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1 Sorption of Europium on Diatom Biosilica as Model of a “Green” 2 Sorbent for *f*-Elements

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8

9 **1. Abstract**

10 Removing *f*-elements from anthropogenically contaminated sites is a challenging, but ecologically
11 important task. Some of these elements are not only radioactive, but also chemically toxic and can
12 spread through various pathways in the environment. The present work investigates *f*-element
13 sorption on biogenic silica, which may be a promising “green” material for remediation. Commercially
14 available diatomaceous earth (DE) and the cleaned cell walls of the diatom species *Stephanopyxis turris*
15 (*S.t.*) and *Thalassiosira pseudonana* (*T.p.*) are compared with artificial mesocellular foam (MCF) as
16 porous silica reference material. Trivalent europium was chosen as model sorptive for chemically
17 similar trivalent actinides. Accordingly, Eu(III) in concentrations of 10⁻³ M and 10⁻⁵ M was sorbed on
18 the four silica materials at varying pH values. The zeta potentials of the implemented sorbents under
19 the same conditions were determined. With time-resolved laser-induced fluorescence spectroscopy
20 (TRLFS), two different uptake mechanisms can be discerned, surface adsorption and
21 incorporation/precipitation.

22

23 KEYWORDS: biosilica; diatoms; europium; fluorescence; sorption

24

25

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26 2. Introduction

27 The recovery of 4f-elements (lanthanides) and 5f-elements (actinides) from the environment is
28 important from different perspectives. While these elements should be removed from
29 anthropogenically contaminated sites, they also constitute valuable raw materials. These might be of
30 increasing value as the natural resources become scarcer and more difficult to retrieve in the future.¹
31 Furthermore, studying the environmental interactions of lanthanides yields important information on
32 the behavior of their radioactive analogs in the actinide series.

33 A possible approach for scavenging dissolved substances from the environment is to accumulate them
34 via sorption. It is therefore indispensable to identify suitable sorbents, which should not only be
35 efficient in accumulating the desired elements, but also offer ecological and economic advantages.^{2,3}
36 In this regard, biogenic materials often surpass artificial materials.⁴

37 The silica cell walls of diatoms exhibit several beneficial properties: They are hierarchically structured
38 and porous, chemically and physically stable, and non-toxic.⁵ Fossilized diatom cell walls (frustules) are
39 frequently evaluated and applied as sorbents in the form of diatomite or diatomaceous earth (DE).⁶
40 For example, this material has been considered for the pretreatment of radioactive wastewater.⁷ Its
41 specific surface area (SSA) is in the order of 30 to 40 m² g⁻¹.⁸ Apart from a high percentage of frustules
42 of various diatom species, DE contains a considerable amount of other mineral compounds.⁶

43 In contrast, the cleaned cell wall material of axenically cultivated and harvested diatoms is much more
44 homogeneous in terms of chemical composition as well as morphology (i.e. shape and size) of the
45 particles. Furthermore, fresh diatom biosilica contains a higher amount of silanol groups (Si-OH).
46 These are partly fused to siloxane groups (Si-O-Si) in aged biosilica like diatomite.⁵ Consequently, fresh
47 frustules constitute a more defined and thus preferable object for fundamental research like the
48 luminescence spectroscopic studies in the current work. Fresh diatom biosilica is currently scarce, but
49 it may become available as large-scale by-product of future food and oil production.⁹ In contrast,
50 diatomite is easily available as it can be extracted from abundant natural deposits.

51 In the present study, the sorption of trivalent lanthanide ions on both aged biosilica (diatomite) and
52 fresh biosilica of two different diatom species was examined. To gain fresh biosilica, the two centric
53 species *Stephanopyxis turris* (*S.t.*) and *Thalassiosira pseudonana* (*T.p.*) were axenically cultured in
54 artificial seawater (ASW). *Stephanopyxis turris* is a wide-spread diatom species, inhabiting mainly
55 temperate waters.¹⁰ The cells are 20–100 μm long¹⁰ and, therefore, suitable for diverse microscopical
56 analysis methods. Their frustules exhibit a hierarchical structure of hexagonal pores, resulting in an
57 SSA of ~60 m² g⁻¹ for extracted biosilica.⁸ *Thalassiosira pseudonana* grows fast in a wide temperate
58 range and is resistant to environmental stress, resulting in an almost worldwide distribution of this
59 diatom species.¹¹ The cylindrical cells are comparatively small with a diameter of 2–15 μm.¹¹ The
60 cleaned frustules of this species exhibit an SSA of about 60–100 m² g⁻¹, slightly higher than *S.t.*^{8,12} The
61 biogenic materials were compared with mesocellular foam (MCF), an abiogenic, synthetic silica.¹³ Due
62 to its mesoporous structure with pore diameters of 20–50 nm, it has a very high internal porosity with
63 a SSA of 680 m² g⁻¹.¹⁴

64 To evaluate these sorbents, europium was chosen as model sorptive. Eu(III) is often used as analog of
65 trivalent actinide ions such as Cm(III) or Am(III).^{15,16} Eu(III) also exhibits excellent luminescent
66 properties, facilitating the structural analysis of its coordination compounds by fluorescence
67 spectroscopy. The structure and surface charge of the sorbents as well as the Eu(III) loading and
68 speciation were elucidated through scanning electron microscopy (SEM), zeta potential
69 measurements, inductively coupled plasma optical emission spectroscopy (ICP-OES), and TRLFS.

70

71 3. Materials and Methods

72 3.1. Diatom Cultivation and Biosilica Extraction

73 DE (p.a.) was purchased from Merck and used as received.

74 Axenic diatom cultures were grown in 20 L batches of sterile-filtered artificial seawater (ASW) with a
75 composition according to **Table A3** (appendix) at 20 °C. The cultivation vessels were illuminated with
76 1000 Lux in a 12 h/12 h light/dark cycle. To monitor cell growth, the Si concentration was analyzed
77 colorimetrically via the molybdenum blue method.¹⁷ After the Si concentration decreased below 5 µM,
78 algae were harvested by centrifugation with a Hereaus Megafuge at 4000 rpm.

