

Environmentally safe ZVI/ZnS-based polymer composite for lindane degradation in water: Assessment of photocatalytic activity and eco-toxicity

Original

Environmentally safe ZVI/ZnS-based polymer composite for lindane degradation in water: Assessment of photocatalytic activity and eco-toxicity / Rescigno, Raffaella; Sacco, Olga; Pragliola, Stefania; Albarano, Luisa; Libralato, Giovanni; Lofrano, Giusy; Romano Spica, Vincenzo; Tammaro, Olimpia; Montalbano, Giorgia; Esposito, Serena; Vaiano, Vincenzo; Venditto, Vincenzo. - In: SEPARATION AND PURIFICATION TECHNOLOGY. - ISSN 1383-5866. - 330 A:(2024), pp. 1-10. [10.1016/j.seppur.2023.125246]

Availability:

This version is available at: 11583/2982813 since: 2023-10-06T09:08:43Z

Publisher:

Elsevier

Published

DOI:10.1016/j.seppur.2023.125246

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

Elsevier postprint/Author's Accepted Manuscript

© 2024. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>. The final authenticated version is available online at:
<http://dx.doi.org/10.1016/j.seppur.2023.125246>

(Article begins on next page)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

**Environmentally safe ZVI/ZnS-based polymer composite
for lindane degradation in water: assessment of
photocatalytic activity and eco-toxicity**

Raffaella Rescigno¹, Olga Sacco^{1*}, Stefania Pragliola¹, Luisa Albarano², Giovanni Libralato², Giusy Lofrano^{3*}, Vincenzo Romano Spica³, Olimpia Tammaro⁴, Giorgia Montalbano⁴, Serena Esposito⁴ Vincenzo Vaiano⁵ and Vincenzo Venditto¹

¹Department of Chemistry and Biology “A. Zambelli”, INSTM research unit, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano (Salerno), Italy

²Department of Biology, University of Naples Federico II, Monte Sant'Angelo University Complex - Building 7, Via Vicinale Cupa Cintia 26, 80126, Naples, Italy

³Department of Movement, Human and Health Sciences, University of Rome Foro Italico, Piazza Lauro De Bosis, 15, 00135 Roma, Italy

⁴Department of Applied Science and Technology and INSTM Unit of Torino – Politecnico, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy.

⁵Department of Industrial Engineering, INSTM research unit, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano (Salerno), Italy

25 *Corresponding authors: Olga Sacco (osacco@unisa.it); Giusy Lofrano
26 (giusy.lofrano@uniroma4.it)

27 **Abstract**

28 Monolithic composite aerogel based on a photocatalytic system, constituted by Fe⁰
29 (ZVI) coupled with ZnS (FZ), embedded into syndiotactic polystyrene (sPS) matrix
30 was used, for the first time, in the lindane degradation under UV light. The content of
31 FZ photocatalyst inside the monolithic composite aerogel (FZsPS) composite was 3
32 wt%. FESEM images of FZsPS indicate that the FZ photocatalyst is well dispersed in
33 the polymer matrix. EDS analyses and temperature-programmed reduction (TPR-H₂)
34 measurements revealed an interpenetrated structure of the ZVI and ZnS phases as
35 well the presence of some iron in an oxidized form. Photocatalytic activity data
36 showed that in presence FZsPS aerogel, the almost complete lindane degradation was
37 achieved after only 30 min of UV irradiation time. FZsPS was also effective in the
38 lindane mineralization since a TOC removal of about 94% was detected after 180
39 min of treatment time. Remarkably, based on the toxicity evaluation on *Artemia*
40 *franciscana*, while the bare FZ photocatalyst showed significant toxicity per se, no
41 toxicity or genotoxicity was found in the water treated with the FZsPS composite
42 system where FZ is immobilized into the sPS aerogel matrix. Therefore the proposed
43 composite photocatalyst can be considered as a model for a strategy to eliminate the
44 environmental impact of catalysts that would otherwise be harmful to water.

45 **Keywords:** ZVI/ZnS polymer composite; polymeric aerogel; lindane; photocatalytic
46 degradation; toxic and genotoxic effects

47

48

49

50 **1. Introduction**

51 Lindane is the common name of the γ -isomer of hexachlorocyclohexane (HCH), an
52 organochlorine pesticide (OCP) widely used from 1950s to 1980s for both
53 agricultural and non-agricultural purposes (USEPA, 2006 [1]). It has been used for
54 example on fruits and vegetables, to control insects and pests, but also for seed and
55 soil treatment, for the treatment of trees and wood, especially in coniferous forests
56 and for the treatment against ectoparasites in both veterinary and human applications
57 [2-4]. Its global production was around 600,000 tonnes during the period from 1950s
58 to 2000s [5]. Italy was one of the top 10 countries with the highest usage of Europe
59 [6].

60 The persistence of lindane in aquatic environments has been widely documented, as
61 well as its toxicity to aquatic organisms [7]. The (L(E)C50) and chronic (NOEC)
62 toxicity values are at the level of $\mu\text{g/L}$ for several type of fishes and aquatic
63 invertebrates. Several concerns have been reported regarding human health. AMAP
64 reported an increase in HCH isomers in human tissues and breast milk [8]. It has
65 been identified as a potential endocrine-disrupting chemical [9]. The United States
66 Environmental Protection Agency (US EPA) and the World Health Organization
67 (WHO) classify lindane as a potent carcinogen and teratogen agent [10, 11]. The
68 International Agency for Research on Cancer (IARC) has associated its exposure
69 with one of the causes of non-Hodgkin's lymphoma (NHL) (IARC, 2016).

70 For these reasons, lindane was listed within the persistent organic pollutants by the
71 2009 Stockholm Convention [12]. As a result, its production and agricultural use
72 were banned in more than 50 countries worldwide by 2010 [5], but pharmaceutical
73 use is permitted as a second-line treatment for scabies and lice [13]. Therefore, HCH
74 concentrations have been detected in water bodies all over the world (ranging from

75 0.087 to 5509 $\mu\text{g/L}$), as well as in drinking water, also due to its strong refractory
76 degradation [14], becoming a concern of global relevance.

77 Traditional methods require long treatment times for lindane degradation because it
78 is a hydrophobic organic molecule ($\log K_{ow} > 3.5$) [15, 16]. Thus, much effort is
79 being made in developing more efficient and sustainable technologies to remove
80 lindane from water.

81 Among several processes allowing the breaking of the C-Cl bond, technologies based
82 on zero-valent iron (ZVI), which reacts with halogenated organic pollutants (RX)
83 acting as a very powerful reducing agent [17], result as the most promising. In recent
84 decades, the use zero-valent iron (ZVI) has been proposed for depolluting soils and
85 aquifers because ZVI is highly reactive and inexpensive [18, 19]. However, the
86 halogenated organic pollutants degradation rates in presence of ZVI decrease over
87 time [20] because Fe^0 is easily oxidized to Fe^{2+} [21] according to the following
88 general reaction [21-24]:



90 On the other hand, advanced oxidation processes (AOPs), such as heterogeneous
91 photocatalysis, can degrade organic pollutants into harmless end products, including
92 lindane [13, 25-28], but the degradation performance is generally low when
93 photocatalysis is used for the treatment of water polluted by chlorinated organic
94 compounds (such as perchloroethylene and lindane) [26, 29-33]. Indeed, in the case
95 of lindane, it is reported that treatment times higher than 2 h are required for the
96 almost complete pollutant degradation. Hence to improve the efficiency of
97 photocatalytic processes for the degradation of halogenated organic pollutants, some
98 authors have proposed to couple semiconductor photocatalysts, such as TiO_2 , ZnO ,
99 $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4/\text{MoS}_2$, with ZVI to simultaneously exploit the photocatalytic

100 degradation properties with the reductive action of ZVI [34-38]. In this perspective,
101 Sacco et al. selected ZnS as a suitable semiconductor to be coupled with ZVI and
102 demonstrated as it is possible to obtain a powder composite capable of degrading
103 chlorobenzene more efficiently than ZnS and ZVI alone, evidencing that the
104 simultaneous presence of UV light and ZnS avoid the ZVI oxidative corrosion
105 phenomena, also preserving a high reactivity after several reuse cycles [39].
106 However, despite the interesting degradation performances reported by such
107 photocatalytic composites, it must be considered that they have been used in slurry
108 photoreactors in which the catalytic powders are dispersed within the aqueous
109 medium. Therefore, the need for a post-treatment step for the separation of catalysts
110 from the treated water remains the main constraint to the full-scale application of
111 photocatalytic systems [40-43]. Moreover, the use of suspended particles for
112 wastewater treatment implies their possible release into the environment, inducing a
113 health risk due to the possible toxicity of these nanoparticles [44-49].

