorption process. Therefore, the knowledge of species distribution of both the  
270 adsorbent and the metal ion provides a necessary starting point to discuss the adsorption results  
271 properly, and to obtain information about the adsorption mechanisms. Thus, we preliminary  
272 performed a speciation study of the four CyCaNSs and the  $\text{Pb}^{2+}$  ion, by using the stability  
273 constants from literature. More in detail, the protonation constants of ionizable sites of the  
274 CyCaNSs had already been calculated in a previous work according to the Diprotic-Like Model  
275 (DLM (Crea et al., 2009)), in NaCl medium, at  $I = 0.1 \text{ mol L}^{-1}$  and  $T = 298.15 \text{ K}$  (see Supporting  
276 Information, Table S1) (Di Vincenzo et al., 2019). It is worth mentioning here that the average  
277 amount of ionizable groups in CyCaNSs determined by potentiometric titration techniques  
278 results significantly lower than that provided by solid-state NMR characterization. This peculiar  
279 finding was explained by admitting the existence of highly hydrophobic regions within the  
280 framework of the materials, which are hardly accessible to aqueous media.

281 The stability constants of  $\text{Pb}^{2+}$  species in NaCl, at different ionic strengths were taken from  
282 Cataldo et al. (Cataldo, Lando, et al., 2018), whilst the stability constants of hydrolytic species in  
283  $\text{NaClO}_4$   $0.1 \text{ mol L}^{-1}$ , considered a non-interacting medium like  $\text{NaNO}_3$ , and at  $I \rightarrow 0 \text{ mol L}^{-1}$   
284 were taken from the references (Supporting Information, Table S2)(Baes & Mesmer, 1976). The  
285 speciation diagrams of CyCaNSs were drawn by using the concentrations of ionizable groups  
286 (triazole, amino and carboxyl groups) reported in Cataldo et al. (Cataldo, Lando, et al., 2018).



287 Conversely, those of  $\text{Pb}^{2+}$  were drawn at  $c_{\text{Pb}^{2+}} = 30 \text{ mg L}^{-1}$ , that was the initial concentration of  
288 the solution used in adsorption experiments. The percentages of  $\text{Pb}^{2+}$  and of CyCaNSs species  
289 formed at pH 3 and 5, calculated from the distribution diagrams drawn at the different  
290 experimental conditions are reported in Table 2 (see Figures 1S and 2S in the Supporting  
291 Information for complete details). The acid-base properties of the triazole unit of the CyCaNSs  
292 and of the amino unit of NS3 are well described by two protonation constants (di-functional  
293 units, according to the theory of DLM (Crea et al., 2009). Looking at the percentages of  
294 protonated and unprotonated species of CyCaNSs at pH 3 and 5, the only considerable variation  
295 regards the carboxylic units of NS4 (% of NS4-2 = 77.2 and 3.3 at pH 5 and 3, respectively).  
296 Also in the case of  $\text{Pb}^{2+}$  speciation, irrelevant differences were noted at the two pH values at the  
297 same experimental conditions. On the contrary, the concentration of chloride in metal ion  
298 solution completely changes the speciation of  $\text{Pb}^{2+}$  in the pH range 3~5 (e.g., % of  $\text{Pb}^{2+} = 99.8$   
299 and 24.3 at pH = 5.0, at  $I = 0.1 \text{ mol L}^{-1}$ , in  $\text{NaClO}_4$  and  $\text{NaCl}$ , respectively). The percent decrease  
300 for the aquo ion in solution containing  $\text{NaCl}$  background is due to the gradual increase of Pb-  
301 chloride complex species, in particular the positively charged  $\text{PbCl}^+$  and the neutral  $\text{PbCl}_2$ , on  
302 increasing medium concentration.

303

### 304 *3.2. Modelling of $\text{Pb}^{2+}$ adsorption equilibria into NS3 and NS4 adsorbent materials*

305 Preliminary adsorption tests, aimed at generally assessing the sorption abilities of the materials,  
306 enabled to select the best adsorbents to be used in further isotherm and kinetic experiments. We  
307 observed that pristine CyCaNSs NS1 and NS2 showed very poor performances. In fact, 8 %  
308 adsorption was found for NS1, whereas NS2 did not adsorb  $\text{Pb}^{2+}$  ion at all. Conversely, post-  
309 modified materials NS3 and NS4 were able to remove 70 % and 55 % of  $\text{Pb}^{2+}$  ion, respectively,  
310 under the conditions used (see Experimental).

311  
 312 **Table 2.** Percentage of CyCaNSs species and of Pb<sup>2+</sup> species formed at pH = 5.0 and 3.0 (in  
 313 parentheses), at *T* = 298.15 K

CyCaNSs	% of NSx-1 Species <sup>a</sup>			% of NSx-2 Species <sup>b</sup>		
	(NSx-1)H <sub>2</sub>	(NSx-1)H	NSx-1	(NSx-2)H <sub>2</sub>	(NSx-2)H	NSx-2
NS1	96 (100) <sup>c</sup>	4 (0)	0 (0)	-	-	-
NS2	96.1 (100)	3.9 (0)	0 (0)	-	-	-
NS3	-	97.7 (100)	2.3 (0)	99.9 (100)	0.1 (0)	0 (0)
NS4	99.7 (100)	0.3 (0)	0 (0)	-	22.8 (96.7)	77.2 (3.3)

Conditions	Pb <sup>2+</sup>	PbCl <sup>+</sup>	PbCl <sub>2</sub>	PbCl <sub>3</sub> <sup>-</sup>	Pb(OH) <sup>+</sup>
<i>I</i> → 0 mol L <sup>-1</sup>	99.8 (100)	-	-	-	0.2 (0)
NaClO <sub>4</sub> 0.1 mol L <sup>-1</sup>	99.8 (100)	-	-	-	0.2 (0)
NaCl 0.01 mol L <sup>-1</sup>	75.6 (76.2)	22.7 (22.9)	0.9 (0.9)	0 (0)	0.8 (0)
NaCl 0.05 mol L <sup>-1</sup>	38.7 (39.1)	50.7 (51.3)	9.2 (9.3)	0.2 (0.2)	1.2 (0)
NaCl 0.1 mol L <sup>-1</sup>	24.3 (24.5)	55.6 (56.0)	18.4 (18.5)	0.9 (0.9)	(0)

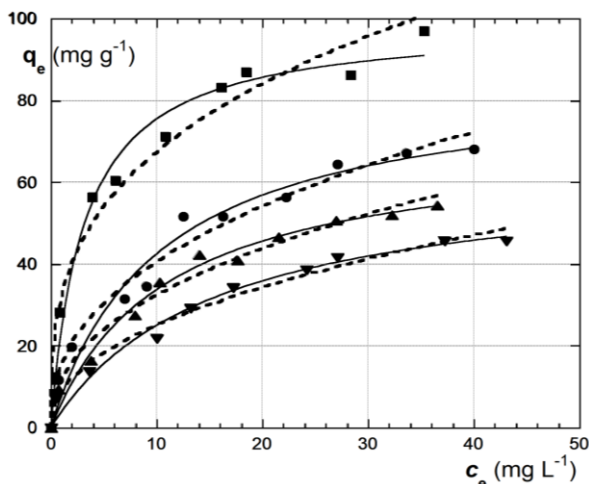
314 <sup>a</sup> triazole unit, in NaCl 0.1 mol L<sup>-1</sup>; <sup>b</sup> amino or carboxyl unit, in NaCl 0.1 mol L<sup>-1</sup>; <sup>c</sup> in parenthesis  
 315 the percentages of species at pH = 3.

316  
 317 These observations are interesting because they indicate that the participation of possible -NH<sub>2</sub>  
 318 or -COOH groups in the metal ion binding process is specifically involved. Moreover, this even  
 319 implies that the other possible binding sites present in the materials, namely the secondary  
 320 hydroxyl groups of the cyclodextrin subunits, the *soft* and electron-rich calixarene cavities and  
 321 the electron-donor N atoms of the 1,2,4-triazole linkers, are not effective in accomplishing the  
 322 Pb<sup>2+</sup> ion binding process. Therefore, considering the affinity and the higher adsorption ability of

323 NS3 and NS4, the kinetic and thermodynamic studies were continued only on these latter two  
324 adsorbents.

325 The adsorption equilibria of NS3-Pb<sup>2+</sup> and NS4-Pb<sup>2+</sup> systems were studied in aqueous solution  
326 at different experimental conditions, namely, pH 3.0 and 5.0, at  $I \rightarrow 0 \text{ mol L}^{-1}$  or with the  
327 addition of an ionic medium (either NaCl or NaNO<sub>3</sub>) at different ionic strengths ( $0.01 \leq I / \text{mol}$   
328  $\text{L}^{-1} \leq 0.1$ ) and in the temperature range  $283.15 \leq T / \text{K} \leq 323.15$ . The experimental data, i.e.  $q_e$  vs  
329  $c_e$ , have been fitted with both the Langmuir and Freundlich isotherm models. Typical trends are  
330 depicted in Figure 2 (the complete data plots are reported in the Supporting Information, Figures  
331 3S-7S; the relevant fitting parameters are reported therein, Tables 3S – 6S).

332

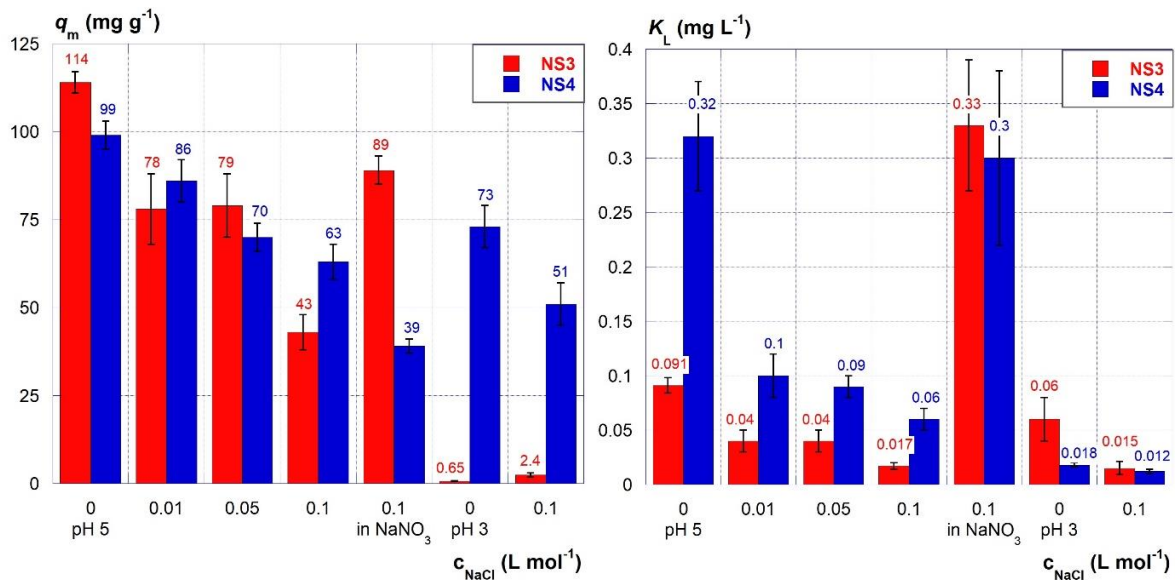


333  
334 **Figure 2.** Adsorption isotherms of Pb<sup>2+</sup> onto material NS4 from aqueous solutions at pH = 5.0  
335 without ionic medium (■), in NaCl 0.01 (●), 0.05 (▲), 0.10 (▼) mol L<sup>-1</sup> and at  $T = 295.15 \text{ K}$ .  
336 Experimental data fitted with Langmuir (continuous lines) and Freundlich (dashed lines) models.