79 The resulting cell pellets were lysed to remove organic material from the silica frustule. For this
80 purpose, 20 mL buffer solution (20 g L⁻¹ sodium dodecyl sulfate (SDS), 37 g L⁻¹ sodium ethylenediamine-
81 tetraacetic acid (Na₂EDTA)) were added to the pellet, mixed and heated to 95 °C for 10 min. The
82 suspension was centrifuged for 10 min at 4000 rpm in a Hereaus Biofuge primo and the supernatant
83 was discarded afterwards. This lysis step was repeated until the supernatant appeared clear.
84 Subsequently, the pellet was washed 5 times with Millipore water and then dried at -55 °C and
85 0.47 mbar in a Christ Alpha 1-4 LSCbasic freeze dryer.

86 In order to remove tightly bound or embedded organic residues from the lysed cells, the material was
87 calcined in a muffle furnace for 5 h at 550 °C under air atmosphere.

88

89 3.2. Synthesis of MCF

90 MCF was synthesized according to the preparation method of Schmidt-Winkel et al.¹³ Pluronic® P-123
91 (PEG-PPG-PEG block copolymer), ammonium fluoride, and 1,3,5-trimethylbenzene were heated to
92 35–40 °C in hydrochloric acid for at least 45 min. After adding tetraethoxysilane and retaining the
93 temperature for another 20 h, the suspension was heated to 100 °C for 24 h. The solid material was
94 filtered, dried, and calcined for 8 h at 500 °C.¹³

95

96 3.3. Zeta Potential Measurements

97 Zeta potentials of the silica sorbents were measured with a Zetasizer Nano Series device by Malvern
98 Instruments. Therefore, about 5 mg of the solid was suspended in 2 mL 0.1 M NaClO₄. The pH values
99 were adjusted to 2, 3, 4, 5, 6, 6.5, and 7 with NaOH and HClO₄.

100

101 3.4. Batch Sorption Experiments

102 For sorption experiments, Eu(III) solutions with a concentration of 10⁻³ M and 10⁻⁵ M were prepared
103 from EuCl₃ · 6 H₂O (99.99%, Sigma-Aldrich) and ultrapure water. 0.1 M NaClO₄ · H₂O (≥99.0% p.a.,
104 VWR) was chosen as background electrolyte. After adding 10 mL of the solutions to 10 mg of the
105 respective sorbents, the suspensions were immediately adjusted to pH 3, 4, 5, 6, 6.5, and 7,
106 respectively, with NaOH and HClO₄. After 3 days shaking at room temperature, the mixtures were
107 centrifuged for 10 min at 4000 rpm in a Hereaus Biofuge primo.

108

109

110 3.5. SEM and EDX

111 After sorption, a small amount of the silica material was suspended in n-hexane and pipetted onto an
112 aluminum pin stub. The dried samples were sputter-coated with gold and visualized in a Hitachi
113 SU 8000 microscope (Hitachi). For energy-dispersive X-ray (EDX) spectroscopy, the peaks of the K series
114 were used for Si and the peaks of the L series for Eu. The acceleration voltage was adjusted to 2–4 keV
115 for imaging and 15–20 keV for EDX analysis/mapping. Exemplary results are shown in the appendix
116 (**Figure A1, Figure A2**).

117

118 3.6. ICP-OES

119 The concentration of Eu in the supernatants after sorption was determined via ICP-OES. Therefore,
120 samples with an initial Eu concentration $c_0(\text{Eu})$ of 10^{-3} M and 10^{-5} M were diluted in HNO_3 (5%) 1:1000
121 and 1:10, respectively. The resulting liquids were analyzed with an Optima 7000DV spectrometer
122 (Perkin Elmer) utilizing the following parameters: high frequency power 1300 W, liquid flow 1.6 L min^{-1} ,
123 plasma gas flow 15 L min^{-1} , auxiliary gas flow 0.2 L min^{-1} , and nebulizer gas flow 0.65 L min^{-1} . The
124 spectral line was 412.970 nm for radial detection of Eu.

125

126 3.7. TRLFS

127 All Eu species were indirectly and, thus, simultaneously excited at 394 nm to get an overview of their
128 speciation in each sample as influenced by the conditions during sorption. TRLFS measurements were
129 conducted at room temperature with a Nd:YAG pumped OPO laser system (Powerlite Precision II 9020
130 - PANTHER EX OPO, Continuum), a monochromator with a grating of 300 or 1200 lines mm^{-1} (Oriel
131 MS 257) and a CCD camera (Andor iStar).

132 Fluorescence lifetimes were collected by monitoring the luminescence intensity as a function of delay
133 time between laser pulse and acquisition. By integrating the individual spectra and plotting the results
134 as a function of delay time, the fluorescence decay curves could be acquired. This data was analyzed
135 with MATLAB (The MathWorks), OriginPro (OriginLab) and Andor Solis (Andor). To each lifetime value,
136 the confidence interval of the fit (95% confidence level) is given.

137 In aqueous solution, the hydration shell effectively quenches Eu fluorescence lifetimes through an
138 energy transfer to the OH vibrational overtones of the water molecules.¹⁸ H_2O is progressively replaced
139 when Eu ions coordinate with more sites to a sorbent material. Thus, the luminescence decay
140 mechanism becomes less effective and luminescence lifetimes increase. The semi-empirical Horrocks
141 equation¹⁹ approximates the number of water molecules in the first coordination sphere as a function
142 of the measured luminescence lifetime τ in ms as:

$$143 \quad n(\text{H}_2\text{O} \pm 0.5) = 1.07 \tau^{-1} - 0.62$$

144 Furthermore, luminescence decay curves (depicted in **Figure A4**, appendix) can be described using an
145 exponential fit. The number of decay modes commonly corresponds to the number of luminescent
146 species formed in a given sample. The integral band intensity ratio of the emission bands at about
147 620 nm and 590 nm, further denoted as ${}^7\text{F}_2/{}^7\text{F}_1$,¹⁸ can be interpreted as an indicator of the strength of
148 complexation. As the ${}^7\text{F}_2$ band is a hypersensitive transition, its increasing integral intensity changes
149 the ${}^7\text{F}_2/{}^7\text{F}_1$ emission-band ratio of less than one (i.e., ${}^7\text{F}_1 > {}^7\text{F}_2$) for the non-complexed aquo ion to more
150 than one upon sorption (i.e., ${}^7\text{F}_1 < {}^7\text{F}_2$).¹⁸