114 To overcome these drawbacks, the catalytic materials could be immobilized on the
115 surface of suitable macroscopic supports [50, 51] or dispersed within the porous
116 structure of supports having a high affinity towards the target pollutant [52, 53].

117 To date, among the different supports for photocatalysts (such as glass, ceramic or
118 zeolites [54-56]) polymers are attracting more and more attention in the literature
119 concerning heterogeneous photocatalysis [57-60].

120 Recent research papers reported that monolithic syndiotactic polystyrene (sPS)
121 aerogels are promising supports for photocatalytic applications due to their good
122 mechanical properties and the nanoporous crystalline phase which confers high
123 surface areas and good sorption properties [59, 61-66].

124 This research aimed at investigating for the first time the behavior of a composite
125 aerogel (FZsPS) based on sPS and Fe⁰/ZnS, in the photocatalytic degradation of
126 lindane. The kinetic of degradation was fully characterized from a chemical and
127 ecotoxicological viewpoint. In particular, embryo-larval and adult-related effects on
128 *Artemia franciscana* were evaluated. Genotoxicity testing was also performed to
129 determine potential hazards for direct or indirect DNA interaction.

130 It is worthwhile to note that to date no scientific paper reports toxicological results
131 on the treated water coming from the photocatalytic degradation of lindane by using
132 composite aerogels.

133

134 **2. Materials and methods**

135 *2.1. Materials*

136 Sodium borohydride (NaBH₄), zinc sulfide (ZnS) particles, iron (II) sulfate
137 heptahydrate (FeSO₄ • 7H₂O) and Lindane (C₆H₆Cl₆) were provided by Sigma–
138 Aldrich. Syndiotactic polystyrene (sPS) used for the aerogels preparation was
139 purchased from Idemitsu Kosan Co., Ltd. under the trademark XAREC© 90ZC.

140

141 *2.2. Preparation of Fe⁰ and Fe⁰/ZnS photocatalyst*

142 Fe⁰/ZnS (FZ) photocatalyst in powder form were prepared following the procedure
143 reported by Sacco et al. [39]. Specifically, 1 g of ZnS was added to 100 mL of
144 distilled water where 4 g of FeSO₄•7H₂O was previously dissolved. The suspension
145 was stirred for 10 minutes in the presence of an N₂ stream (flow rate: 30 NL/h) to
146 remove dissolved oxygen. Subsequently, 1.4 g of reducing agent (NaBH₄) was added
147 to the suspension, which was stirred in the presence of N₂ flow for 1 h, washed three

148 times with ethanol and finally dried at room temperature overnight to obtain the FZ
149 sample (Fe^0 content in the FZ photocatalyst was 45 wt % [39]).

150 Fe^0 particles were prepared following the same procedure but without adding ZnS in
151 the aqueous solution.

152 FZ, ZnS and Fe^0 particles were deeply characterized in our previous work [39]. In
153 detail, Wide-angle X-ray diffraction (WAXD) analysis of FZ evidenced diffraction
154 patterns (at $2\theta = 28.6, 33.2, 47.6$ and 56.5°) due to ZnS [67, 68]. Moreover, the
155 characteristic peak of Fe^0 , at about $2\theta = 45^\circ$, was also detectable [39] with no signals
156 related to iron oxides whose presence was instead shown by Raman spectra [39].

157

158 *2.3 Preparation of FZsPS monolithic composite aerogel*

159 The monolithic composite aerogel (FZsPS) was prepared according to the
160 experimental procedure described by Sacco et al. [66]. Syndiotactic polystyrene
161 (sPS) and the FZ photocatalyst with a weight ratio of 97/3 were dispersed in
162 chloroform (chloroform/sPS weight ratio equal to 90/10) and inserted in a
163 hermetically sealed test tube, which was then heated up to 100°C . The formation of
164 a gel was obtained after cooling the suspension from 100°C to room temperature.
165 The chloroform was extracted from the obtained gel through treatment with
166 supercritical carbon dioxide (using an ISCO SFX 220 extractor) for 3 h at 40°C and
167 at a pressure of 20 MPa, obtaining the FZsPS monolithic composite aerogel in a
168 cylindrical shape (diameter=5.6 mm; height= 3 cm) (Figure S1 of Supplementary
169 Material).

170 The content of FZ photocatalyst inside the FZsPS composite was 3 wt%.

171 Only for toxicity data analysis, monolithic composite aerogels containing Fe⁰ and
172 ZnS particles at 3 wt% (named Fe⁰sPS and ZsPS, respectively) were also prepared
173 with the same method used for the preparation of FZsPS.

174 *2.4. Characterization techniques*

175 Wide-angle X-ray diffraction (WAXD) patterns of the photocatalysts were obtained
176 with a Bruker D8 Advance diffractometer, using a nickel filtered Cu-K α radiation
177 and Bragg–Brentano θ – θ geometry. The 2θ acquisition interval was 5–80°, with a
178 step size of 0.0303° and a scanning acquisition time of 0.200 s/point.

179 To investigate the effect of iron on optical properties of ZnS powder, a Perkin Elmer
180 Spectrofluorometer LS55 was used to collect the photoluminescence spectra with an
181 excitation wavelength $\lambda_{\text{ex}} = 285$ nm and slits 10 nm, recorded in the λ range of 300–
182 550 nm.

183 The specific surface area (SSA) of the composite aerogel was obtained by dynamic
184 N₂ adsorption measurements at –196 °C, using a Nova Quantachrome 4200e
185 instrument analyzer and evaluated by the BET method.

186 Field emission scanning electron microscopy (FE-SEM) enabled the morphological
187 analysis of the aerogel pellet. A ZEISS MERLIN instrument (Oberkochen, Germany)
188 was used; the samples were deposited on a carbon-coated stub and then coated with a
189 7 nm Pt layer.

190 In order to investigate the presence and distribution of FZ powders throughout the
191 aerogel sample, energy-dispersive X-ray spectroscopy (EDS) analyses by using
192 Aztec Software (Oxford Instruments) were performed on the same instrumentation.

193 Temperature programmed reduction (TPR-H₂) measurements were carried out in
194 AMI-300 (Altamira Instrument). The FZ sample was reduced in 5% H₂–95% Ar with

195 a flow rate of $50 \text{ Ncm}^3 \text{ min}^{-1}$ and a heating rate of $10^\circ\text{C min}^{-1}$. TPR- H_2 profile was
196 recorded using a thermo-conductive detector [69].

197

198 *2.5 Photocatalytic activity tests*

199 The photocatalytic tests were out carried in presence of UV light using a Pyrex
200 cylindrical reactor (ID = 3.5 cm, h = 28 cm, V = 269 mL). A UV-LEDs strip
201 (nominal power: 10 W, main wavelength emission: 365 nm, provided by LED
202 lighting hut, Shenzhen, China) was used as light source. The UV-LEDs strip was
203 placed around and in contact with the outer surface of the photoreactor. The
204 photocatalytic tests were performed on 100 mL of aqueous solution at a lindane
205 concentration of $100 \mu\text{g/L}$ and using a photocatalyst dosage equal to 0.09 g/L for FZ,
206 Fe^0 and ZnS in powder form, whereas the used FZsPS dosage was 3 g/L
207 (corresponding to an FZ dosage of 0.09 g/L). Fe^0 degradation efficiency was instead
208 analysed in the absence of light [39].

209 In the case of the tests with the FZsPS monolithic composite aerogel, a volume (2
210 mL) of solution was taken at different times to analyze the lindane concentration. In
211 the case of the tests with powder photocatalysts, before the analysis, the taken
212 suspension (2 mL) was filtered through $0.45 \mu\text{m}$ membrane to separate the
213 photocatalyst from the solution. An Agilent Gas Chromatograph (model 7820 A)
214 equipped with an Electron Capture Detector (ECD) was used to evaluate the lindane
215 concentration. The used analytical method was that one described by the EPA (U.S.
216 Environmental Protection Agency, SW-846 Test Method 8081B, Organochlorine
217 Pesticides by Gas Chromatography). The total organic carbon (TOC) of aqueous
218 solutions was measured with a TOC analyzer (Multi N/C 3100S, Analytik Jena),
219 which used an air flow of $160 \text{ Ncm}^3/\text{min}$ and drew $500 \mu\text{L}$ per sample.