337 As a preliminary observation, better fitting quality was in general achieved by means of the  
338 Langmuir model, rather than with the Freundlich one. Although the satisfactory fitting of an  
339 isotherm does not necessarily give information on the mechanisms of the metal ion adsorption, it  
340 can be a useful parameter to predict or optimize the sorption processes. In fact, the calculation of

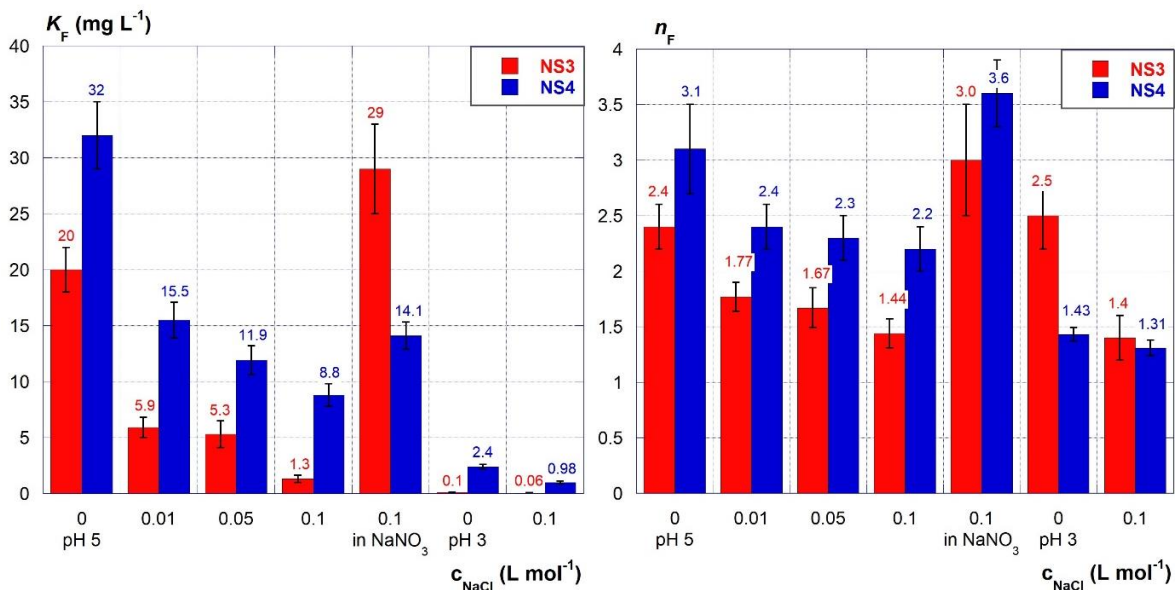
341 the Langmuir parameters  $K_L$  and  $q_m$  are related to the affinity of the material towards metal ion  
342 and to the maximum amount of metal ion that is adsorbed. Noticeably, in batch experiments  
343 carried out at pH = 5.0, we observed a decrease in the solution pH at equilibrium as large as ca.  
344 0.8~1.2 units, depending on the amount of adsorbent used. This can be attributed to an ionic  
345 exchange between the  $Pb^{2+}$  ions and the  $H^+$  ions of protonated functional groups (i.e. - OH,  
346 triazole,  $-NH_2$  or  $-COOH$ ) present in the CyCaNS materials, during the adsorption processes.  
347 Conversely, when the starting pH was 3.0 no significant pH variation was found. Trends of the  
348 of  $q_m$ ,  $K_L$ ,  $K_F$  and  $n_F$  values as a function of pH, nature of the ionic medium, ionic strength and  
349 temperature are depicted as histograms in Figures 3 and 4.

350 For both adsorbent materials, the best adsorption capacities ( $q_m$ ) and affinities ( $K_L$ ) towards  
351  $Pb^{2+}$  were observed at pH 5.0 in the absence of the ionic medium. In details,  $q_m$  values as large as  
352 114  $mg\ g^{-1}$  for NS3 and 99  $mg\ g^{-1}$  for NS4 are found, corresponding to 0.55 and 0.48  $mmol\ g^{-1}$   
353 respectively. These results, in turn, can be compared with the amount of amine and carboxyl  
354 groups present in the materials, obtained in a previous study by potentiometric titration, i.e. 0.68  
355 and 0.75  $mmol\ g^{-1}$  respectively (Di Vincenzo et al., 2019). It is worth recalling here that this  
356 result was significantly lower than the theoretical amount of ionizable groups obtained from  
357 solid state NMR characterization. This finding was explained by admitting the existence of  
358 highly hydrophobic, non-water-accessible microdomains in the matrix. Hence, our results  
359 provide good support to the aforementioned hypothesis.



360

361 **Figure 3.**  $q_m$  (left) and  $K_L$  (right) values of  $\text{Pb}^{2+}$  adsorption onto NS3 and NS4 materials from  
 362 aqueous solutions at different experimental conditions: initial pH = 5.0, ionic medium NaCl or  
 363  $\text{NaNO}_3$ ;  $0 \leq I/\text{mol L}^{-1} \leq 0.1$ ; at  $T = 298.15$  K.



364

365 **Figure 4.**  $K_F$  (left) and  $n_F$  (right) values of  $\text{Pb}^{2+}$  adsorption onto NS3 and NS4 materials from  
 366 aqueous solutions at different experimental conditions: initial pH = 3.0 or 5.0, ionic medium =  
 367 NaCl or  $\text{NaNO}_3$ ;  $0 \leq I/\text{mol L}^{-1} \leq 0.1$ ; at  $T = 298.15$  K.

368 A noticeable decrease in  $q_m$  values occurs on going from pH 5.0 to pH 3.0. In fact, the NS3  
369 adsorption ability almost drops down to zero, whereas the one for NS4 decreases to 73.4 at  $I \rightarrow 0$   
370 mol L<sup>-1</sup>, and to 51.1 mg g<sup>-1</sup> in NaCl 0.1 mol L<sup>-1</sup>, respectively. It is worth recalling here that the  
371 variation of percentages of protonated/unprotonated NS3 and NS4 species and of Pb<sup>2+</sup> species  
372 between pH 3 and 5 is almost negligible (see values reported in Table 1). Therefore, the  
373 reduction of the adsorption ability of NS3 and NS4 towards Pb<sup>2+</sup> at pH = 3.0 may be ascribed to  
374 the higher H<sup>+</sup> concentration, which is in competition with Pb<sup>2+</sup> in the feasible ion exchange  
375 adsorption mechanism.

376 Addition of NaCl to the solution causes a significant effect in the adsorption abilities ( $q_m$ ) and  
377 affinities ( $K_L$  or  $K_F$ ), both of which gradually decrease on increasing the concentration of the ionic  
378 medium. Again, it must be considered that NaCl causes negligible variations in the percentages of  
379 protonated/unprotonated forms of the adsorbent (e.g. through the formation of weak complexes  
380 between Na<sup>+</sup> and carboxylate groups of the nanosponge). Therefore, the observed decrease of the  
381 adsorption capacity can be confidently attributed to the decrease of the percent of the free aquo  
382 ion of lead, which is partly converted into complex chlorinated species (in particular PbCl<sup>+</sup> and  
383 PbCl<sub>2</sub>, the percentages of which increase with chloride concentration, see Table 1). These species  
384 (in particular the neutral PbCl<sub>2</sub>) have a lower affinity for the binding sites of the CyCaNSs.  
385 Moreover, in the case of NS3, the greater decrease in sorption ability with respect to NS4 can be  
386 attributed to the hydrochloride form of the -NH<sub>2</sub> groups, which contributes to hinder their  
387 interaction with the Pb<sup>2+</sup> ions. These considerations are supported by the fact that affinities for  
388 Pb<sup>2+</sup> ( $K_L$  and  $K_F$ ) increase on changing the ionic medium from NaCl to NaNO<sub>3</sub>, the ionic strength  
389 being equal ( $I = 0.1$  mol L<sup>-1</sup>). In particular,  $K_L$  and  $K_F$  values are on average about twenty and  
390 twenty-two times larger for NS3 and about five and two times larger for NS4, respectively.

391 The comparison between the two different CyCaNSs reveals interesting differences. At pH = 5  
392 in the presence of NaCl, NS4 shows a better affinity than NS3 ( $K_L$  and  $K_F$ ) towards the metal ion.  
393 In particular,  $K_F$  values are on average ca. three times larger for NS4 than for NS3. On increasing  
394 the NaCl concentration up to 0.1 mol L<sup>-1</sup>, absorption capacities ( $q_m$ ) decrease on a larger extent  
395 for NS3 (62 %) than for NS4 (36 %). Noticeably, changing the ionic medium from NaCl to  
396 NaNO<sub>3</sub> ( $I = 0.1$  mol L<sup>-1</sup>) causes an increase in the adsorption capacity for NS3, whereas the  
397 opposite occurs for NS4. At the same time, a larger increase of  $K_L$  occurs for NS3 (ca. 20 times)  
398 than for NS4 (ca. 5 times). Finally, comparison between data at  $I = 0$  with those in the presence  
399 of NaNO<sub>3</sub> at  $I = 0.1$  mol L<sup>-1</sup>, showed a large increase in the  $K_L$  value for NS3, whereas  $K_L$  was  
400 substantially unchanged for NS4. All these observations outline, in general, a larger sensitivity to  
401 environmental conditions for NS3 (as already observed for what concerns the effect of pH  
402 variation). This is the effect of the different average charge status of the functional groups  
403 present in the different materials (positive ammonium groups for NS3 vs. negative carboxylate  
404 groups for NS4). In fact, neutral amine groups are less able than anionic carboxylate groups in  
405 competing with water molecules and chloride ions for the positions in first coordination shell of  
406 the metal ion. This finding is consistent with the fact that monocarboxylic acids possess a much  
407 larger coordination ability towards Pb<sup>2+</sup> ion (i.e. larger stability constants for complex formation)  
408 than monoamines (Cataldo, Lando, et al., 2018). Therefore, the behavior differences between the  
409 two CyCaNS discussed above can be ultimately justified on the grounds of the aforementioned  
410 intrinsic coordination abilities of the functional groups, in perfect agreement with the well-  
411 known reactivity-selectivity principle. Noticeably, the larger decrease in  $q_m$  values on changing  
412 the ionic medium observed for NS4 can be also partly ascribed to a shielding effect of the Na<sup>+</sup>  
413 ion towards the anionic carboxylate groups, which does not occur for NS3.

414        3.3. *Thermodynamic parameters for Pb<sup>2+</sup> adsorption onto NS3 and NS4.*

415        The study of the adsorption abilities of Pb<sup>2+</sup> onto NS3 and NS4 at equilibrium was  
416        complemented by the estimation of the relevant thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ,  
417        which was performed by applying Gibbs and van't Hoff equations to the data recorded at  
418        different temperatures (in the range 283.15~323.15 K). Data are collected in Table 3 and  
419        depicted in Figure 5.