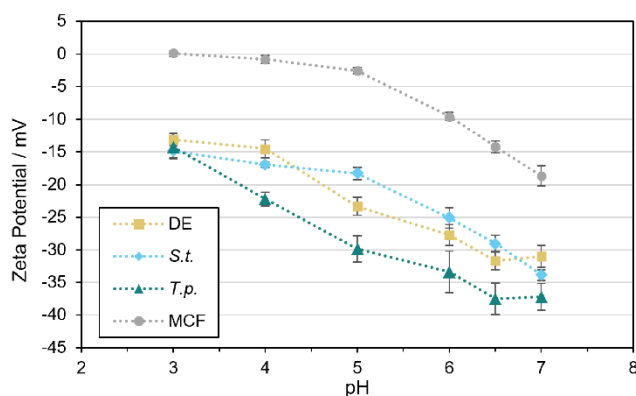
151 In addition to the ${}^7F_2/{}^7F_1$ ratio, some of the collected spectra show significant differences at varying
152 pH values pointing towards the formation of more than one surface-sorbed Eu(III) species. Thus, the
153 recorded spectra were deconvoluted as described in the literature to identify individual species.^{16,20}
154 Therefore, the spectrum of the Eu^{3+} aquo ion was subtracted from the original spectra. Alternatively,
155 two spectra measured at consecutive pH values were compared with one another, i.e. the spectrum
156 measured at a lower pH was subtracted from the spectrum at a higher pH. Some of the resulting
157 difference spectra can be considered as single component spectra. These difference spectra were
158 further subtracted from recorded spectra with additional species. Major species are further denoted
159 as consecutively numbered species.

160

161 4. Results and Discussion

162 4.1. Zeta Potentials of the Sorbent Materials

163 Electrostatic interactions strongly affect the sorption of ions. Thus, not only the speciation of the
164 sorptive, but also the charge of the sorbent is pivotal. The isoelectric point (pH(I)), i.e., the pH value at
165 zero net electric charge, can be determined through zeta potential measurements.²¹ In the current
166 study, zeta potentials of the sorbent materials were measured at the same buffer concentrations and
167 pH values as applied during the sorption experiments to assess possible changes in charge. The
168 investigated pH range covers the mostly near-neutral pH of natural water bodies as well as acidic
169 conditions characteristic for mine waters.²² The zeta potentials of all sorbent materials (see **Figure 1**)
170 above pH 4 are negative, facilitating the sorption of cations. Within the studied pH range of pH 3–7, a
171 pH(I) can only be determined for MCF at pH 3–4. The zeta potential measurements of the diatom
172 materials indicate an overall negative charge of the surface at any pH in the studied range. These
173 findings agree with literature data reporting that the pH(I) of silica materials can vary from below 1 to
174 4 or may not exist.²³



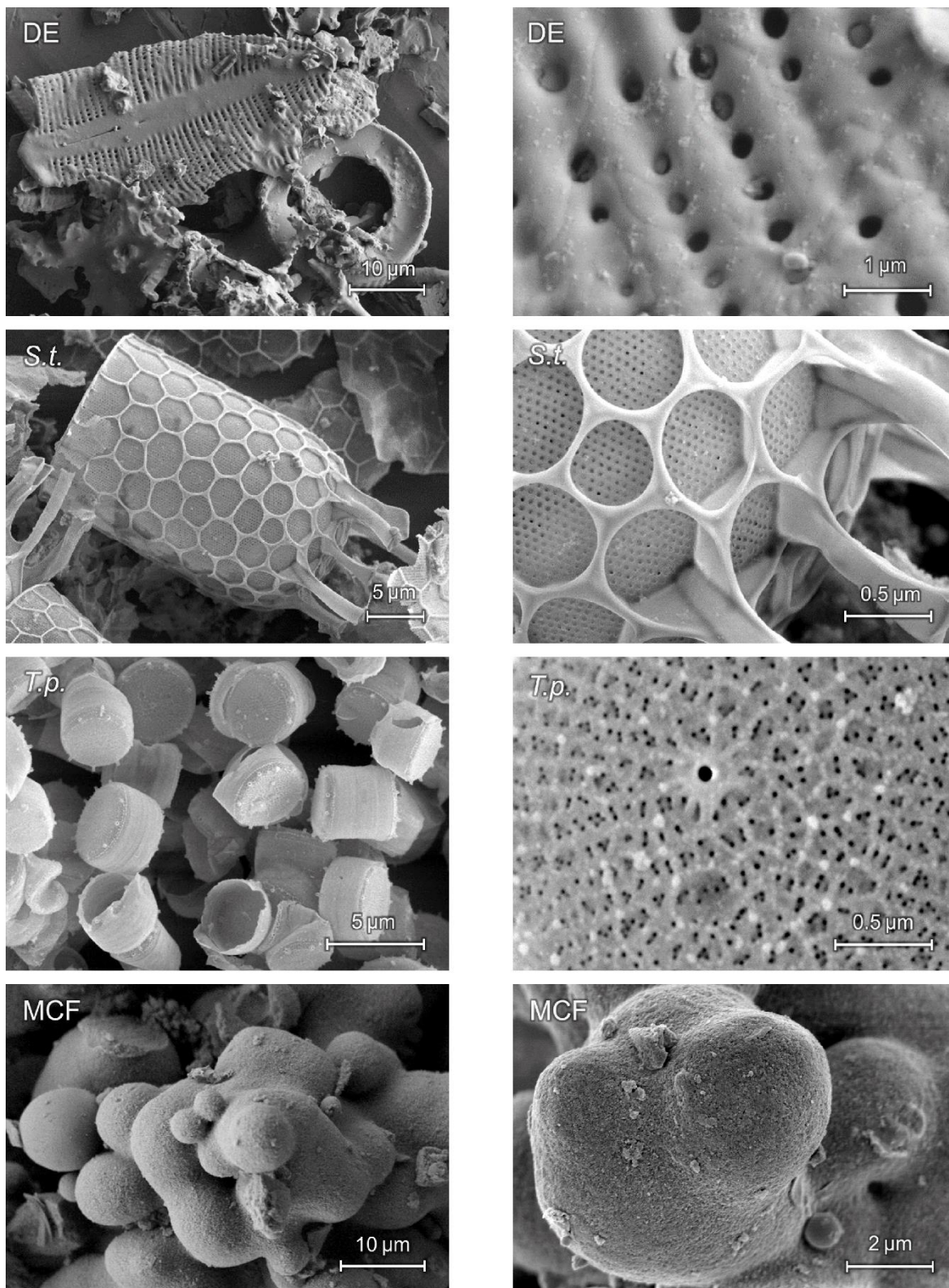
175

176 **Figure 1.** Zeta potential of different types of silica in 0.1 M NaClO_4 with varying pH value (error bars
177 indicate the confidence interval at 95% confidence level, t-distribution).