220 2.6. Bioassays and toxicity data analysis

221 The bioassays carried out with *Artemia franciscana* and data analysis were in
222 accordance with [70, 71]. Ten nauplii, metanauplii, and juvenile, and five adults
223 were exposed to increasing percentage concentrations of three experimental
224 conditions ((i) negative control – synthetic seawater (SSW, prepared in according to
225 ISO 10253/16) plus amendments (distilled water + FZ or distilled water + FZsPS);
226 (ii) positive control – seawater spiked with lindane (100 µg/L) (distilled water +
227 lindane) to check the toxic impact of lindane; (iii) seawater spiked with treatments
228 effluents (distilled water + lindane + Fe⁰ or distilled water + lindane + FZ or distilled
229 water + lindane + FZsPS or distilled water + lindane + Fe⁰sPS or distilled water +
230 lindane + ZsPS).

231 About RNA extraction and cDNA synthesis, two hundred nauplii and metanauplii,
232 one hundred juvenile and ten adults of *Artemia franciscana* were exposed to 100%
233 non-diluted aqueous solutions of distilled water + FZsPS, distilled water + lindane
234 and distilled water + lindane + FZsPS. All details about the experimental plan and
235 materials are provided in Supplementary Materials.

236

237 **3. Results and Discussion**

238 3.1 Characterization results

239 The WAXD results of the FZsPS aerogel (before and after use) and the FZ
240 photocatalyst in powder form are shown in Figure S2 of Supplementary Material.
241 The WAXD spectrum of bare sPS has been included for comparison.

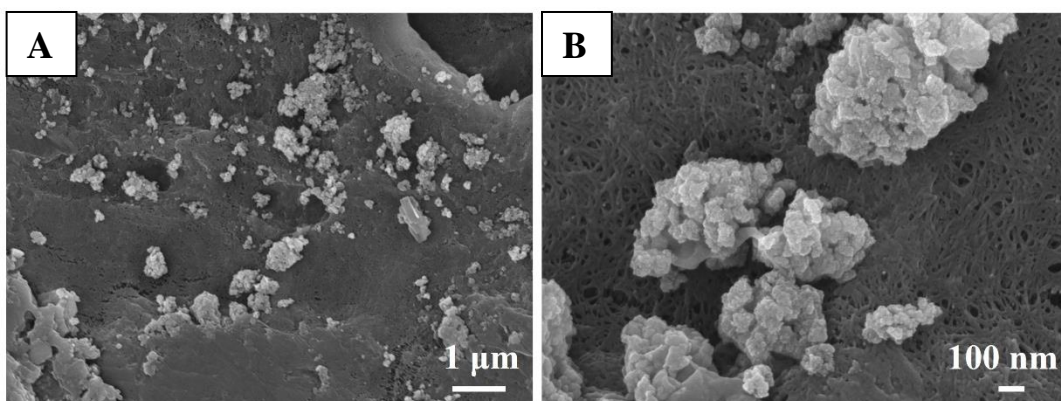
242 The diffraction patterns of the FZsPS composite aerogel show both the diffraction
243 peaks of the δ crystalline form of sPS ($2\theta = 10 - 23.6^\circ$) [62] and of the crystalline

244 phase of ZnS ($2\theta = 28.6, 47.7, 56.6^\circ$) [39]. Moreover, the characteristic peak of Fe⁰
245 ($2\theta = 45^\circ$) [39] is also detectable for both FZ and FZsPS composite aerogel,
246 confirming the presence of FZ photocatalyst within the sPS matrix and evidencing
247 that the inclusion of FZ particles within the polymer framework did not alter the δ
248 crystalline form of sPS.

249 FZsPS specific surface area (SSA), evaluated by BET method, was 309 m²/g, while
250 for FZ photocatalyst in powder form and bare sPS, the SSA was 44 and 340 m²/g,
251 respectively. The observed slight reduction of the FZsPS composite SSA compared
252 to that of bare sPS aerogel, as a result of the photocatalyst particle embedding within
253 the sPS framework, is in agreement with SSA values commonly observed in sPS
254 aerogel-based composite materials [39].

255 Morphological evaluation performed on the FZsPS aerogel by means of Field
256 Emission Scanning Electron Microscopy (FESEM) confirmed the presence of FZ
257 photocatalyst throughout the sample. FESEM images, shown in Figure 1, highlight
258 the distribution and morphology of FZ powders in FZsPS aerogel.

259



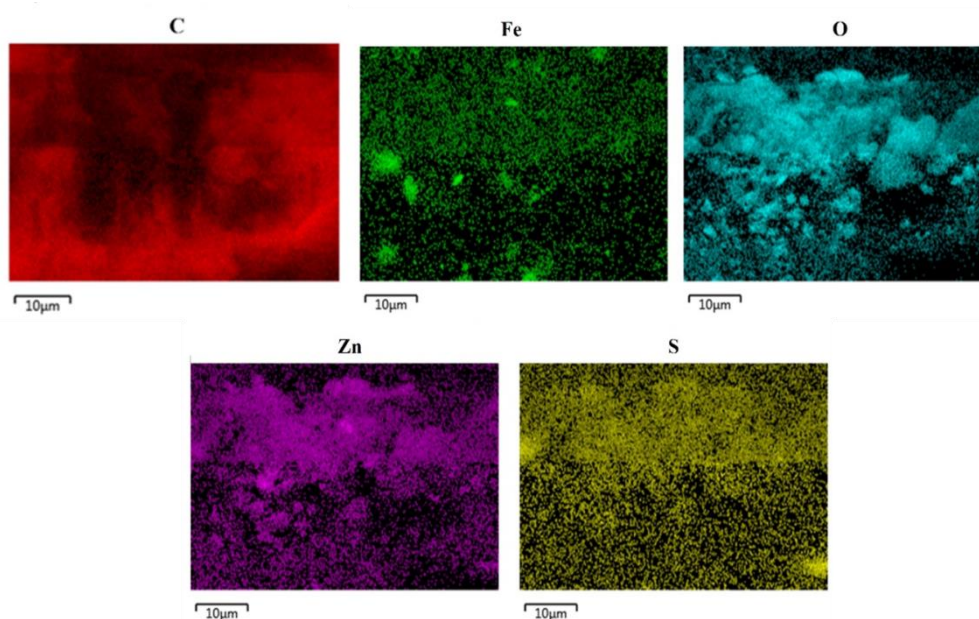
260
261 **Figure 1:** FESEM images of the FZsPS monolithic composite aerogel at two
262 different magnifications.

263

264 At lower magnification (Figure 1A) the sample overview shows that FZ particles are
265 well dispersed and incorporated into the polymer matrix, although particle
266 agglomerates are also present in some areas. At higher magnification (Figure 1B) the
267 morphology of FZ particles and porosity of the polymeric phase, having a fibrillar
268 structure [66] are better highlighted. The FZ particle morphology observed in the
269 composite, is different from that of the unsupported FZ powders (Figure S3 of
270 Supplementary Material), characterized by sphere-like aggregates composed of
271 flakes. This difference may be ascribed to the processing conditions involved during
272 aerogel formation [72].

273 EDS analysis on the FZsPS composite aerogel sample was exploited to confirm the
274 chemical composition of the material where the mapping of the different elements
275 composing the catalyst powders enabled to explore their distribution onto the aerogel
276 surface.

277



278

279

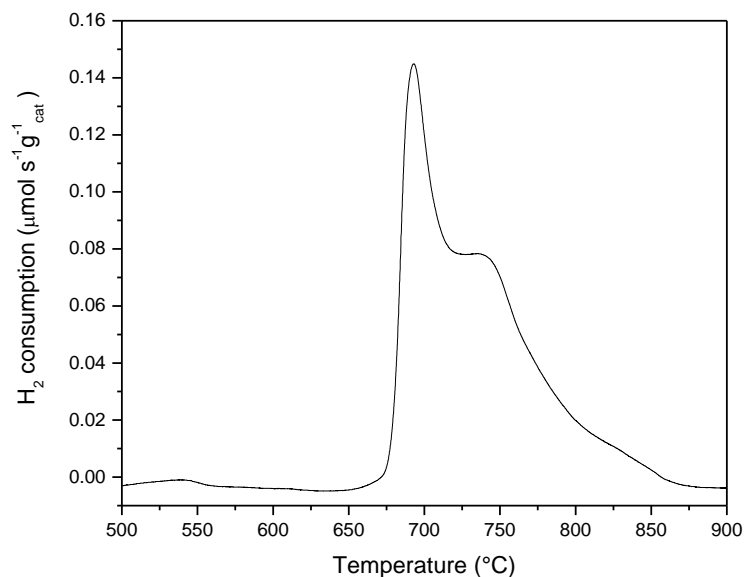
280 **Figure 2:** EDS analysis performed on the composite aerogel FZsPS. Mapping of Fe,

281 O, C, Zn and S elements.

282

283 As shown in Figure 2, elements such as Zn, S, Fe and O were found in the FZ
284 particle agglomerates, while C was localized in surrounding area corresponding to
285 the sPS polymeric matrix. The mapping of Fe, Zn and S has highlighted both a
286 homogeneous distribution of these elements and an interpenetration of them,
287 although areas with higher Fe concentrations are also present. The homogeneous
288 interpenetration of Fe and ZnS is in agreement with the distribution of elements
289 observed in unsupported FZ powders (Figure S4 of Supplementary Material), where
290 the EDS elemental analysis highlights the tendency of iron to organize itself in chain
291 structures surrounding the ZnS, phase. Finally, the EDS mapping also evidenced
292 greater concentrations of O in areas characterized by higher Fe concentrations,
293 suggesting the possible presence of iron in its oxidized form.