420        For both materials, the metal ion adsorption is a spontaneous process (negative  $\Delta G$  values) in  
421        the temperature range explored. Adsorption capacities of both NS3 and NS4 undergo only minor  
422        decrease on increasing the temperature. A similar, but more noticeable trend occurs for  $K_L$   
423        values. Consequently, the adsorption process results to be exothermic, with a small and positive  
424        entropy variation ( $\Delta H^\circ = -18$  and  $-11.4$  kJ mol<sup>-1</sup>,  $\Delta S^\circ = 25$  and  $4$  J mol<sup>-1</sup> K<sup>-1</sup> for NS3 and NS4,  
425        respectively). The occurrence of positive  $\Delta S$  values suggests a structural changing in the  
426        adsorbent and an increasing randomness at the adsorbent – solution interfaces (Aksu, 2002; Yu  
427        Liu & Liu, 2008; Tran et al., 2016). In the temperature range investigated, the  $\Delta G$  values vary in  
428        the ranges  $-26.5 - -28.6$  and  $-26.8 - -28.0$  kJ mol<sup>-1</sup> for NS4 and NS3, respectively, which are  
429        comparable with other literature data (El-Kafrawy, El-Saeed, Farag, El-Saied, & Abdel-Raouf,  
430        2017). Indeed,  $\Delta G$  values in the range  $-20\sim-80$  kJ mol<sup>-1</sup> are considered typical of an adsorption  
431        based on ion exchange (Gereli, Seki, Murat Kuşoğlu, & Yurdakoç, 2006; Önal, Akmil-Başar, &  
432        Sarıcı-Özdemir, 2007; Tran et al., 2016). Therefore, also  $\Delta G$  values suggest an ion exchange  
433        mechanism, which is in perfect agreement with hypothesis done on the basis of acid-base  
434        properties of binding groups of NS3 and NS4 and of the Pb<sup>2+</sup> species present in the aqueous  
435        solution at the studied experimental conditions.

436

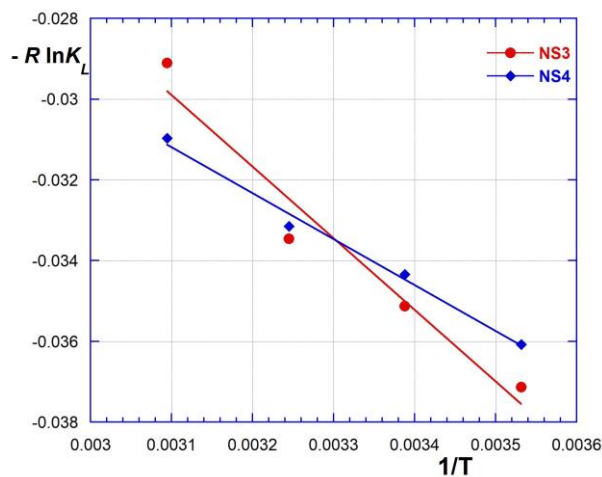


437 **Table 3.** Thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the  $\text{Pb}^{2+}$  adsorption onto NS3 and NS4  
 438 from aqueous solution at  $\text{pH} = 5$ , in  $\text{NaNO}_3$ , at  $I = 0.1 \text{ mol L}^{-1}$ , in the temperature range  
 439 283.15~323.15 K.

Adsorbent	$T$ (K)	$q_e^a$	$-\Delta G^b$	$\Delta H^b$	$\Delta S^c$
NS3	283.15	$92.9 \pm 3.9$	$26.8 \pm 0.2$	$-18 \pm 3$	$25 \pm 9$
	295.15	$88.8 \pm 4.3$	$27.3 \pm 0.3$		
	308.15	$86.6 \pm 6.1$	$28.0 \pm 0.5$		
	323.15	$81.0 \pm 4.2$	$28.0 \pm 0.5$		
NS4	283.15	$37.6 \pm 1.9$	$26.5 \pm 0.5$	$-11.4 \pm 0.8$	$4 \pm 3$
	295.15	$39.4 \pm 2.2$	$27.1 \pm 0.5$		
	308.15	$34.9 \pm 2.5$	$27.9 \pm 0.4$		
	323.15	$32.0 \pm 2.8$	$28.6 \pm 0.4$		

440 <sup>a</sup>  $\text{mg g}^{-1}$ ,  $\pm$  std. dev.; <sup>b</sup>  $\text{kJ mol}^{-1}$ ,  $\pm$  std. dev.; <sup>c</sup>  $\text{J mol}^{-1} \text{K}^{-1}$ ,  $\pm$  std. dev.

441



442

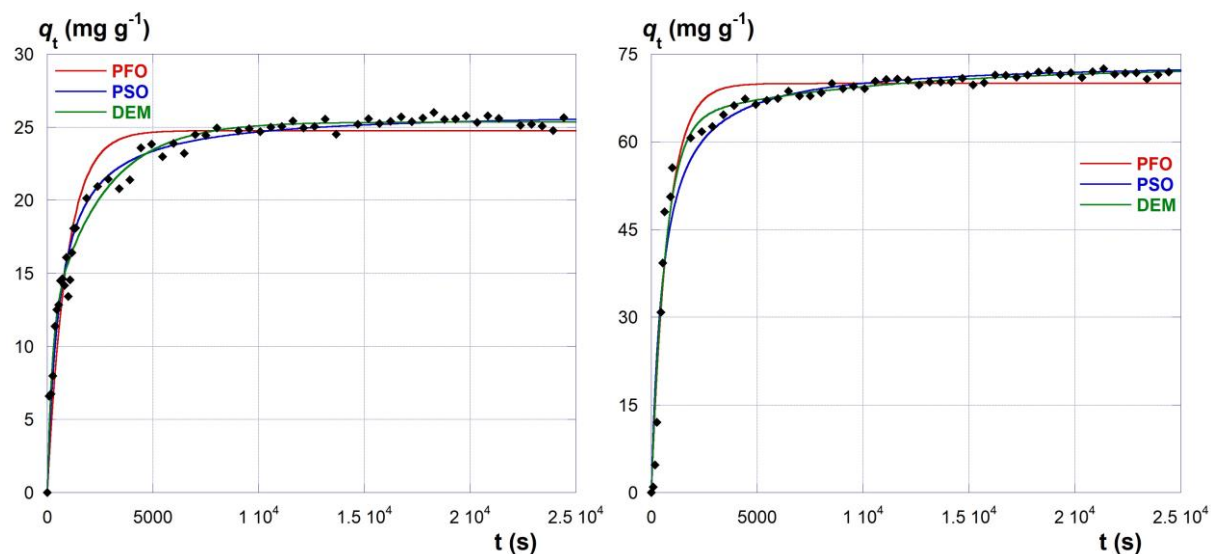
443 **Figure 5.** plot of  $-R \ln K_L$  vs.  $1/T$  for the calculation of thermodynamic parameters  $\Delta H$  and  $\Delta S$  for  
 444  $\text{Pb}^{2+}$  adsorption onto NS4 at  $\text{pH} = 5.0$ , in  $\text{NaNO}_3$   $0.1 \text{ mol L}^{-1}$ , by using van't Hoff equation.

445

446        3.4. Kinetics of  $Pb^{2+}$  adsorption onto NS3 and NS4.

447        The kinetics of  $Pb^{2+}$  adsorption onto NS3 and NS4 was studied at  $pH = 5.0$ , in  $NaNO_{3aq}$  at  $I =$   
448         $0.1 \text{ mol L}^{-1}$  and  $T = 298.15 \text{ K}$ . In both kinetic experiments were used the same amount of  
449        adsorbent, i.e. ca 15 mg, and the same metal ion solution ( $20 \text{ mL}$ ,  $c_{Pb^{2+}} = 35 \text{ mg L}^{-1}$ ). Relevant  
450        data are illustrated in Figure 6. The PFO and PSO kinetic models were first used to fit the  
451        experimental data. However, visual observation of the data plots suggested us to use also a  
452        double-exponential DEM fitting model as a suitable alternative. Fitting parameters obtained are  
453        collected in Table 4. A quick overview of results collected in Table 4 clearly shows that the PFO  
454        model affords an inferior fitting of experimental data. Conversely, in both cases, statistical  
455        testing parameters indicated that the DEM model was the best model. The latter finding is  
456        interesting, because it mirrors the kinetic profiles observed for the release of some organic guests  
457        from CyCaNSs composites. (Guernelli, Cariola, Baschieri, Amorati, & Lo Meo, 2020; Massaro et  
458        al., 2016) This suggests the idea that adsorption occurs through the superimposition of two  
459        different processes, a “fast” and a “slow” one, probably accounting for the occurrence of mass  
460        transfer phenomena within the material texture.

461        Both the PSO and the DEM models agree in indicating that NS4 is faster than NS3 in  
462        accomplishing adsorption. More in detail, as long as the PSO model is concerned,  $k_2$  is ca. 2.5  
463        times larger for the former material. For the DEM model,  $k_1$  and  $k_2$  result ca. 4 times and 3 times  
464        larger, respectively. Conversely, NS3 shows a much larger adsorption capacity (ca. 3 times) than  
465        NS4. It is worth noting, at this purpose, that the value for the  $\alpha$  parameter found in the case of  
466        NS3 (i.e. 0.87) suggests that most of the metal ion is absorbed during the “fast” step of the  
467        process. Differently, the  $\alpha$  value for NS4 (0.44) indicates that both steps equally contribute to  
468        overall adsorption.



469  
 470 **Figure 6.** Dependence of  $q_t$  ( $\text{mg g}^{-1}$ ) on contact time for the  $\text{Pb}^{2+}$  adsorption onto NS3 (left) and  
 471 NS4 (right). Data were fitted with the PFO (red), PSO (blue) and DEM (green) kinetic models.

472 **Table 4.** Parameters of PFO and PSO and DEM kinetic equations for  $\text{Pb}^{2+}$  adsorption onto NS4  
 473 anNS3 in aqueous solution at  $\text{pH} = 5.0$ , in  $\text{NaNO}_3$ , at  $I = 0.1 \text{ mol L}^{-1}$  and  $T = 298.15 \text{ K}$

material	PFO	PSO	DEM
NS3	$q_e = 69.9 \pm 0.5 \text{ mg g}^{-1}$ $k_1 = (1.30 \pm 0.07) \cdot 10^{-3} \text{ s}^{-1}$  $R^2 = 0.9618$	$q_e = 73.8 \pm 0.7 \text{ mg g}^{-1}$ $k_2 = (2.5 \pm 0.2) \cdot 10^{-5} \text{ s}^{-1} \text{ mg}^{-1} \text{ g}$  $R^2 = 0.9649$	$q_e = 72.7 \pm 1.8 \text{ mg g}^{-1}$ $\alpha = 0.87 \pm 0.03$ $k_1 = (1.53 \pm 0.12) \cdot 10^{-3} \text{ s}^{-1}$ $k_2 = (1.0 \pm 0.7) \cdot 10^{-4} \text{ s}^{-1}$ $R^2 = 0.9781$
NS4	$q_e = 24.7 \pm 0.3 \text{ mg g}^{-1}$ $k_1 = (1.10 \pm 0.06) \cdot 10^{-3} \text{ s}^{-1}$  $R^2 = 0.9421$	$q_e = 26.1 \pm 0.2 \text{ mg g}^{-1}$ $k_2 = (6.4 \pm 0.3) \cdot 10^{-5} \text{ s}^{-1} \text{ mg}^{-1} \text{ g}$  $R^2 = 0.9813$	$q_e = 25.3 \pm 0.2 \text{ mg g}^{-1}$ $\alpha = 0.44 \pm 0.03$ $k_1 = (4.7 \pm 0.7) \cdot 10^{-3} \text{ s}^{-1}$ $k_2 = (4.0 \pm 0.4) \cdot 10^{-4} \text{ s}^{-1}$ $R^2 = 0.9858$

474

475 As a final remark, it is worth noting that, as long as the PSO model is concerned, the  $k_2$   
476 values found in our case appear a little lower in comparison with other literature reports  
477 (Taka, Fosso-Kankeu, Pillay, & Mbianda, 2018; Zhao et al., 2019).