178 For Eu(III), the Eu^{3+} aquo ion dominates the speciation in acidic media up to a pH of 6 ($200 \mu\text{M Eu}$)²⁴ or
179 7 ($6.6 \mu\text{M Eu}$)²⁵. Small amounts of hydrolysis species, mainly $\text{Eu}(\text{OH})^{2+}$, are also present at these
180 pH values. At about pH 8, $\text{Eu}(\text{CO}_3)^+$ prevails in solutions in contact with air.²⁵ Negatively charged ions
181 like $\text{Eu}(\text{CO}_3)_2^-$ and $\text{Eu}(\text{CO}_3)_3^{3-}$ become predominant only at higher pH values.²⁵ Thus, Eu sorption is
182 favored in the pH range considered here. The zeta potential also provides information on the behavior
183 of the particles in solution. Suspensions of small particles are considered as stable for zeta potentials
184 with a modulus of 30 mV or higher. Between +30 mV and -30 mV, particles tend to agglomerate.²⁶ The

185 accessible surface area may then decrease. This threshold is at pH 6.0–6.5 for DE, at pH 6.5–7.0 for *S.t.*
186 and at pH 5.0–6.0 for *T.p.*

187 **4.2. Morphology of the Sorbent Materials**



188
189 **Figure 2.** SEM images of the sorbent materials in different magnifications (2,500x up to 50,000x);
190 acceleration voltage 2–4 kV.

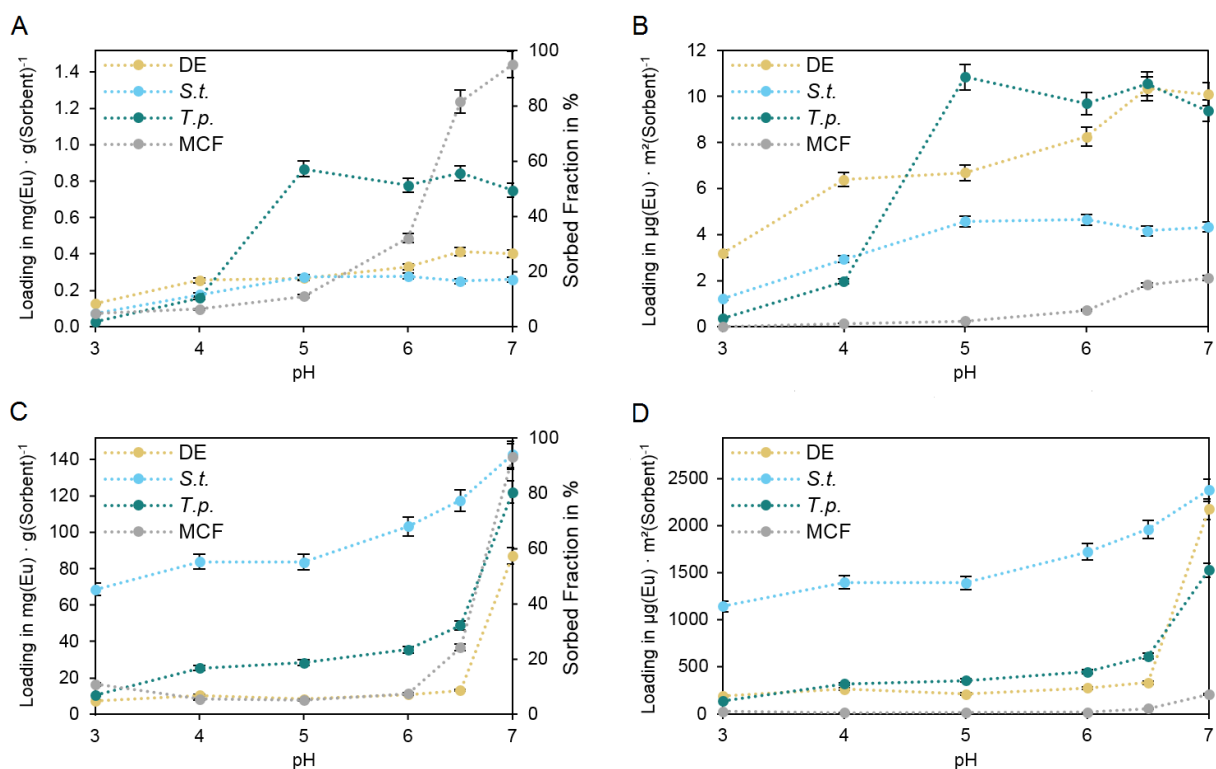
191 The morphology of the utilized sorbent materials is very diverse, as can be seen from **Figure 2**.
 192 Diatomite consists of the cell walls originating from many different sedimented diatom species, which
 193 are fragmented to a large degree. The *S.t.* sample contains up to 100 μm long valves, i.e., comparably
 194 large particles. These cell walls exhibit three-dimensional, chamber-like pores with a larger opening on
 195 the outer side and a sieve plate with smaller pores on the inner side. In contrast, the smaller and flatter
 196 valves of *T.p.* with a diameter of about 5 μm contain a non-hierarchical pore system and are radially
 197 furrowed. Generally, the comparatively large pore diameters of the implemented sorbents DE,⁸ *S.t.*,²⁷
 198 *T.p.*²⁷ and MCF²⁷ should not restrict the sorption of the smaller Eu(III) ion. Only a negligible percentage
 199 below 3% of the pores is smaller than 2 nm, whereas over 50% of the pores are macropores.²⁷

200

201 4.3. Batch Sorption – Quantitative Results

202 In general, the sorption of Eu(III) is influenced not only by the pH but also by the concentration of the
 203 sorptive. The sorption experiments were thus carried out at two different initial Eu(III) concentrations:
 204 10^{-5} M and 10^{-3} M. Furthermore, the amount of sorbed Eu(III) on mixed silica materials can decrease
 205 at higher ionic strength through an increased number of ions that can screen the sorbent's surface or
 206 compete with sorptive ions.²⁸ This issue is taken into account in the current study by adding 0.1 M
 207 NaClO_4 as background electrolyte.