294 In order to ascertain the presence of oxidised iron, the FZ sample was studied by
295 means of the TPR technique. The TPR profile of FZ presents reduction peaks located
296 at high temperature, 690 and 740°C (Figure 3). These peaks can be attributed
297 exclusively to iron phases, in agreement with the results of Dutková et al [73].
298 Before 650°C no reduction peaks are detected, indicating that α -hematite like phase
299 (Fe_2O_3) is not present. Considering the adopted heating ramp ($10^\circ\text{C min}^{-1}$), the sharp
300 peaks around 700°C are mainly attributed to the step reduction of the magnetite-like
301 phase (Fe_3O_4) to metallic iron [74]. Correlating this result with the absence of peaks
302 related to iron oxides from the WAXD analysis reported by Sacco et al. [39], we can
303 speculate the presence of nonstoichiometric amorphous phases. The results obtained
304 from TPR profile agree with the presence of iron oxides detected in the Raman
305 spectrum of FZ reported in ref [39].

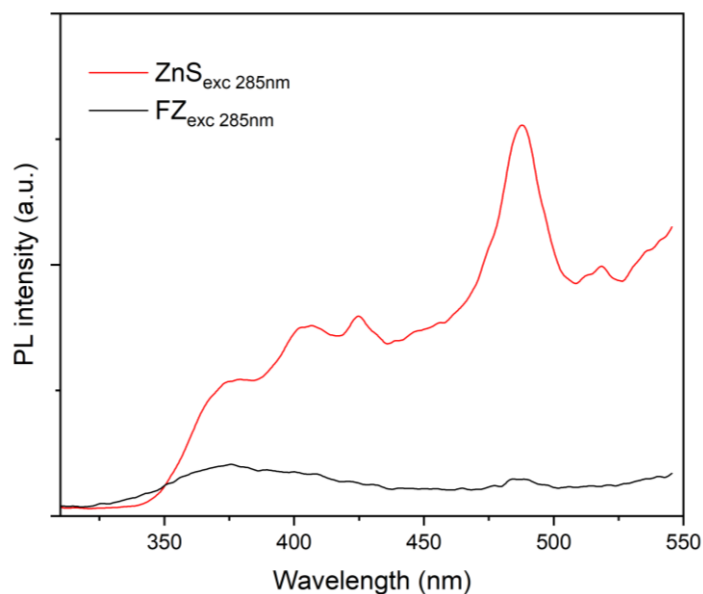


306

307 **Figure 3:** Temperature programmed reduction (TPR) profile of FZ photocatalyst.

308 Photoluminescence (PL) spectral analysis was conducted to verify the impact of iron

309 on the optical properties of the prepared photocatalyst.



310

311 **Figure 4:** Photoluminescence spectra of modified and unmodified system: FZ and
312 ZnS.

313

314 Figure 4 shows the room temperature PL spectra, under 285 nm excitation, for pure

315 ZnS and FZ powder prepared as reported by Sacco et al. [39]. The PL spectrum of

316 ZnS shows a multipeak emission typical of this semiconductor [75]. The blue

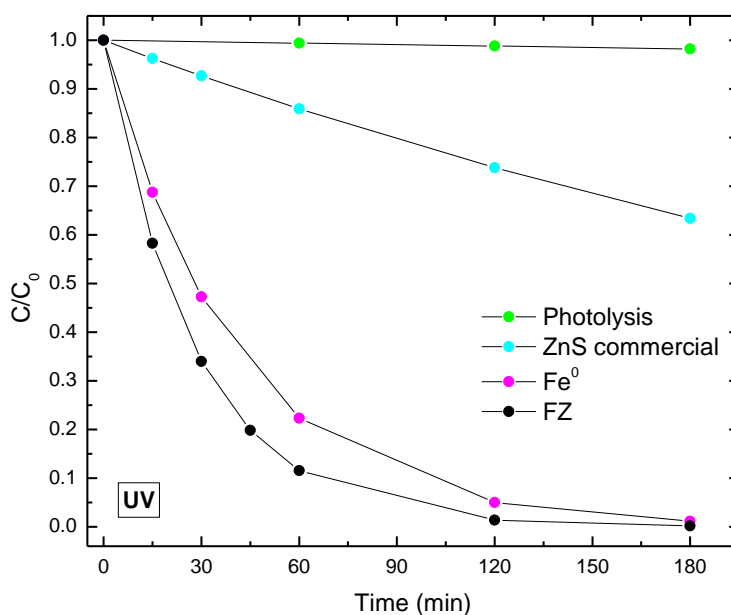
317 emission band is attributed to defect states due to sulfur and zinc vacancies (about
318 425 and 480 nm, respectively). The broad emission band of peaks located between
319 360 nm and 405 nm is generally attributed to interstitial defects (S interstitial at low
320 wavelength and Zn interstitial at higher wavelength) [76]. When the iron is
321 introduced into the system, the PL peaks slightly shift to shorter wavelengths [77]
322 but the main effect is the reduction of their intensity. The doping with iron allows to
323 capture the photoactivated electrons and thus slows down the recombination between
324 the valence and conduction bands, resulting in the decrease of PL intensity [78].

325

326 *3.2 Photocatalytic activity results*

327 The photocatalytic activity of commercial ZnS and FZ in powder form was evaluated
328 in the degradation of lindane under UV light irradiation and compared with the
329 degradation efficiency of Fe⁰ in the absence of light (Figure 5). A sample-free
330 control test, performed to verify the contribution of photolysis, showed no influence
331 during the overall irradiation time, while a decrease in lindane relative concentration
332 was found in the presence of ZnS, Fe⁰ and FZ. In detail, with ZnS, the lindane
333 concentration slowly decreased as a function of irradiation time, achieving a
334 degradation efficiency of only about 35 % after 180 min. The low photocatalytic
335 activity of ZnS could be explained considering that the C-Cl bonds of lindane
336 structure are difficult to break by hydroxyl radicals generated when ZnS is excited by
337 UV light [39, 79, 80], as also reported in some literature papers [33, 81, 82] in which
338 it is shown that the photodegradation efficiency decreases by increasing the number
339 of C-Cl bonds of the pollutants structure. Noticeably, in the absence of UV light, the
340 lindane degradation efficiency by Fe⁰ particles was higher than that of ZnS under
341 irradiation, because of the high ability of Fe⁰ to break the C-Cl bond of chlorinated
342 organic pollutants [39, 83], leading to the complete lindane degradation in 180 min.

343 It is worth to pointing out that, under UV light, the lindane degradation by FZ
344 photocatalyst was enhanced, showing faster degradation kinetics as compared with
345 Fe⁰ alone. Indeed, in the presence of FZ photocatalyst and UV light, the lindane
346 relative concentration was always lower than that achieved with the non-irradiated
347 Fe⁰ particles. It is argued that the higher lindane degradation efficiency of FZ
348 photocatalyst under UV light is due to the continuous reduction of Fe²⁺ (continuously
349 generated from the reductive cleavage of C-Cl bonds by Fe⁰) to Fe⁰ by the electrons
350 promoted in the conduction band of photoexcited ZnS, similarly to what reported for
351 the photocatalytic degradation of chlorobenzene in presence of Fe⁰/ZnS [39]. This
352 assumption is consistent with the outcomes of photoluminescence analyses, which
353 show a decrease in the electron-hole recombination rate for sample FZ.