478

### 479 3.5. Textural features of NS3 and NS4 from FFC-NMR relaxometry.

480 In order to rationalize the whole of the experimental results, we reasoned that, along with the  
481 different chemical functionalization of the materials, the relevant physico-chemical and  
482 morphological features should be accounted for, with particular regard to their permeability to  
483 aqueous media. At this purpose, it is worth mentioning here that the textural/porosimetric  
484 properties of nanosponges can be hardly investigated with the ordinary BET/BJH methodologies  
485 (L. D. Wilson, Mohamed, & Berhaut, 2011; Lee D. Wilson, Mohamed, & Headley, 2011), whereas  
486 interesting and valuable information can be achieved by means of fast-field cycling (FFC) NMR  
487 relaxometric techniques. Investigation of the  $^1\text{H}$  longitudinal relaxation for a micro- or nano-  
488 porous material sample saturated with water, enables to evaluate the fraction  $f_s$  of water molecules  
489 directly interacting with the pore surface (Bird, Preston, Randall, Whalley, & Whitmore, 2005;  
490 Pohlmeier, Haber-Pohlmeier, & Stapf, 2009; Stingaciu et al., 2010). Moreover, the inverse-  
491 Lagrange transform of the relaxation kinetics data can be correlated with pore size distribution (P.  
492 Conte & Ferro, 2018; Pellegrino Conte & Ferro, 2020). In the case of materials such as  
493 nanosponges, which may undergo swelling in the presence of aqueous media, a “*pore connectivity*  
494 *index*” (*PCI*) can be defined, in order to describe the functional mobility of water within the  
495 nanopore network (Paolo Lo Meo et al., 2020).

496 We studied the longitudinal relaxation of materials NS3 and NS4 at three Larmor frequencies  
497 (3, 1 and 0.3 MHz) after equilibration with aqueous  $\text{NaNO}_3$  0.1 mol L<sup>-1</sup> solution at pH 5.0.

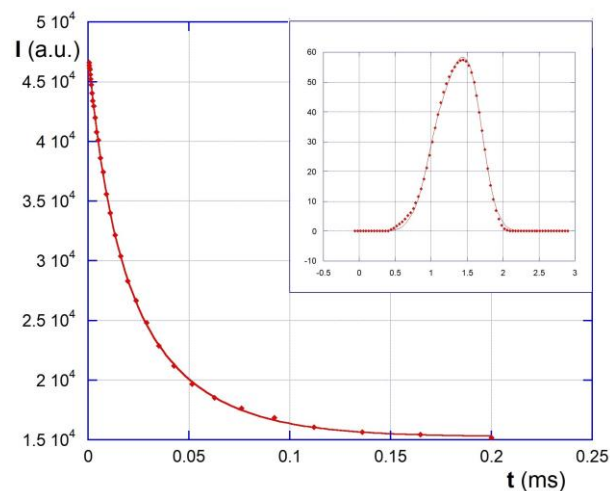
498 According to previous literature, relaxation kinetics follows a double-exponential trend, with a  
 499 “fast” and a “slow” component accounting for the relaxation of water molecules interacting with  
 500 the pore surface or flowing in the nano-channels (a typical trend is shown in Figure 7).  
 501 Accordingly, the relevant inverse-Laplace transform can be fitted as a sum of two Log-normal  
 502 distributions. Relaxometric data (see Experimental for details) are summarized in Table 5.

503

504 **Table 5.** Summary of FFC-NMR relaxometric data.

NS3					NS4			
$\omega_L$ (MHz)	$R_{fast}$ ( $\mu s^{-1}$ )	$R_{slow}$ ( $\mu s^{-1}$ )	$f_s$	$PCI$	$R_{fast}$ ( $\mu s^{-1}$ )	$R_{slow}$ ( $\mu s^{-1}$ )	$f_s$	$PCI$
3.0	$110 \pm 40$	$45 \pm 7$	0.40		$67 \pm 8$	$18 \pm 3$	0.27	
1.0	$140 \pm 40$	$54 \pm 7$	0.40	1.66	$98 \pm 8$	$29 \pm 2$	0.29	2.07
0.3	$170 \pm 60$	$61 \pm 6$	0.36		$88 \pm 5$	$26 \pm 2$	0.30	

505



506

507 **Figure 7.** T1 relaxation kinetics for NS4 at 1.0 MHz; in inset the relevant Inverse-Laplace  
 508 transform (UPEN).

509

510 The results indicate a smaller fraction of pore surface water molecules and a larger *PCI* value  
511 for NS4 than for NS3. Keeping into account the presence in the CyCaNSs of two different co-  
512 monomer units (i.e., the hydrophilic cyclodextrin and the hydrophobic calixarene), these results  
513 suggest that NS3 can be more extensively permeated by the aqueous medium than NS4. This is  
514 consistent with the presence in its composition of a larger amount of cyclodextrin, which can  
515 effectively interact with the medium via H-bonds by means of the –OH groups therein. Because  
516 of this, however, the medium perceives a better mobility in the nanochannels of the most  
517 hydrophobic material NS4, in agreement with the its faster adsorption kinetics.

518

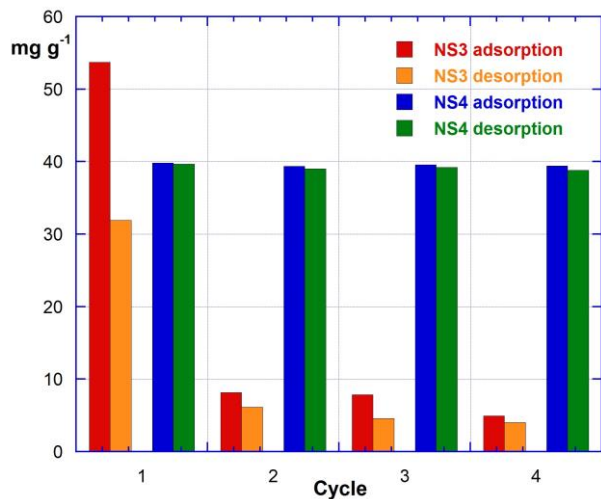
519 *3.6. Recycle and reuse of the absorbent materials.*

520 The possibility of recycling an adsorbent material, makes its application more attractive,  
521 because of possible lowering of the costs for polluted water treatment. Therefore, recycle and  
522 reuse experiments were carried out on both NS3 and NS4 making for each of them four  
523 adsorption/desorption steps (see Experimental for details). A 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> solution was  
524 used as the extraction medium; the results of the four cycles are depicted in Figure 8.

525 The NS4 material showed an excellent reuse capacity with comparable and constant  $q_e$  values  
526 of adsorption and desorption in each of the four cycle. This result is perfectly consistent with the  
527 ion exchange mechanism hypothesized previously. Nevertheless, the adsorption and desorption  
528 of the metal ion may probably be also ascribed to a combination of chemical and physical  
529 processes, the outcome of which varies according to the experimental conditions of the aqueous  
530 solution containing the metal ion. The results obtained for NS3 are quite different. Apparently,  
531 the material showed a scarce reuse capacity. In fact, even in the first desorption step the amount

532 of recovered metal is lower than the amount of adsorbed one. Then, a dramatic drop in the  
533 adsorption capacity occurred, even since the second cycle. Again, for each cycle we observed  
534 that the amount of recovered metal is lower than the adsorbed one, and similar results are  
535 obtained in subsequent cycles. This unsatisfactory result suggests that some significant structural  
536 alteration or degradation occur in the material, after having interacted for the first time with the  
537  $Pb^{2+}$  ion, which can be likely ascribed to the peculiar chemical behavior of the primary amine  
538 groups present

539



540

541 **Figure 8.**  $q_e$  values of  $Pb^{2+}$  adsorption and desorption steps in recycle experiments with NS3 and  
542 NS4. Experimental details: amount of CyCaNSs in column = 12.1 mg (NS3), 10.2 mg (NS4);  
543 treated solution:  $V = 20$  mL;  $c_{Pb^{2+}} = 35$  mg L<sup>-1</sup>; pH = 5.0; extracting solution: HNO<sub>3</sub> 0.1 mol L<sup>-1</sup>.

544

#### 545 4. Conclusions and further remarks

546 Four pre- and post-modified cyclodextrin-calixarene nanosponges (CyCaNSs) have been  
547 employed as adsorbents for  $Pb^{2+}$  ions from aqueous solutions. Preliminary adsorption tests  
548 showed very poor performances of the NS1 and NS2 materials; conversely, the post-modified

549 materials NS3 and NS4, functionalized with amino and carboxyl groups, respectively, showed a  
550 very good affinity and adsorption ability towards the metal ion. Then, several batch kinetic and  
551 thermodynamic experiments were carried out in order to study the adsorption performances of  
552 NS3 and NS4 as function of ionic medium (NaNO<sub>3</sub>, NaCl), ionic strength ( $0 \leq I / \text{mol L}^{-1} \leq 0.1$ ),  
553 pH (3.0, 5.0) and temperature ( $283.15 \leq T / \text{K} \leq 323.15$ ). Our materials showed the highest  
554 adsorption ability at pH = 5.0 ( $q_m = 114$  and  $99 \text{ mg g}^{-1}$  at  $I \rightarrow 0 \text{ mol L}^{-1}$  for NS3 and NS4,  
555 respectively). The addition of NaCl to the metal ion solution causes a lowering of their  
556 adsorption ability ( $q_m$ ) and affinity ( $K_L, K_F$ ) mainly attributable to the formation of chloride  
557 species of Pb<sup>2+</sup> ions. Moreover, the hydrochloride form of amino groups of NS3, especially at pH  
558 3.0, hinders their interaction with the metal ion causing a higher lowering of adsorption  
559 parameters. The addition of NaNO<sub>3</sub> causes, in general, a smaller reduction of the adsorption  
560 capacity that, however, is more pronounced for NS4 suggesting a shielding effect of the Na<sup>+</sup> ions  
561 towards the anionic carboxylate groups of the adsorbent. The negative  $\Delta G$  values confirm that  
562 the adsorption onto both materials is a spontaneous process predominantly based on ion  
563 exchange mechanism. Moreover, it is exothermic with low and positive entropy variations  
564 suggesting a structural changing in the adsorbents and an increasing randomness at the adsorbent  
565 – solution interfaces. For both post modified CyCaNSs, statistical testing parameters agree in  
566 indicating the DEM model as the best kinetic equation in terms of data fit. NS4 is faster than  
567 NS3 in accomplishing adsorption with  $k_1$  and  $k_2$  values about 4 times and 3 times larger  
568 respectively. The later result can be rationalized in terms of a better functional mobility of water  
569 within the nanopores of the nanosponge matrix, as accounted for by the relaxometric  
570 determinations. Finally, the NS4 material showed an excellent reuse capacity with comparable



571 adsorption and desorption abilities in each of the four cycles. By contrast, worse reuse  
572 performances were shown by NS3.

573 As a final remark, we can also conclude that our CyCaNSs actually appear interesting and  
574 promising materials for environmental remediation purposes. Indeed, their ability in  
575 sequestering organic pollutants has been already accounted for elsewhere (Cinà et al., 2017; P.  
576 Lo Meo et al., 2014). Here we positively showed the possibility to extend their use to inorganic  
577 pollutants at the same time. It is worth noting here that, as long as adsorption capacities ( $q_m$ ) are  
578 concerned, the performances of materials NS3 and NS4 appear comparable or even better to  
579 other recent literature reports on cyclodextrin-based materials (El-Kafrawy et al., 2017; Li et al.,  
580 2020; Rubin Pedrazzo et al., 2019; Taka et al., 2018; Zhao et al., 2019; Zheng et al., 2019), and  
581 even superior to materials such as activated carbon (M. M. Rao, Ramana, Seshaiyah, Wang, &  
582 Chien, 2009), iron oxide (Nassar, 2010) or carbon nitride (Hu et al., 2015). Of course, further  
583 studies are needed to investigate the sequestration of different metal species and the molecular  
584 mechanisms involved in the process.