208 The surface site density and SSA determine the sorption capacity of sorbents. Considering the wide
 209 range of surface site density values reported in the literature for silica materials, a complete sorption
 210 of the Eu ions even at the higher initial concentration of 10^{-3} M is theoretically possible (see **Table A1**,
 211 appendix). The sorption efficiency is further influenced by the kind of available sites.



212

213 **Figure 3.** Quantitative analysis of the Eu sorption on different silica materials at varying pH value;
 214 **A,B:** $c_0(\text{Eu}) = 10^{-5}$ M; **C,D:** $c_0(\text{Eu}) = 10^{-3}$ M; **A,C:** sorbent loading normalized by mass; **B,D:** sorbent
 215 loading normalized to the SSA of the sorbents, whereby the following SSA values were used: DE

216 $40 \text{ m}^2 \text{ g}^{-1}$, *S.t.* $60 \text{ m}^2 \text{ g}^{-1}$, *T.p.* $80 \text{ m}^2 \text{ g}^{-1}$, MCF $680 \text{ m}^2 \text{ g}^{-1}$ (error bars indicate the confidence interval at
217 95% confidence level, t-distribution).

218 As shown in **Figure 3**, the sorbent loadings tend to increase with higher pH values at both initial Eu
219 concentrations. One reason is the charge of the sorbent surfaces. According to the zeta potential
220 measurements, the overall negative charges increase in the observed pH range at higher pH. In
221 general, the loading scales with the initial Eu concentration. For biosilica, highest loadings are about
222 $0.8 \mu\text{g g}^{-1}$ for 10^{-5} M (**Figure 3A,B**) and about 140 mg g^{-1} for 10^{-3} M Eu (**Figure 3C,D**). Remarkably, though
223 the artificial MCF exhibits a high SSA, its loading is not generally higher than that of the biogenic
224 materials (except above pH 6 for $c_0(\text{Eu}) = 10^{-5} \text{ M}$). *S.t.* shows high loadings over a large pH range for
225 10^{-3} M Eu. *T.p.* removes about half of the Eu at pH 5–6 and is thus the most effective sorbent under
226 these conditions.

227 The determined sorbent loadings up to 140 mg g^{-1} are in the order of $1\text{--}100 \text{ mg g}^{-1}$ that is usual for
228 biosorbents.^{29,30} As initial experiments with the used diatom species and general studies with living
229 microalgae and dead algae biomass indicate,⁴ the removal of Eu by diatoms may be increased if
230 complete cells instead of cleaned cell walls were implemented. Containing amine, amide, carbonyl,
231 and carboxyl among other functional groups, the organic compounds of the external cell surface
232 exhibit a multitude of potential ligands.^{4,31} Therefore, the sorption on whole diatom cells is a
233 fascinating, but even more complex issue.

234 In **Figure 3B,D**, loadings are normalized to the SSA. This allows comparing the sorbent materials with
235 respect to the quality of the sorbent surface rather than its size. Accordingly, the loading of the highly
236 porous MCF is lower in this visualization (**Figure 3B,D**). At $c_0(\text{Eu}) = 10^{-5} \text{ M}$, *T.p.* and DE are more efficient
237 than *S.t.* biosilica. This situation changes at $c_0(\text{Eu}) = 10^{-3} \text{ M}$, where *S.t.* accumulates the highest amount
238 of Eu relative to the SSA. The comparatively large loadings of the diatom biosilica normalized to the
239 SSA may also arise from a higher amount of silanol groups and other functionalities resulting from
240 impurities. The presence of “foreign elements” such as Fe and Al – especially in DE – also influence the
241 surface charge depending on mass ratio and pH.^{32,33} Hence, the chemical advantages of the biosilica
242 with respect to Eu sorption become evident.

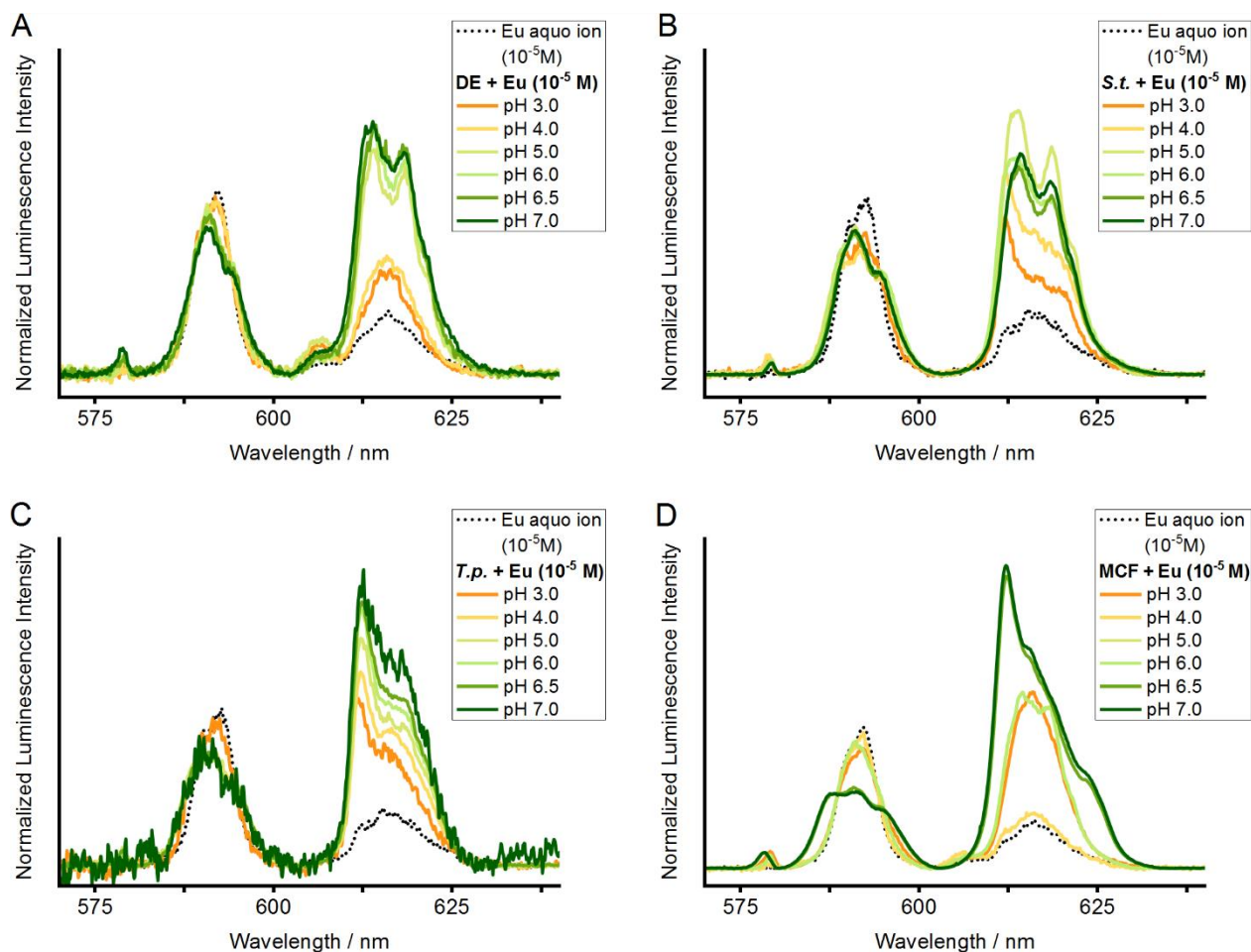
243 Besides the sorption of Eu onto silanol groups and other functionalities, a precipitation of Eu can occur,
244 for example in the form of Eu hydroxides. A similar mechanism is the partial dissolution of silica and
245 reprecipitation or coprecipitation of Eu and Si containing compounds like Eu(III) silicate complexes.³⁴
246 Fresh diatom frustules like *S.t.* at $c_0(\text{Eu}) = 10^{-3} \text{ M}$ may act as a more effective seed for the formation of
247 Eu salts. Especially the rapid uptake of Eu(III) visible in all sorption curves from pH 6.5 to 7.0 shows that
248 the solubility limit is exceeded in this neutral region. This behavior has been reported in studies with a
249 high Eu concentration before.³⁵ For this reason, the following TRLFS studies will focus on the lower
250 initial Eu concentration of 10^{-5} M (for samples with $c_0(\text{Eu}) = 10^{-3} \text{ M}$, see **Figure A3**, appendix).