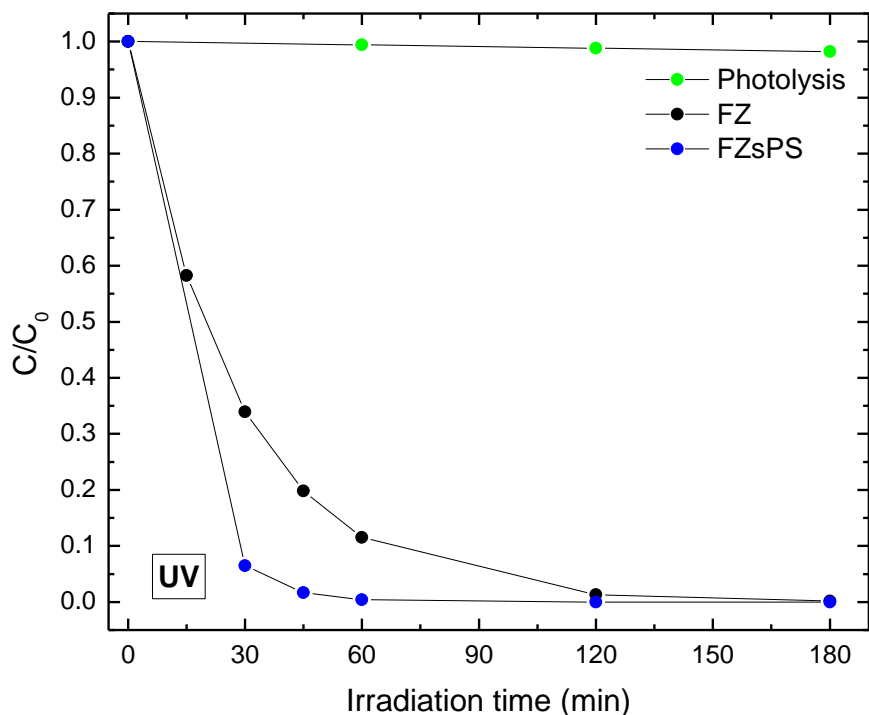
354

355 **Figure 5:** Photocatalytic degradation of lindane by ZnS and FZ under UV light
356 irradiation and in the presence of Fe⁰ in the absence of light.

357

358 Figure 6 reports the comparison of the lindane photocatalytic degradation obtained in
359 the presence of FZ photocatalyst in powder form and FZsPS monolithic composite

360 aerogel.



361

362 **Figure 6:** Photocatalytic degradation of lindane by FZ and FZsPS under UV light
363 irradiation.

364

365 Despite both FZ powder and FZsPS composite completely degraded lindane after
366 180 min of UV irradiation, the decreasing rate of lindane relative concentration as a
367 function of irradiation time clearly evidenced a photodegradation activity of FZsPS
368 significantly higher than that observed in the presence of FZ photocatalyst. Indeed,
369 using the FZsPS aerogel, the lindane degradation was about 95% after only 30 min
370 of irradiation time whereas the FZ photocatalyst exhibited a lindane degradation of
371 about 65% after the same irradiation time. These data underline that the
372 photodegradation activity is strongly promoted when the FZ photocatalyst in powder
373 form is dispersed in the polymer matrix.

374 The enhanced photocatalytic activity observed in the presence of FZsPS could be due
375 to the higher SSA of FZsPS (309 m²/g) with respect to FZ (44 m²/g) but also to the

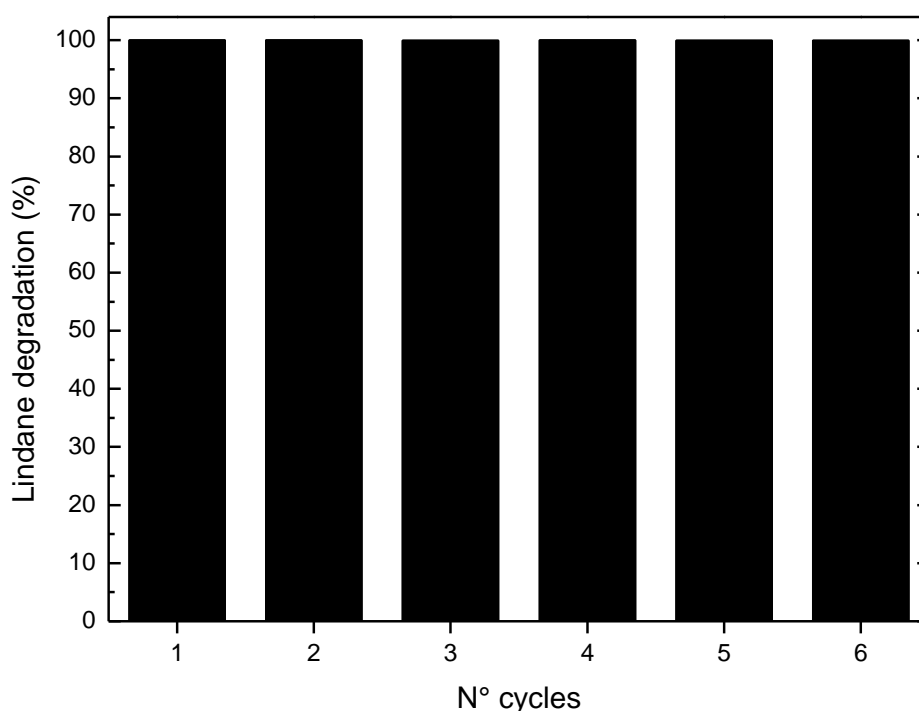
376 affinity of lindane with the non-polar polymer matrix, which results in a
377 concentration of lindane in the matrix itself. To confirm such hypothesis, an
378 additional experiment was carried out to measure the amount of lindane absorbed by
379 bare sPS monolithic aerogel in dark conditions performed with the same
380 experimental conditions used for the photodegradation tests (solution volume: 100
381 mL; initial lindane concentration: 100 $\mu\text{g/L}$; sPS dosage: 3 g/L). (Figure S5 of
382 Supplementary Materials). sPS aerogel showed an uptake of 30 % after 180 min.
383 This result confirms the good affinity of the polymer matrix towards non-polar
384 organic compounds (such as lindane), in agreement with the available literature [61,
385 65, 84, 85]. Therefore, it is possible to argue that the higher photodegradation
386 efficiency of FZsPS aerogel is mainly due to the lindane absorption ability of the
387 polymer matrix since the number of lindane molecules in contact with FZ particles
388 embedded into sPS aerogel is increased. Thus, the photocatalytic degradation rate is
389 enhanced.

390 The aqueous solution recovered after the photocatalytic treatment with the FZsPS
391 aerogel was analysed by inductively coupled plasma optical emission spectrometry
392 (ICP-OES Optima 7000DV, PerkinElmer). This analysis revealed the almost total
393 absence of Fe (<0.01 mg/l) and a slight presence of Zn (3 mg/L), probably due to the
394 partial leaching of the FZ particles immobilized on the external surface of sPS and
395 not of those dispersed within the polymer framework.

396 To test whether such leaching phenomenon could negatively affect the stability of
397 the FZsPS aerogel, photocatalytic experiments were repeated six times (Figure 7)
398 using the same FZsPS monolithic composite aerogel and without any regeneration
399 step of the photocatalyst.

400 The obtained results did not evidence any significant decrease in the lindane

401 photocatalytic degradation performance, demonstrating the stability and the
402 possibility of reusing the FZsPS aerogel. Furthermore, WAXD analysis was
403 performed on the FZsPS composite aerogel recovered from the photoreactor after the
404 sixth reuse cycle. The obtained result is shown in Figure S2 of Supplementary
405 Material. No substantial difference with respect to the WAXD spectrum of FZsPS
406 before its use in the photocatalytic degradation of lindane was observed.