585  
586 **Supporting Information.** Protonation constants of ionisable groups of CyCaNSs; Formation  
587 constants of  $Pb^{2+}$  species in aqueous solutions; Langmuir and Freundlich isotherm parameters for  
588 the  $Pb^{2+}$  adsorption onto CyCsNSs; Distribution diagrams of the NSx-1 and NSx-2 species vs pH  
589 and Adsorption isotherms are reported.

590

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593

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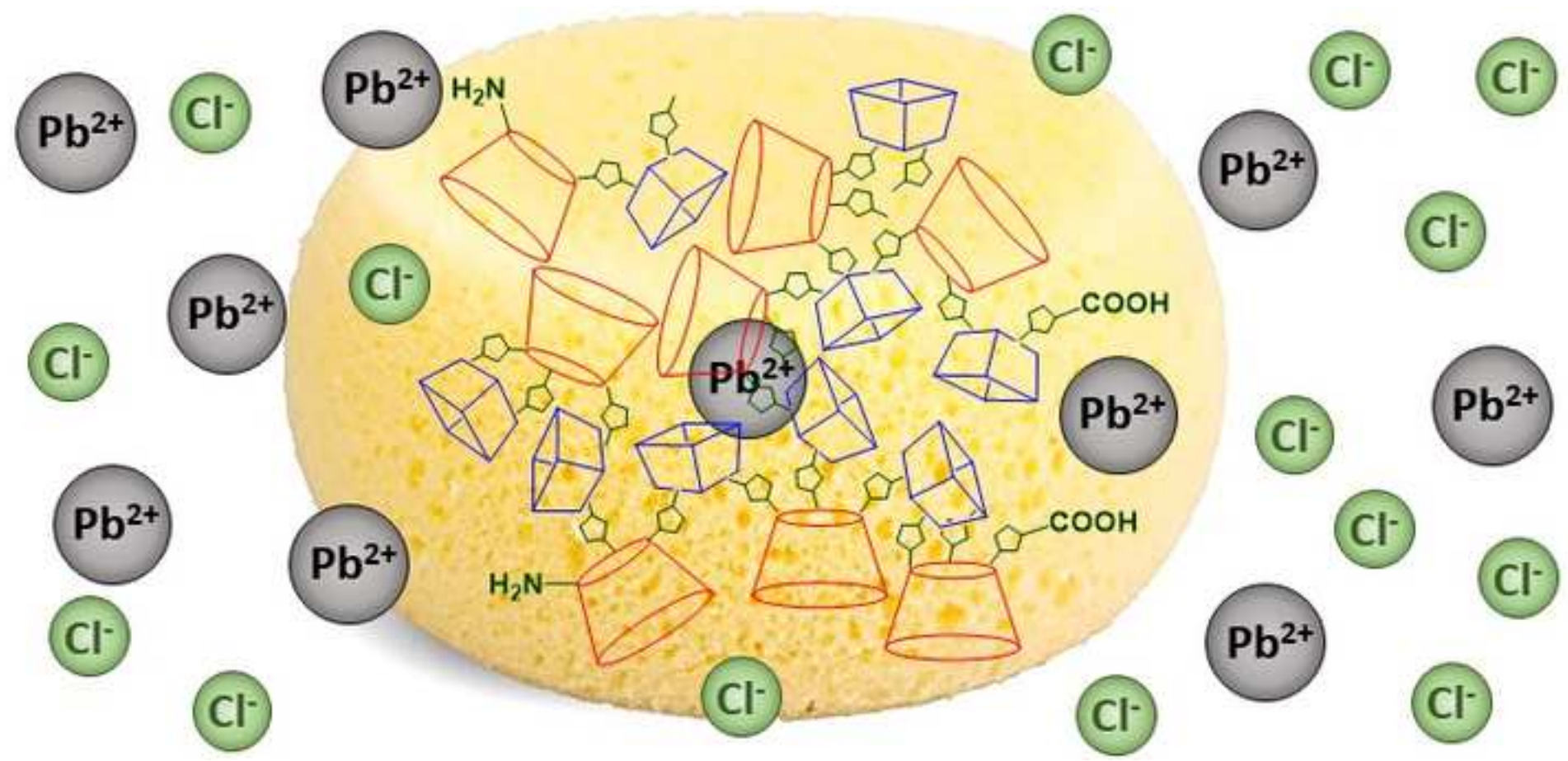
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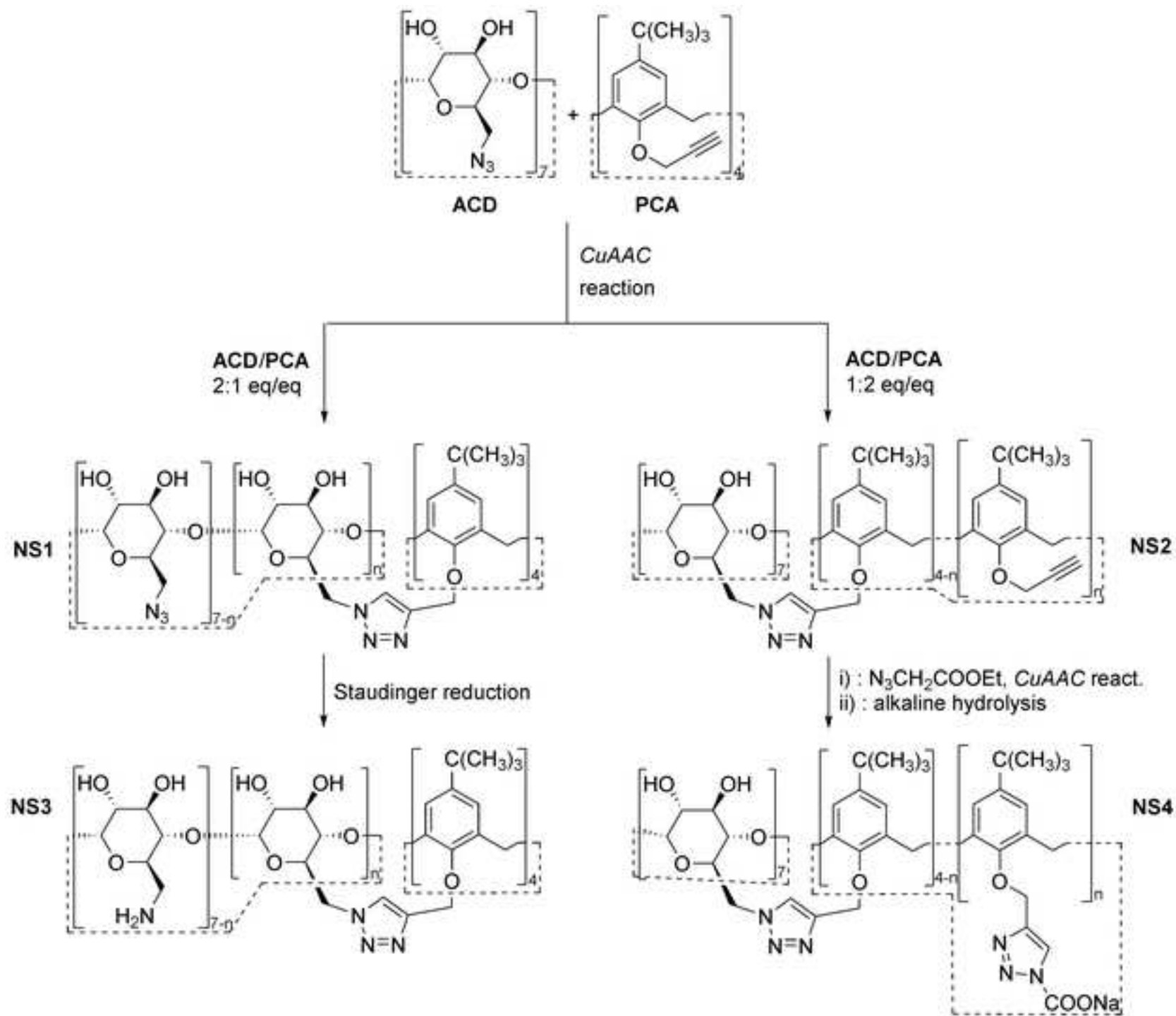
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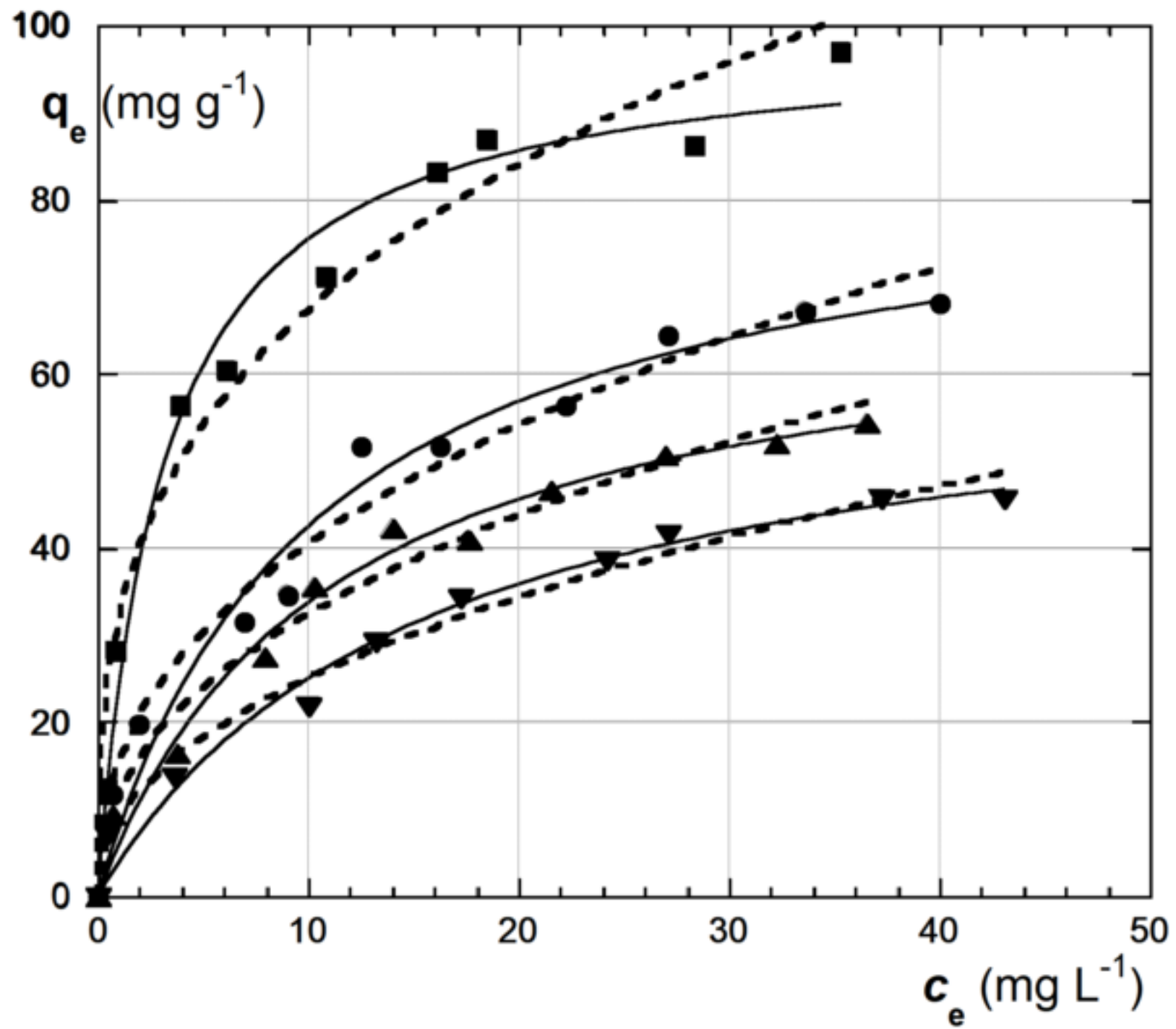
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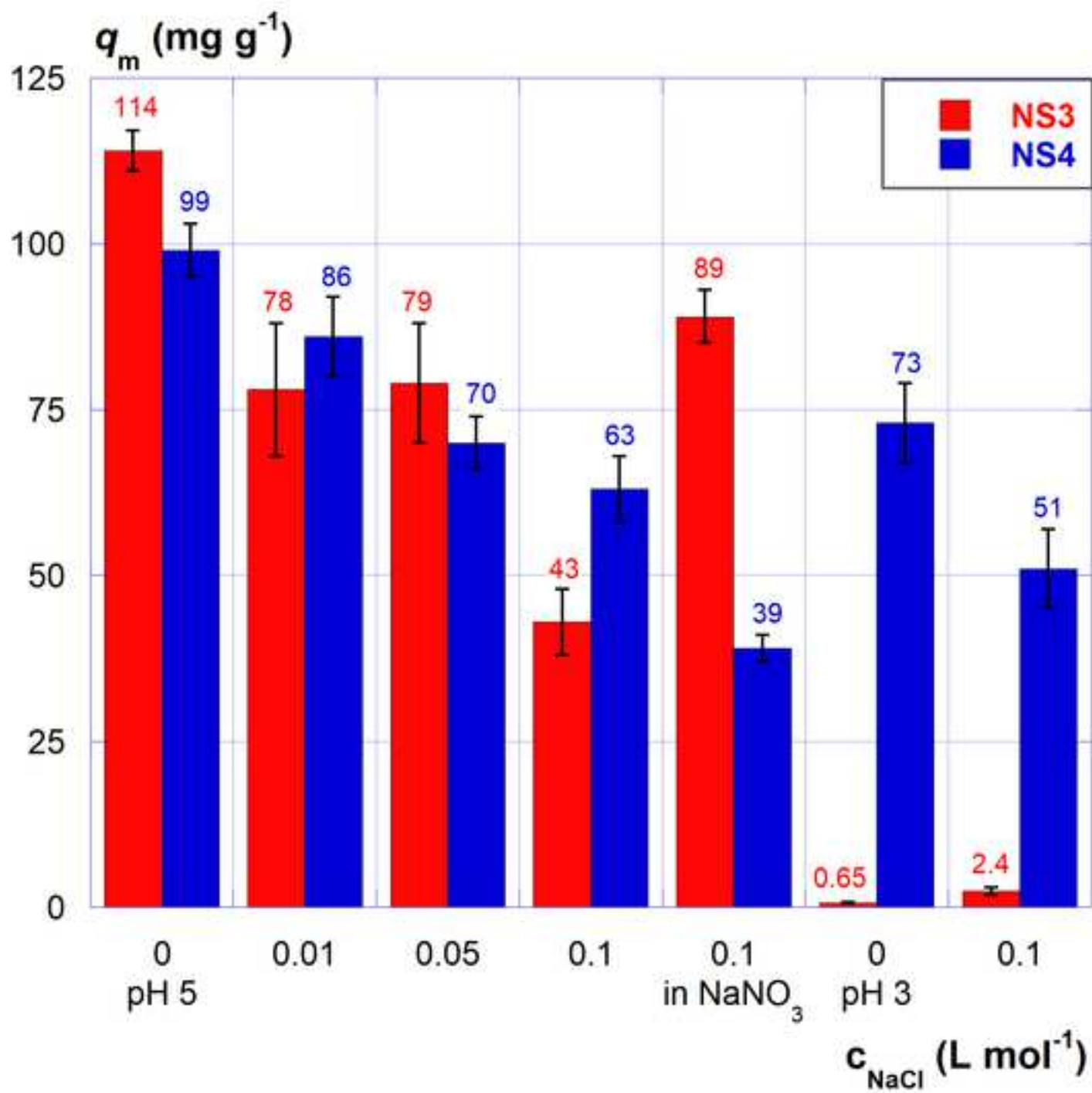
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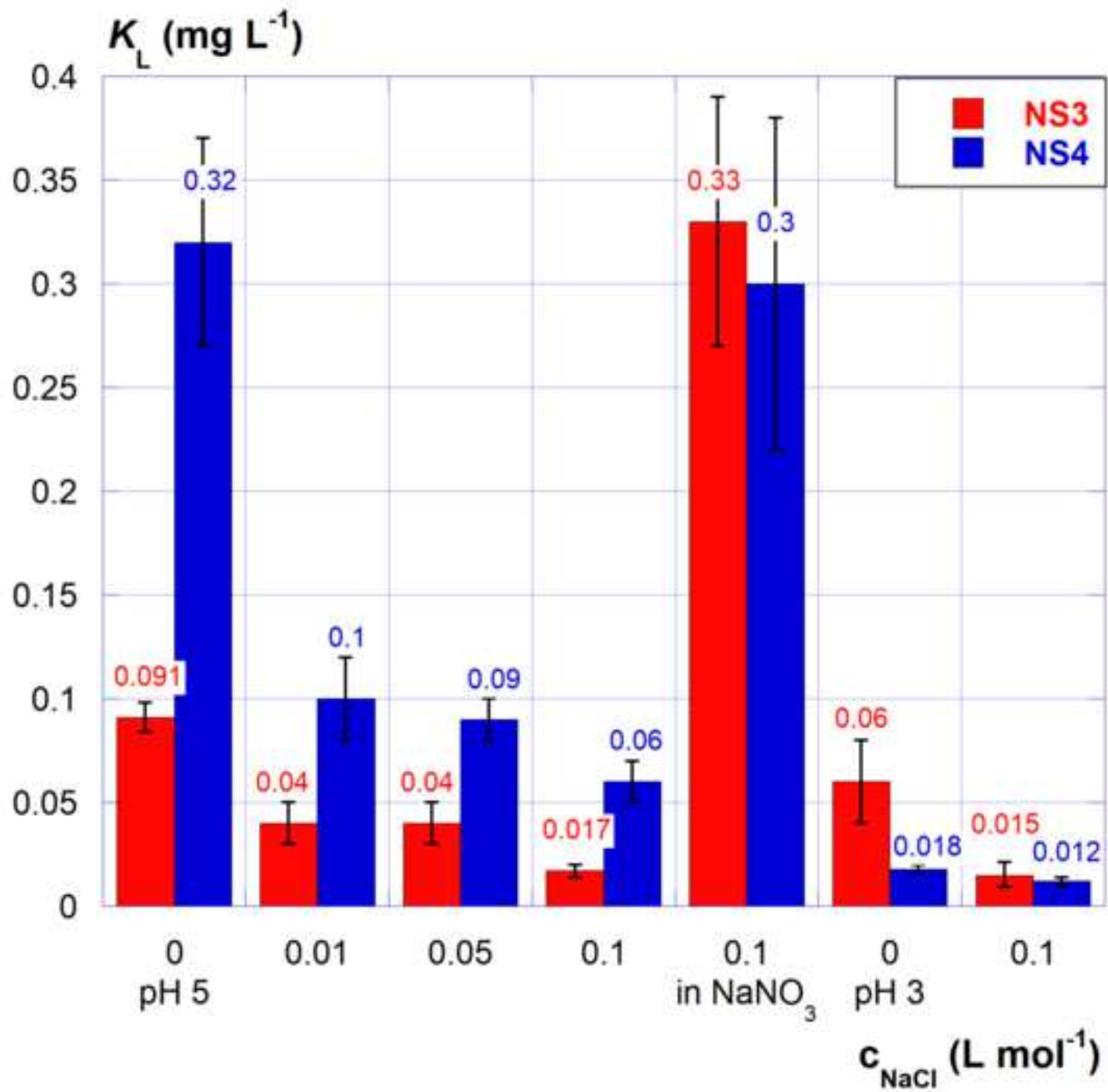