251

252 **4.4. TRLFS – Emission Spectra and Lifetimes**

253 TRLFS was employed to gain further insight into the speciation of the Eu-silica sorbates. Eu(III)
254 luminescence emission spectra collected at various pH values for the different silica materials are
255 presented in **Figure 4**. Sorbent spectra show a considerably higher ${}^7\text{F}_2/{}^7\text{F}_1$ band intensity ratio
256 compared with the spectra of the Eu^{3+} aquo ion (**Figure 4**). This implies a change in the coordination
257 environment of the sorbed cation and subsequent attachment at the surface by inner-sphere sorption.

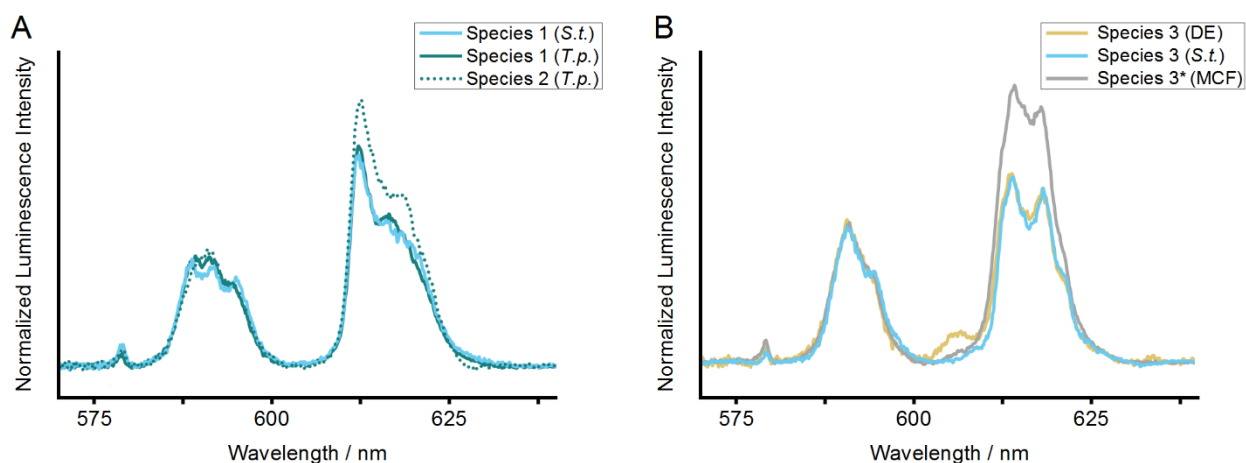
258 The spectra of the *T. p.* sorbate closely resemble each other over the entire investigated pH range
 259 (**Figure 4C**). However, these composite spectra reveal some minor changes in the shoulder, visible in
 260 the 7F_2 band at approximately 620 nm, indicating the presence of two Eu(III) species at the *T. p.* silica
 261 surface. In the deconvolution process, a single component spectrum of “species 1” could be extracted
 262 from the spectra measured at pH 3 and 4 (**Figure 5A**).



263
 264 **Figure 4.** Luminescence emission spectra of the solid biosilica samples after sorption of $c_0(\text{Eu}) = 10^{-5} \text{ M}$
 265 at different pH values; spectra normalized to 7F_1 integrated band intensity. A: DE, B: *S.t.*, C: *T.p.*, D:
 266 MCF.