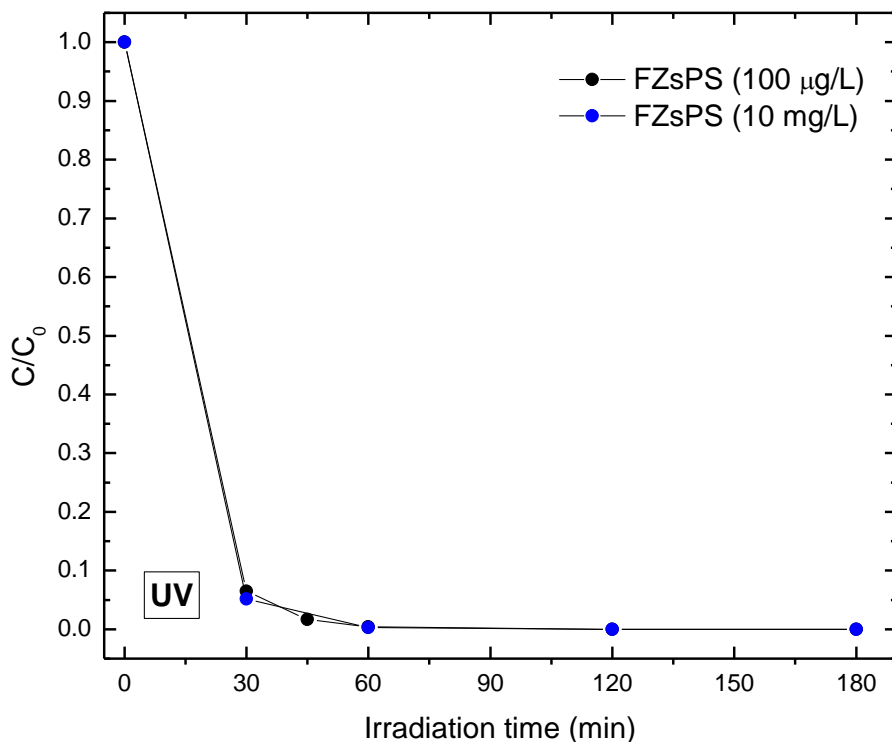


407

408 **Figure 7:** Lindane degradation after 180 min of UV irradiation using FZsPS aerogel
409 in six reuse cycles.

410

411 An additional photocatalytic test was carried out with the FZsPS monolithic
412 composite at a higher concentration of the pollutant (10 mg/L). The results were
413 comparable to the test at a concentration of 100 $\mu\text{g/L}$ (Figure 8).



414

415 **Figure 8:** Photocatalytic degradation at two different lindane initial concentrations
 416 (100 µg/L and 10 mg/L) by FZsPS under UV light irradiation.
 417

418 For both initial lindane concentrations, a TOC removal of about 94% after 180
 419 minutes of UV irradiation was achieved, underlining the strong ability of FZsPS in
 420 the mineralization of lindane. Considering the literature findings concerning the
 421 photoactivity of Fe⁰/ZnS in powder form [39], it is possible to argue that the holes
 422 generated in the ZnS valence band promote the formation of hydroxyl radicals,
 423 which further oxidize the organic intermediates (such as benzene and cyclohexene
 424 [86, 87]) generated from the cleavage of C-Cl bonds of lindane structure by Fe⁰
 425 supported on ZnS surface, leading to the almost complete TOC removal from
 426 aqueous solution.

427 The photocatalytic degradation efficiency of the FZsPS monolithic composite
 428 aerogel was compared with the performance of photocatalysts immobilized on
 429 different supports and tested in the lindane photodegradation (Table 1).

430

431 **Table 1:** Comparison with literature papers dealing with different immobilized
432 photocatalysts for lindane degradation.

Photoactive phase	Support	Light source	Lindane degradation (%)	Treatment time	Ref
TiO ₂	Hollow glass microspheres	UV	68	30 min	[27]
N-doped TiO ₂	Pyrex glass tube	UVA	~ 20	30 min	[30]
ZnO	Bio-nano hybrid system (<i>Candida</i> VITJzN04).	Sunlight	~ 70	24 h*	[31]
CeO ₂ -TiO ₂	Stainless steel substrates	Simulated solar light	~ 50	2 h*	[88]
Fe ⁰ /ZnS	sPS aerogel	UVA	~ 95	30	This paper

433 *no data at 30 min is available

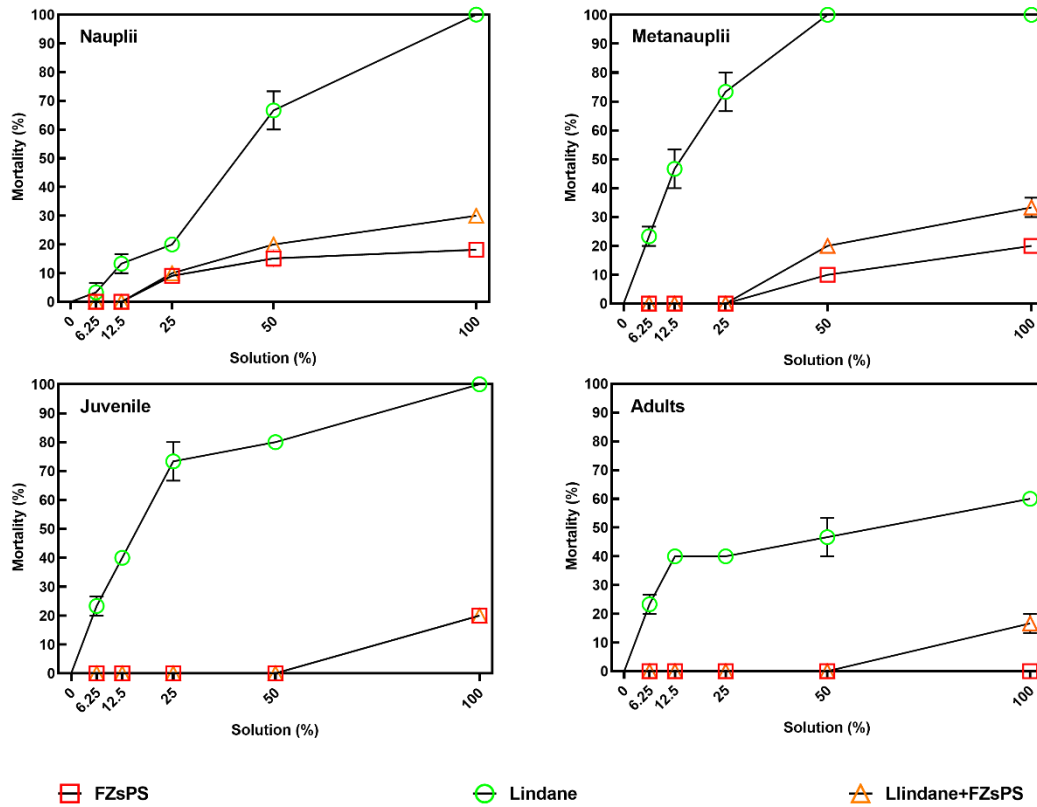
434

435 It is worth noting to underline that the literature about lindane degradation by
436 immobilized photocatalysts is very scarce. However, from the data reported in Table
437 1, it is possible to observe that the FZsPS monolithic composite aerogel used in our
438 study shows the best performance in lindane degradation since an efficiency of 95 %
439 is reached after only 30 min of irradiation time.

440

441 3.3. Toxicity results

442 As reported in Figure 9, after 48 h of exposure to different percentages of aqueous
443 solutions of FZsPS, an increase of nauplii, metanauplii, juvenile and adult mortality
444 (about 20%) was observed only at higher tested percentages, represented by 50% and
445 100%. These data were statistically significant with respect to the control and the
446 others used concentrations ($p < 0.0001$; see Table S1 of Supplementary Material).



447 □ FZsPS ○ Lindane △ Lindane+FZsPS

448 **Figure 9:** After 48 h, the percentage of dead nauplii, metanauplii, juvenile and adults

449 detected both in control (0%) and treated samples with 6.25%, 12.5%, 25%, 50%,

450 and 100% of FZsPS solution (distilled water+ FZsPS), Lindane solution (100 µg/L),

451 Lindane + FZsPS (Treated effluents after 180 min of UV irradiation). Data are

452 reported as a mean ± standard deviation.

453

454 Lindane solution (100 µg/L) caused mortality (about 10-20%) in all life stages

455 already at 6.25% that was statistically significant with respect to the control and all

456 other concentrations ($p < 0.0001$; Figure 9; Table S1). Except for adults, the mortality

457 in all life stages at 100% solution involved all organisms.

458 Considering nauplii and metanauplii exposure to treated effluent (Lindane + FZsPS)

459 (Figure 9), a low percentage of about 20% of dead was observed at 50%. At 100%, a

460 significant increase of toxicity (about 30%) compared to lower (0%, 6.25%, 12.5%,

461 and 25%; $p < 0.0001$) and higher concentrations (50%; $p < 0.01$) was detected.

462 Considering juvenile and adult exposure to the same condition, a low percentage of
463 about 20% of death was observed only at 100%. These data were statistically
464 significant compared to the control and all other concentrations ($p < 0.0001$; see also
465 Table S1).

466 Only the 50% and 100% of FZ and treated effluent by FZ (Lindane +FZ)
467 (Supplementary Figure S6), caused a significant increase of toxicity in four different
468 life stage (about 20% and 30%, respectively) with respect all tested concentrations (p
469 < 0.0001).