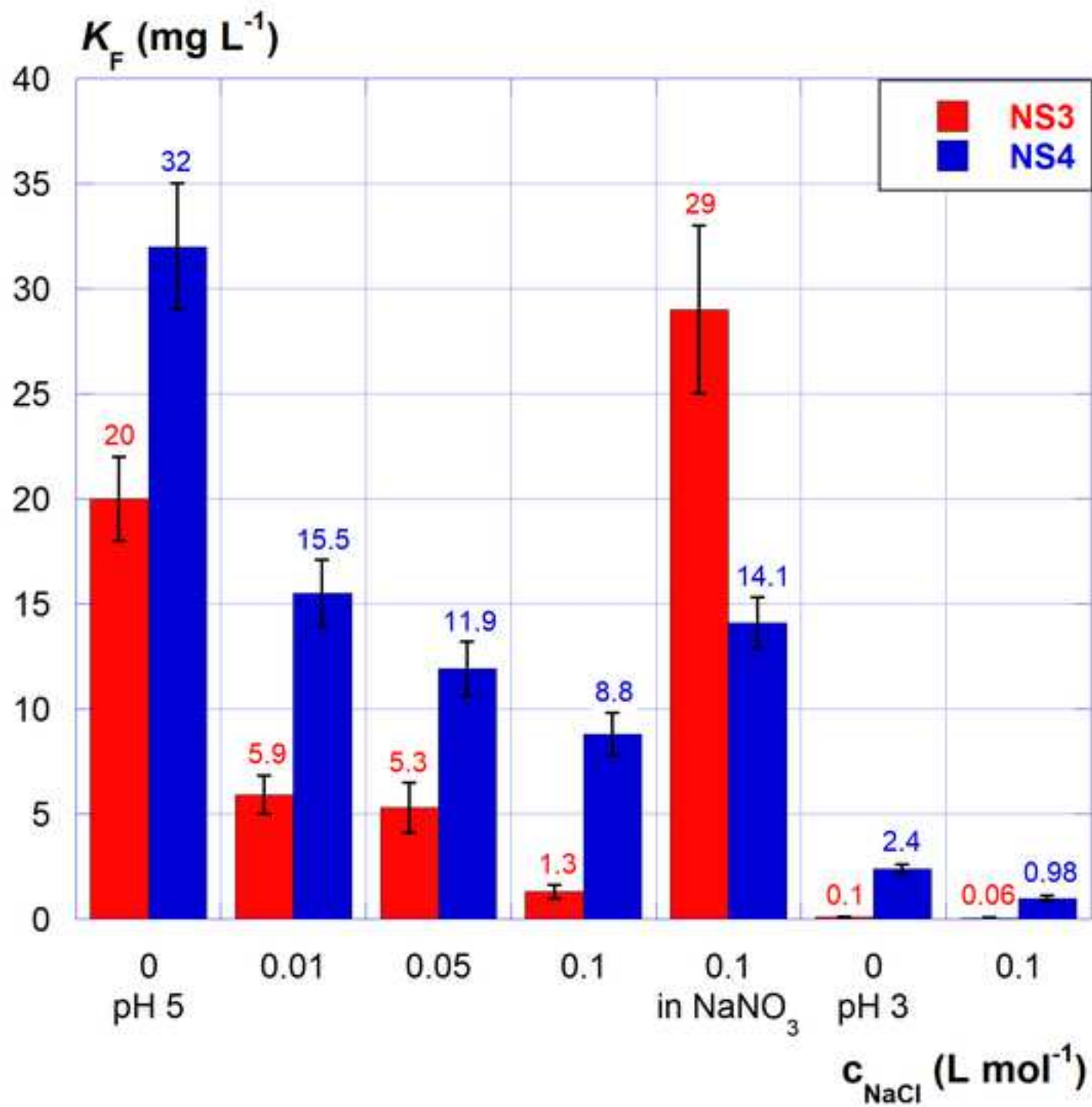


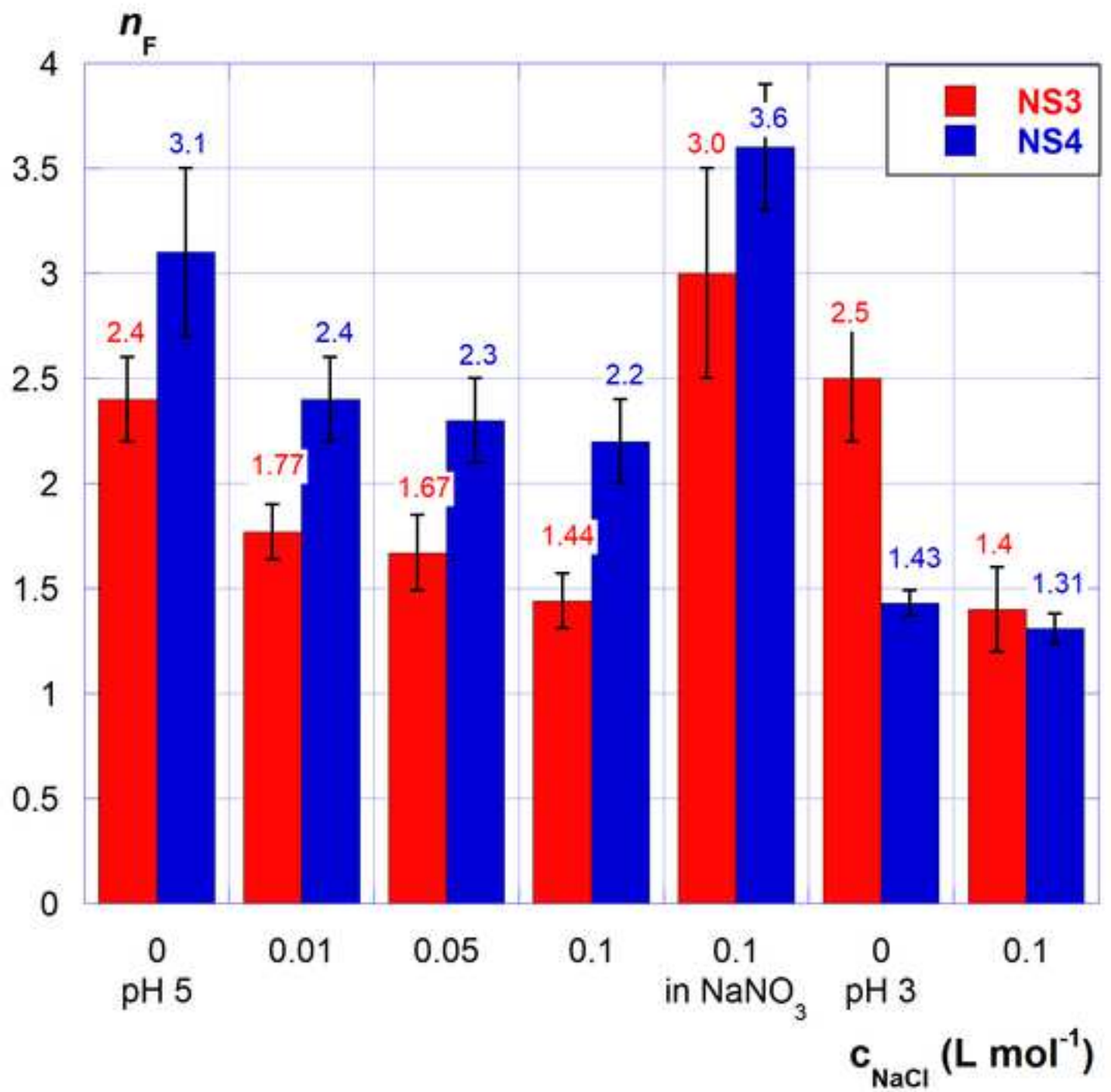


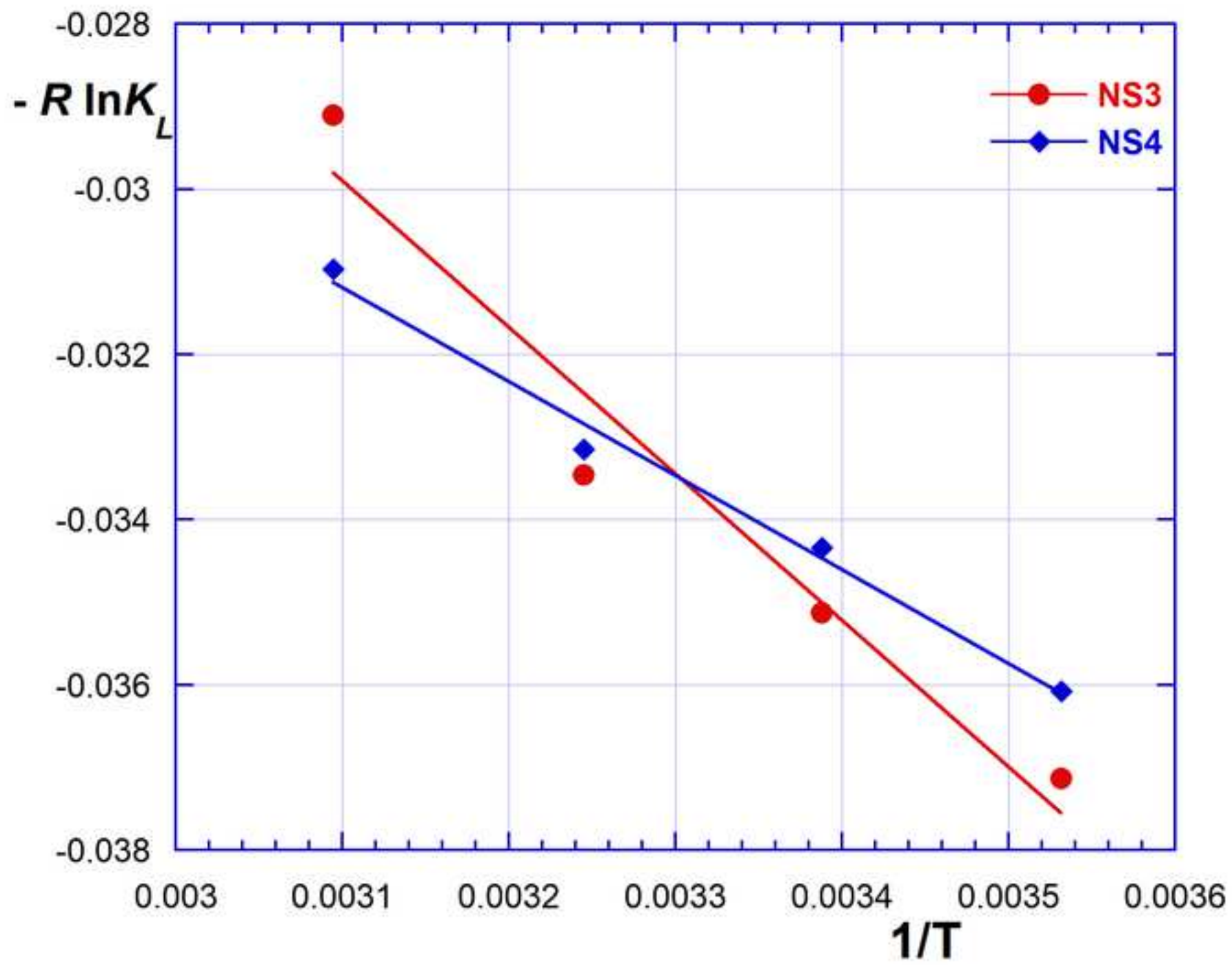


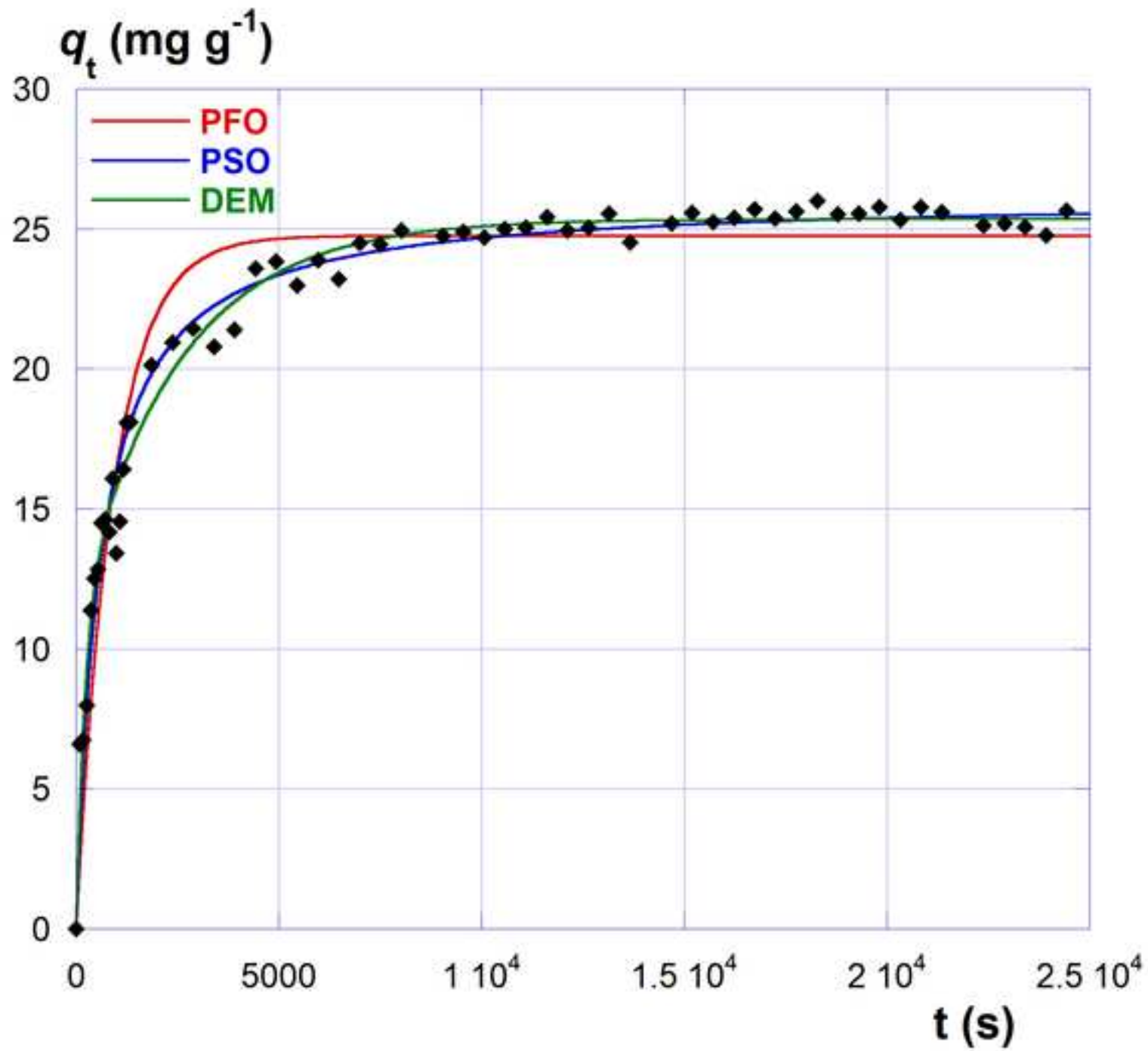