267 Above pH 4, the spectra cannot be explained solely with this single component spectrum, indicating
 268 the presence of a second Eu(III) species further denoted as “species 2” (**Figure 5A**). The Eu(III)
 269 luminescence for the *T. p.* silica solid phase decays biexponentially with a short-lived and a long-lived
 270 component with lifetimes of about $230 \mu\text{s} \pm 20 \mu\text{s}$ (species 1) and $740 \mu\text{s} \pm 50 \mu\text{s}$ (species 2),
 271 respectively. This corroborates the presence of two species in the system. Though additional
 272 quenching mechanisms might be introduced by transition metals such as iron due to the sorbent
 273 materials’ natural origin,³⁶ the Horrocks equation is tentatively applied to calculate the number of
 274 water molecules in the first coordination sphere. For species 1, $4.0 \pm 0.5 \text{ H}_2\text{O}$ entities could be
 275 calculated, indicating the loss of half of the hydration sphere. Thus, this short-lived species is consistent
 276 with an inner-sphere complex found for Eu(III) sorption on inorganic sorbents like kaolinite.³⁷ In
 277 accordance, the emission spectrum of this component is similar to Eu(III) spectra sorbed on non-
 278 biogenic silica reported in the literature.^{34,35}

279 In contrast, species 2 is surrounded by approximately 0.8 ± 0.5 H₂O in the first coordination sphere.
 280 Incorporation processes typically lead to a full loss of the primary hydration sphere as found for Cm(III)
 281 incorporation in siliceous bulk³⁸ or Eu(III) incorporation in hectorite³⁴. However, partial hydration of
 282 one to two water molecules has been described e.g. for Eu(III) incorporation at grain boundaries of
 283 bioapatite³⁹ or in calcite⁴⁰. Other reasons for a small number of H₂O in the first coordination sphere
 284 are surface precipitation of Eu(III) species or additional coordination of the Eu(III) surface complex to
 285 silicates. The latter phenomenon has been reported for Cm(III) complexes on the surfaces of kaolinite²⁰
 286 and illite⁴¹. Based on the collected luminescence data for Eu(III) attachment on *T.p.*, a final conclusion
 287 about the attachment mode at the interface cannot be drawn.



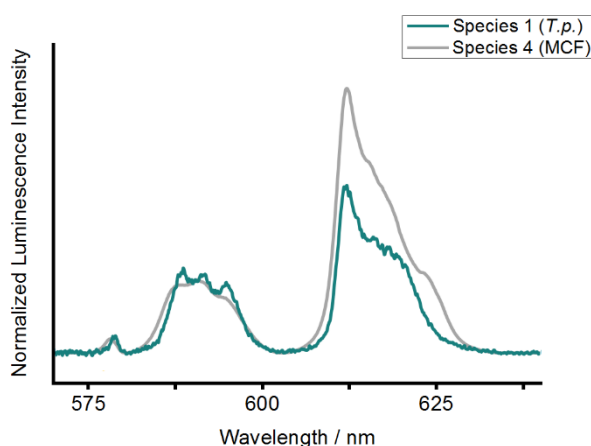
288
 289 **Figure 5.** Extracted luminescence emission spectra; spectra normalized to ⁷F₁ integrated band
 290 intensity. A: examples for species 1 in *S.t.* and *T.p.* (solid line) and example for species 2 in *T.p.* (dotted
 291 line), B: examples for species 3 in DE and *S.t.* and species 3* in MCF.

292 For the second diatom species *S.t.* (**Figure 4B**) below pH 5, spectra similar to those extracted for *T.p.*
 293 (species 1 and 2) can be obtained after deconvolution (**Figure 5A**). The corresponding lifetimes of
 294 $230 \mu\text{s} \pm 20 \mu\text{s}$ and $740 \mu\text{s} \pm 50 \mu\text{s}$ indicate that a surface-sorbed Eu(III) complex and an
 295 incorporated/precipitated species are both present, as found in *T.p.* Hence, the fresh, biogenic silica
 296 materials exhibit the same two Eu species, but their ratios differ. At near neutral pH, only a small
 297 amount of species 1 and 2 can be detected in the *S.t.* material compared to a more acidic suspension.

298 In addition, *S.t.* exhibits an additional species further denoted as “species 3” (**Figure 5B**). At pH 5 and
 299 higher, this species is dominating the spectra of the *S.t.* sorbates. Upon the formation of this species,
 300 the luminescence lifetimes change to a long-lived component of $940 \mu\text{s} \pm 30 \mu\text{s}$ and a short-lived
 301 component of $58 \mu\text{s} \pm 4 \mu\text{s}$. The extraordinarily short lifetime of the second component – below that
 302 of the non-complexed Eu³⁺ aquo ion (about $110 \mu\text{s}$)¹⁸ – must be caused by a luminescence quenching
 303 effect. As mentioned above, quenching may occur in the presence of certain transition metal
 304 impurities such as iron,³⁶ but also between Eu centers when the local Eu concentration is high enough,
 305 e.g. in a precipitate. In the relevant aqueous system with SiO₂ and Eu, a precipitate can be composed
 306 of Eu hydroxides, Eu silicates or mixed/ternary forms thereof. For example, Eu hydroxides exhibit an
 307 extremely short lifetime due to quenching of the hydroxyl groups in addition to the short-range Eu-Eu
 308 self-quenching effects.⁴² Especially Eu self-quenching has previously been shown to result in
 309 biexponential lifetimes despite the presence of only one Eu(III) environment.⁴³ Using the Horrocks
 310 equation, the lifetime of $940 \mu\text{s}$ would yield 0.5 ± 0.5 H₂O molecules in the first coordination sphere.
 311 As the longer component of a precipitated species is likely to be influenced by self-quenching, the
 312 actual lifetime can be expected to be even higher. This implies a full loss of the Eu³⁺ hydration sphere.

313 Generally, these (co-)precipitated and incorporated/intercalated species can result from a partial
314 dissolution of the silica surface. While silica dissolves faster in bases, the dissolution rate is similar
315 within an acidic medium from pH 3–6, as previously shown for quartz and silica glass.^{44,45} Foreign ions
316 can influence the dissolution process depending on their ionic radius⁴⁶ or the frequency of solvent
317 exchange around the aqueous cations.⁴⁷ For example, aluminum – which is a typical component of DE
318 – can reduce the dissolution of silica.⁴⁸ In contrast, Eu(III) can promote the dissolution of silica, as is
319 known for alkaline and earth alkaline metal ions.³⁵ Dissolved Si can form Eu(III) silicate complexes like
320 $[\text{Eu}(\text{OSi}(\text{OH})_3)_2]^{2+}$ and $[\text{Eu}(\text{OSi}(\text{OH})_3)_2]^+$.⁴⁹ Thus, an increased dissolution of impure silica materials at high
321 Eu concentrations may result in a higher amount of intercalated Eu, e.g., through co-precipitation and
322 redeposition of Si and Eu on the sorbent surface.