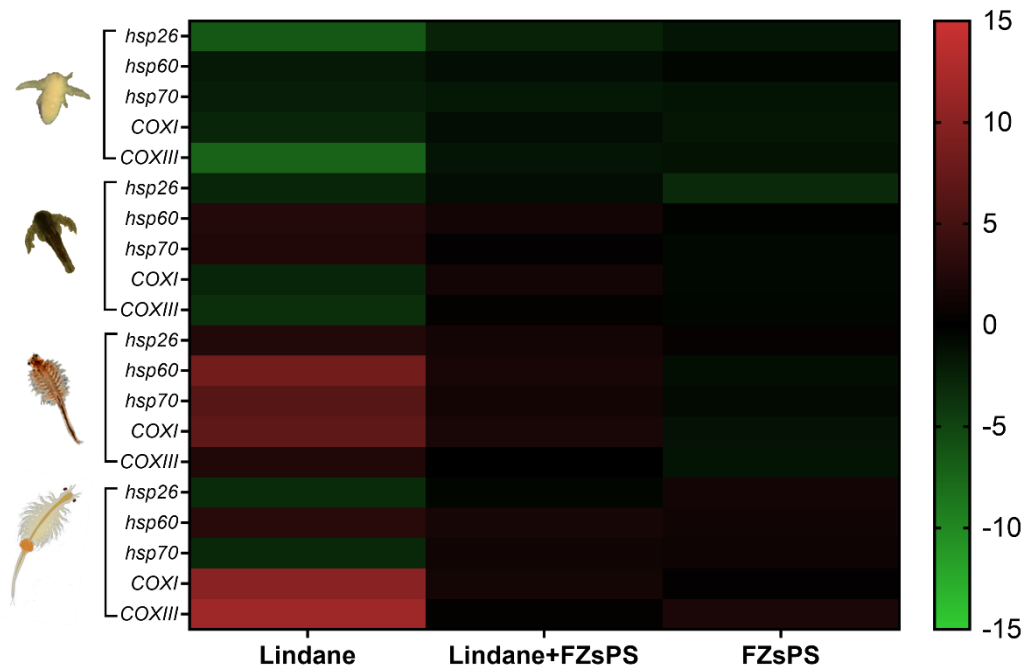
470 Taking into the consideration nauplii and metanauplii exposure to treated effluent by
471 Fe^0 (Lindane + Fe^0) at 25% (Figure S6), a significant percentage of mortality (about
472 20% and 35%, respectively) was observed respecting lower (0%, 6.25%, 12.5%; $p <$
473 0.0001). At 50% and 100%, a significant increase in toxicity (about 40-50%) was
474 shown respecting all tested concentrations ($p < 0.0001$). Considering juvenile and
475 adult exposure, only at 100%, Lindane + Fe^0 solution caused a significant increase in
476 mortality (about 40%) with respect to all tested concentrations ($p < 0.0001$).

477 Finally, Lindane + Fe^0 sPS and Lindane + ZsPS treated effluents (Figure S6) were
478 able to significantly impact the survival of *Artemia* only at 100% with respect to all
479 tested concentrations ($p < 0.0001$; see also Table S1).

480

481 *3.4. Effects of FZsPS on gene expression by real-time qPCR*

482 The expression levels of five genes (Albarano et al., 2022a), involved in stress
483 response, were followed by real-time qPCR after FZsPS treatment experiment
484 (Figure 10; see also Table S2 for the values).



485
 486 **Figure 10:** Heatmap showing the expression profiles and hierarchical clustering of
 487 five genes analyzed through real-time qPCR in nauplii, metanauplii, juvenile and
 488 adult treated with FZsPS solution (distilled water+ FZsPS), Lindane (100 µg/L),
 489 Lindane + FZsPS (Treated effluents after 180 min of UV irradiation). Color code:
 490 red, up-regulated genes with respect to the control; green, down-regulated genes with
 491 respect to the control; black, genes for which there was no variation in expression
 492 with respect to the control.

493 All analyzed genes were targeted in all life stages after lindane exposure with the
 494 exception of *hsp60*. Specifically, *hsp26* was down-regulated in nauplii, metanauplii
 495 and adult (6.40-fold 2.78-fold and 3.20-fold, respectively) and up-regulated in
 496 juvenile (2.46-fold; see Table S2); *hsp70* was down-regulated in nauplii and adult
 497 (2.19-fold and 2.87-fold, respectively) and up-regulated in metanauplii and juvenile
 498 (2.28-fold and 6.32-fold, respectively); *COXI* and *COXIII* were down-regulated in
 499 nauplii (2.77-fold and 7.28-fold, respectively) and metanauplii (2.73-fold and 3.50-
 500 fold, respectively) and up-regulated in juvenile (6.91-fold and 2.30-fold,

501 respectively) and adult (9.96-fold and 11.54-fold, respectively; Table S2); *hsp60* was
502 up-regulated in metanauplii, juvenile and adult (2.50-fold, 8.30-fold and 2.90-fold,
503 respectively; see Table S2).

504 Considering other treatments (Figure 10), *hsp60* was down-regulated (2.55-fold)
505 only in nauplii after the exposure to the treated effluent (lindane + FZsPS), and
506 *hsp26* was down-regulated (3.01-fold) only in metanauplii after the exposure to
507 FZsPS solution (distilled water + FZsPS) (Table S2).

508

509 **4. Conclusions**

510 In this work, a monolithic composite aerogel based on sPS and Fe⁰/ZnS (FZsPS) was
511 tested, for the first time, as a photocatalyst to achieve the complete lindane
512 degradation under UV light. Fe/ZnS powder is well dispersed throughout the
513 polymer matrix even if agglomerates are present and emerge from the surface, as
514 evident from FESEM images and EDS analysis. The mapping of the different
515 elements (Fe, Zn, S, O, C) showed diffuse Fe chain structures interpenetrated with
516 ZnS particles, although iron oxides, in accordance with TPR analyses, were also
517 detected.

518 The photodegradation performance of FZsPS was significantly higher than that
519 observed in the presence of Fe⁰/ZnS photocatalyst in powder form (FZ). In detail,
520 using the FZsPS monolithic composite aerogel, the almost complete lindane
521 degradation was achieved after only 30 min of irradiation time whereas the FZ
522 photocatalyst exhibited a lindane degradation of about 65% after the same irradiation
523 time. Moreover, a TOC removal of about 94% after 180 minutes of UV irradiation
524 was achieved, underlining the ability of FZsPS also in the lindane mineralization.
525 The enhanced photocatalytic activity observed in the presence of FZsPS aerogel is

526 due to the higher SSA of FZsPS (309 m²/g) with respect to FZ (44 m²/g) but also to
527 the concentration of lindane in the sPS matrix. Reusability studies performed on
528 FZsPS showed no significant decrease in the photocatalytic activity, demonstrating
529 the stability of the formulated monolithic composite aerogel. Moreover, the effluent
530 from the photocatalytic treatment based on FZsPs composite aerogel can be
531 considered at low risk of environmental impact since no significant toxic effects on
532 *Artemia franciscana* were evidenced. Therefore, based on the ecotoxicity results, the
533 strategy of dispersing the ZVI/ZnS catalyst in a highly porous polymeric matrix,
534 such as sPS aerogel, can be considered as a model for using otherwise harmful
535 catalysts in water remediation.

536

537 **Acknowledgements**

538 Authors thank Dr Marco Allione (Politecnico di Torino, Italy) for FESEM
539 measurements on Fe⁰/ZnS photocatalyst, Dr. Mariagrazia Napoli and Dr. Ivano
540 Immediata (University of Salerno, Italy) for the technical assistance in gas
541 chromatographic analysis. Authors also thank Dr. Patrizia Iannece (University of
542 Salerno, Italy) for the ICP-OES analysis of water recovered after the photocatalytic
543 treatment.

544

545 **References**

- 546 [1] L.R.E.D. RED, Docket Control Number OPP-2002-0202 Lindane Reregistration
547 Eligibility Decision (RED) Comments Submitted on Behalf of the Natural Resources
548 Defense Council By Gina M. Solomon, MD, MPH Senior Scientist, NRDC, (2002).
549 [2] H. Fu, X. Quan, Z. Liu, S. Chen, Photoinduced transformation of γ -HCH in the
550 presence of dissolved organic matter and enhanced photoreactive activity of humate-
551 coated α -Fe₂O₃, *Langmuir*, 20 (2004) 4867-4873.
552 [3] G. Marko, M. Snezana, B. Jelena, K. Marijana, R. Srdjan, T. Aleksandra, A.
553 Jasmina, Lindane and hexachlorobenzene sequestration and detoxification in
554 contaminated sediment amended with carbon-rich sorbents, *Chemosphere*, (2019).