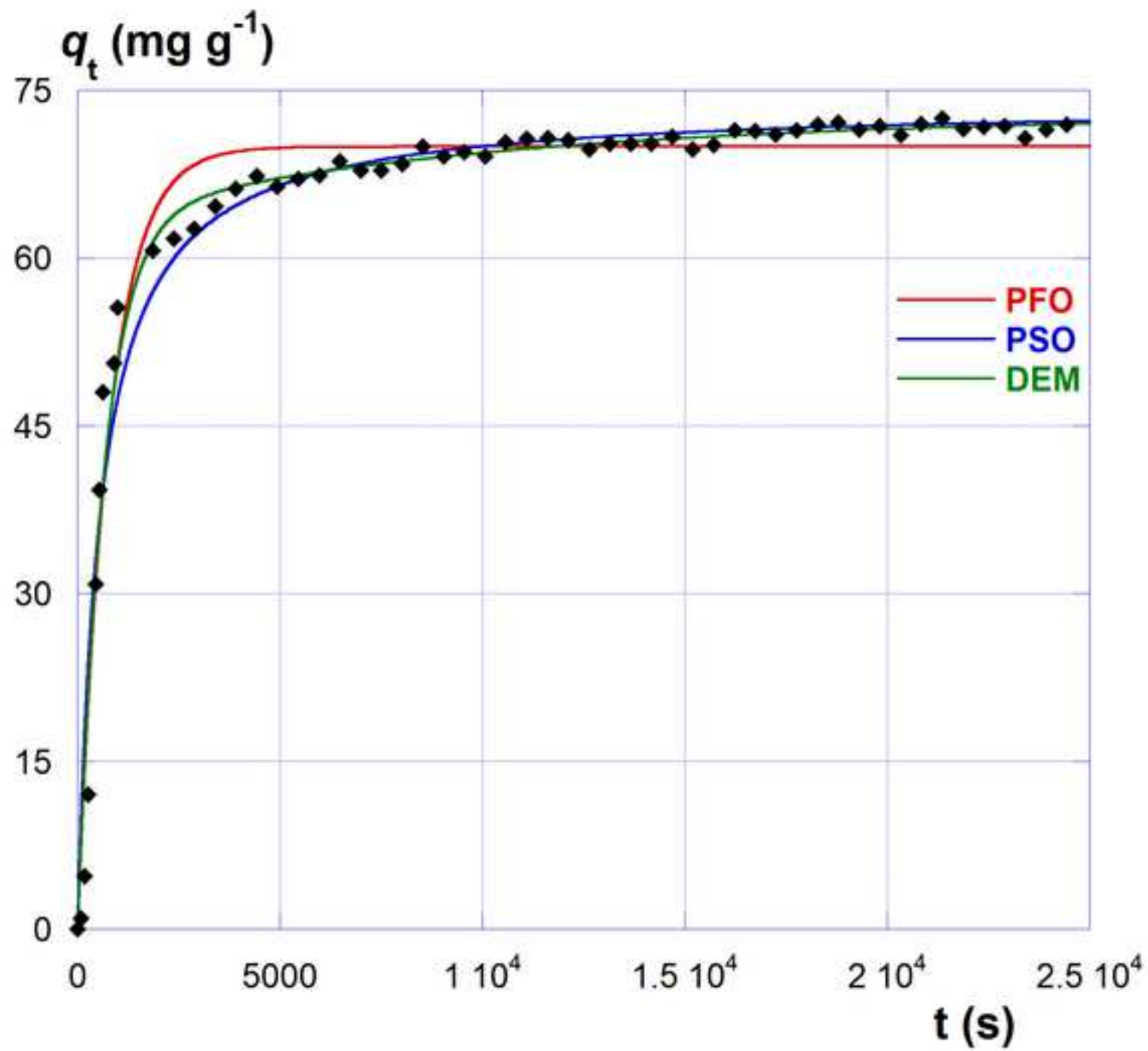


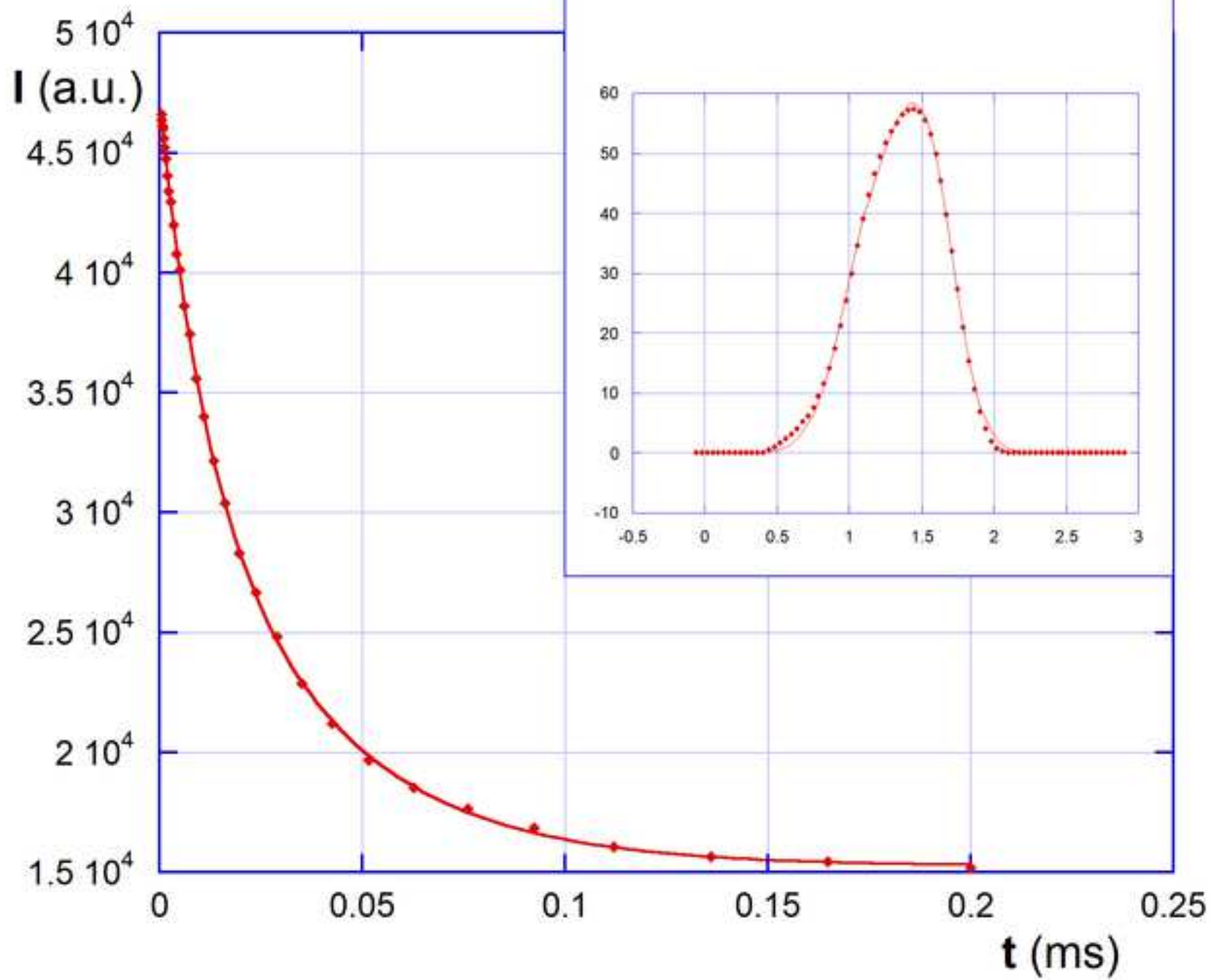




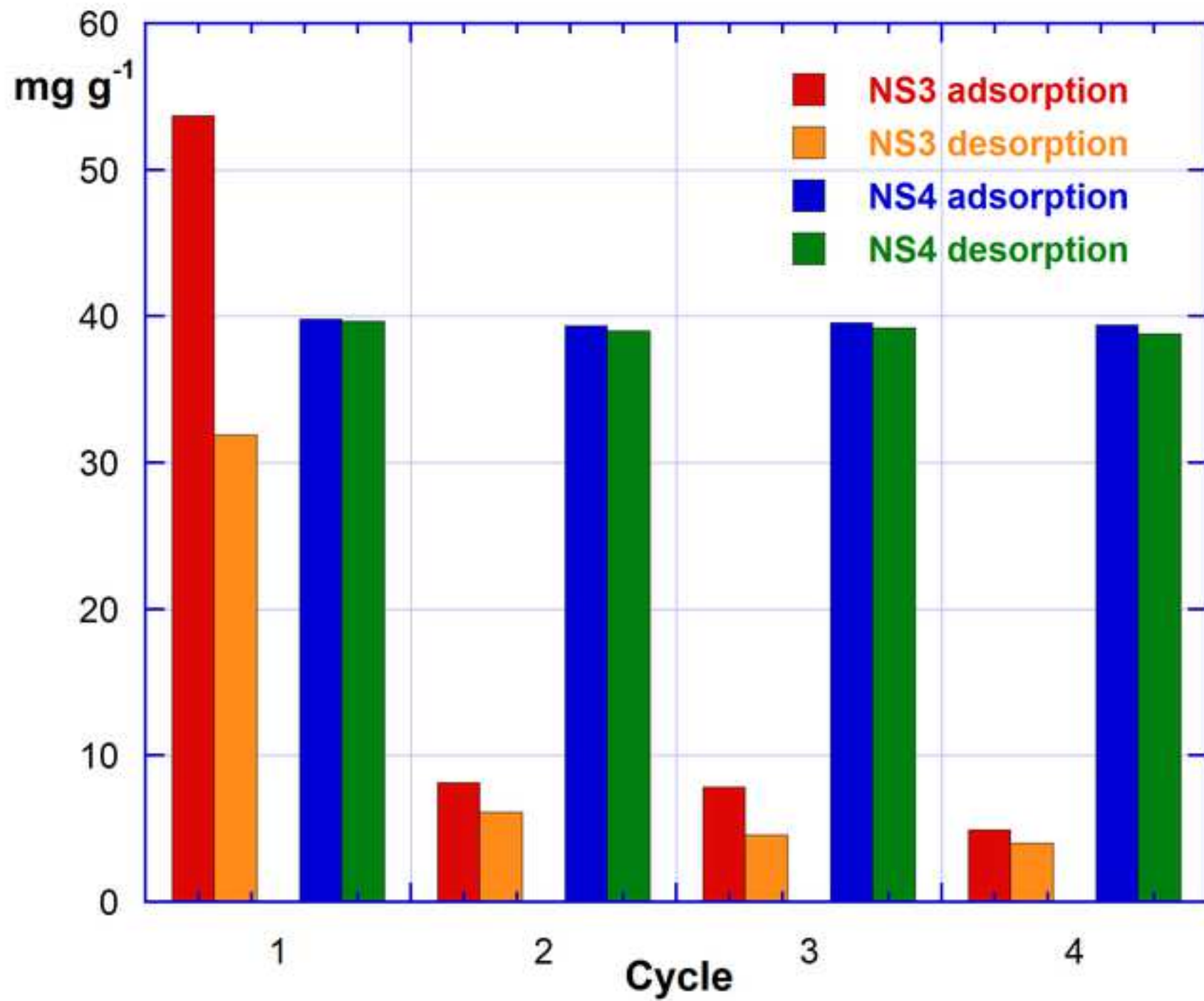














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