323 For the third biogenic silica material, DE (**Figure 4A**), emission spectra resemble mainly those collected
324 for *S.t.* at pH 5 and above. Hence, species 3 dominates the emission spectra of DE samples. In contrast
325 to *S.t.* and *T.p.*, the surface-sorbed species 1 is not apparent in the emission spectra of DE. Though, the
326 time-resolved data indicate the presence of a minor species with a lifetime of $270 \mu\text{s} \pm 30 \mu\text{s}$,
327 corresponding to silanol surface sorption. The reduced amount of this species is probably caused by a
328 lower concentration of silanol groups in diatomite.⁵ Generally, the SSA of DE is comparatively low.
329 Thus, the number of sites on the DE surface is also lower if the site density of the biogenic silicates is
330 similar. In addition to the medium lifetime, an especially short and long lifetime with $27 \mu\text{s} \pm 3 \mu\text{s}$ and
331 $1020 \mu\text{s} \pm 70 \mu\text{s}$ can be found. As previously explained, these lifetimes can result from the same
332 incorporated/precipitated species due to self-quenching.



333
334 **Figure 6.** Extracted luminescence emission spectra; spectra normalized to ${}^7\text{F}_1$ integrated band
335 intensity: examples for species 1 in *T.p.* and species 4 in MCF.

336 Finally, the luminescence spectra of the three aforementioned biogenic silica materials can be
337 compared with the luminescence data obtained for the synthetic silica, MCF (**Figure 4D**). Below pH 5,
338 the spectra of the mesoporous MCF show species equivalent to species 3 with respect to the band
339 shape and particularly the splitting of the ${}^7\text{F}_2$ band (see **Figure 5B**). Though, the ${}^7\text{F}_2/{}^7\text{F}_1$ ratio is higher
340 in the spectra of MCF, indicating a stronger complexation. Accordingly, this species of MCF is referred
341 to as “species 3*”. The corresponding triexponential decay correlates with lifetimes of $46 \mu\text{s} \pm 16 \mu\text{s}$,
342 $180 \mu\text{s} \pm 60 \mu\text{s}$ and $1150 \mu\text{s} \pm 170 \mu\text{s}$.

343 In addition, other species can be identified at pH 5 and above: the luminescence decays biexponentially
344 with lifetimes of $150 \mu\text{s} \pm 10 \mu\text{s}$ and $780 \mu\text{s} \pm 60 \mu\text{s}$, which is further denoted as “species 4”. Its
345 threefold splitting of the ${}^7\text{F}_1$ band resembles the even more pronounced splitting of species 1 as
346 depicted in **Figure 6**. Again, the ${}^7\text{F}_2/{}^7\text{F}_1$ ratio is higher in the spectra of MCF. In addition, the ${}^7\text{F}_0$ band is
347 slightly more pronounced in the spectra of MCF and DE, suggesting a lower degree of symmetry of the

348 formed Eu species. The ${}^7\text{F}_2$ band intensity in the MCF spectra may be increased through a higher Eu
349 loading as MCF exhibits a relatively high SSA and, thus, a higher total amount of silanol groups,
350 i.e. binding sites. The large surface could also lead to a higher partial dissolution of the MCF material
351 and subsequent co-precipitation with Eu.

352 Consequently, multiple differing Eu species are discernable in the silica sorbates (summarized in **Table**
353 **A2**, appendix). The extremely short-lived components with lifetimes below 60 μs in species 3 (DE, *S.t.*)
354 and 3* (MCF) result from self-quenching. The components with lifetimes between 150 μs and 270 μs
355 in species 1 (*T.p.*, *S.t.*), 3 (DE), 3* (MCF) and 4 (MCF) are probably Eu species sorbed on silanol groups.
356 These surface-sorbed species are predominantly found in the *T.p.* samples, coinciding with the highest
357 SSA of the biogenic materials. When the SSA decreases as it is the case for *S.t.* silica, species 1 decreases
358 in abundance until it vanishes for DE with the smallest SSA. Instead, the amount of partially
359 incorporated or precipitated Eu(III) species increases. About one water molecule remains in the inner-
360 sphere of the species with a lifetime of about 740 μs to 780 μs as found in species 2 (*T.p.*, *S.t.*) and 4
361 (MCF). In contrast, the hydration sphere is absent in the species with a lifetime between 940 μs and
362 1150 μs in species 3 (DE, *S.t.*) and 3* (MCF). The long lifetimes are in the range of those reported for
363 Eu incorporated into minerals, suggesting an amorphous Eu-silica phase.³⁴

364

365 5. Conclusions

366 In this study, Eu(III) was sorbed onto diatom biosilica and a synthetic silica material. Due to their
367 negative surface charge, the sorption of cations is facilitated. Resulting sorbent loadings are up to
368 140 mg g^{-1} . With TRLFS, the formed Eu(III) species could be characterized: reversible surface sorption
369 is predominant for *S.t.* (acid conditions) and *T.p.*, while irreversible incorporation or precipitation
370 occurs for *S.t.* (near neutral pH), DE and MCF. Loadings could be increased by modifying the pore
371 system or using whole cells in future studies. Altogether, diatom biosilica is a promising “green”
372 material for scavenging *f*-elements in aqueous solution.

373

374 6. Abbreviations

375 ASW, artificial seawater; DE, diatomaceous earth; EDX, energy-dispersive X-ray spectroscopy; ICP-OES,
376 inductively coupled plasma optical emission spectroscopy; MCF, mesocellular foam; p.a., *pro analysi*;
377 PEG, polyethylene glycol; PPG, polypropylene glycol; SEM, scanning electron microscopy; SSA, specific
378 surface area; *S.t.*, *Stephanopyxis turris*; *T.p.*, *Thalassiosira pseudonana*; TRLFS, time-resolved laser-
379 induced fluorescence spectroscopy.

380

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395

396 9. Declaration of Interest

397 The authors declare that they have no known competing financial interests or personal relationships
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399 10. CRediT Authorship Contribution Statement

400 **Kaitlin Kim Karlotta Kammerlander:** Formal analysis, Investigation, Writing - Original Draft,
401 Visualization; **Lydia Köhler:** Formal analysis, Investigation, Writing - Original Draft, Visualization; **Nina**
402 **Huittinen:** Formal analysis, Writing - Review & Editing; **Robin Steudtner:** Writing - Review & Editing;
403 **Cathleen Oschatz:** Writing - Review & Editing; **Manja Vogel:** Writing - Review & Editing; **Thorsten**
404 **Stumpf:** Resources, Writing - Review & Editing, Supervision; **Eike Brunner:** Resources, Writing - Review
405 & Editing, Supervision; **All authors:** Conceptualization.

406

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