- 555 [4] W.H. Organization, Lindane (gamma-HCH: health and safety guide, (1991).
- 556 [5] J. Vijgen, The Legacy of Lindane HCH Isomer Production: A Global Overview
- 557 of Residue Management, Formulation and Disposal: Main Report. Annexes,
- 558 International HCH & Pesticides Association, 2006.
- 559 [6] M. Vega, D. Romano, E. Uotila, Lindane (Persistent Organic Pollutant) in the
- 560 EU, Best Practices of De-Contamination Exchanged, (2016).
- 561 [7] W.H. Organization, Pesticide Residues in Food-2003: Evaluations, Food &
- 562 Agriculture Org., 2004.
- 563 [8] J.C. Hansen, L.-O. Reiersen, S. Wilson, Arctic Monitoring and Assessment
- 564 Programme (AMAP); strategy and results with focus on the human health
- 565 assessment under the second phase of AMAP, 1998–2003, in, Taylor & Francis,
- 566 2002.
- 567 [9] M. Gmurek, M. Olak-Kucharczyk, S. Ledakowicz, Photochemical decomposition
- 568 of endocrine disrupting compounds—A review, Chemical Engineering Journal, 310
- 569 (2017) 437-456.
- 570 [10] J.O. Babayemi, Overview of levels of organochlorine pesticides in surface water
- 571 and food items in Nigeria, Journal of Environment and Earth Science, 6 (2016) 77-
- 572 86.
- 573 [11] V. Nagpal, A.D. Bokare, R.C. Chikate, C.V. Rode, K.M. Paknikar, Reductive
- 574 dechlorination of γ -hexachlorocyclohexane using Fe–Pd bimetallic nanoparticles,
- 575 Journal of hazardous materials, 175 (2010) 680-687.
- 576 [12] J. Vijgen, P. Abhilash, Y.F. Li, R. Lal, M. Forter, J. Torres, N. Singh, M.
- 577 Yunus, C. Tian, A. Schäffer, Hexachlorocyclohexane (HCH) as new Stockholm
- 578 Convention POPs—a global perspective on the management of Lindane and its
- 579 waste isomers, Environmental Science and Pollution Research, 18 (2011) 152-162.
- 580 [13] B.R. Shah, U.D. Patel, Mechanistic aspects of photocatalytic degradation of
- 581 Lindane by TiO₂ in the presence of Oxalic acid and EDTA as hole-scavengers,
- 582 Journal of Environmental Chemical Engineering, 9 (2021) 105458.
- 583 [14] S. Waclawek, D. Silvestri, P. Hrabák, V.V. Padil, R. Torres-Mendieta, M.
- 584 Waclawek, M. Černík, D.D. Dionysiou, Chemical oxidation and reduction of
- 585 hexachlorocyclohexanes: A review, Water research, 162 (2019) 302-319.
- 586 [15] S. Deng, N. Feng, S. Kang, J. Zhu, B. Yu, J. Chen, X. Xie, Mechanochemical
- 587 formation of chlorinated phenoxy radicals and their roles in the remediation of
- 588 hexachlorobenzene contaminated soil, Journal of Hazardous Materials, 352 (2018)
- 589 172-181.
- 590 [16] I. San Román, A. Galdames, M. Alonso, L. Bartolomé, J. Vilas, R. Alonso,
- 591 Effect of coating on the environmental applications of zero valent iron nanoparticles:
- 592 the lindane case, Science of the Total Environment, 565 (2016) 795-803.
- 593 [17] X. Zhu, Y. Li, B. Han, Q. Feng, L. Zhou, Degradation Characteristics of Carbon
- 594 Tetrachloride by Granular Sponge Zero Valent Iron, International Journal of
- 595 Environmental Research and Public Health, 18 (2021) 12578.
- 596 [18] S. Bajaj, S. Sagar, S. Khare, D.K. Singh, Biodegradation of γ -
- 597 hexachlorocyclohexane (lindane) by halophilic bacterium Chromohalobacter sp. LD2
- 598 isolated from HCH dumpsite, International Biodeterioration & Biodegradation, 122
- 599 (2017) 23-28.
- 600 [19] F.O. Kengara, U. Doerfler, G. Welzl, B. Ruth, J.C. Munch, R. Schroll,
- 601 Enhanced degradation of ¹⁴C-HCB in two tropical clay soils using multiple
- 602 anaerobic–aerobic cycles, Environmental pollution, 173 (2013) 168-175.

603 [20] J.F. Devlin, J. Klausen, R.P. Schwarzenbach, Kinetics of nitroaromatic
604 reduction on granular iron in recirculating batch experiments, *Environmental science*
605 & *technology*, 32 (1998) 1941-1947.

606 [21] H.-J. Lu, J.-K. Wang, S. Ferguson, T. Wang, Y. Bao, H.-x. Hao, Mechanism,
607 synthesis and modification of nano zerovalent iron in water treatment, *Nanoscale*, 8
608 (2016) 9962-9975.

609 [22] T. Pasinszki, M. Krebsz, Synthesis and application of zero-valent iron
610 nanoparticles in water treatment, environmental remediation, catalysis, and their
611 biological effects, *Nanomaterials*, 10 (2020) 917.

612 [23] W. Shen, X. Wang, F. Jia, Z. Tong, H. Sun, X. Wang, F. Song, Z. Ai, L. Zhang,
613 B. Chai, Amorphization enables highly efficient anaerobic thiamphenicol reduction
614 by zero-valent iron, *Applied Catalysis B: Environmental*, 264 (2020) 118550.

615 [24] W. Xu, Z. Li, S. Shi, J. Qi, S. Cai, Y. Yu, D.M. O'Carroll, F. He,
616 Carboxymethyl cellulose stabilized and sulfidated nanoscale zero-valent iron:
617 Characterization and trichloroethene dechlorination, *Applied Catalysis B:*
618 *Environmental*, 262 (2020) 118303.

619 [25] V. Vaiano, O. Sacco, M. Matarangolo, Photocatalytic degradation of
620 paracetamol under UV irradiation using TiO₂-graphite composites, *Catalysis Today*,
621 315 (2018) 230-236.

622 [26] S. Khan, C. Han, M. Sayed, M. Sohail, S. Jan, S. Sultana, H.M. Khan, D.D.
623 Dionysiou, Exhaustive photocatalytic lindane degradation by combined simulated
624 solar light-activated nanocrystalline TiO₂ and inorganic oxidants, *Catalysts*, 9 (2019)
625 425.

626 [27] A. Zaleska, J. Hupka, M. Wiergowski, M. Biziuk, Photocatalytic degradation of
627 lindane, p, p'-DDT and methoxychlor in an aqueous environment, *Journal of*
628 *photochemistry and photobiology A: chemistry*, 135 (2000) 213-220.

629 [28] H.J. Jung, R. Koutavarapu, S. Lee, J.H. Kim, H.C. Choi, M.Y. Choi, Enhanced
630 photocatalytic degradation of lindane using metal-semiconductor Zn@ ZnO and
631 ZnO/Ag nanostructures, *Journal of Environmental Sciences*, 74 (2018) 107-115.

632 [29] D.-K. Lee, I.-C. Cho, Characterization of TiO₂ thin film immobilized on glass
633 tube and its application to PCE photocatalytic destruction, *Microchemical journal*, 68
634 (2001) 215-223.

635 [30] J. Senthilnathan, L. Philip, Photocatalytic degradation of lindane under UV and
636 visible light using N-doped TiO₂, *Chemical engineering journal*, 161 (2010) 83-92.

637 [31] J.A. Salam, N. Das, Degradation of lindane by a novel embedded bio-nano
638 hybrid system in aqueous environment, *Applied microbiology and biotechnology*, 99
639 (2015) 2351-2360.

640 [32] T.S. Jamil, E.S. Mansor, R.A. Nasr, Degradation of Lindane using two
641 nanosized BiOXs and their heterojunction under visible light, *Desalination and*
642 *Water Treatment*, 57 (2016) 14750-14761.

643 [33] S. Khan, C. Han, H.M. Khan, D.L. Boccelli, M.N. Nadagouda, D.D. Dionysiou,
644 Efficient degradation of lindane by visible and simulated solar light-assisted S-
645 TiO₂/peroxymonosulfate process: kinetics and mechanistic investigations, *Molecular*
646 *Catalysis*, 428 (2017) 9-16.

647 [34] X. Wang, M. Hong, F. Zhang, Z. Zhuang, Y. Yu, Recyclable nanoscale zero
648 valent iron doped g-C₃N₄/MoS₂ for efficient photocatalysis of RhB and Cr (VI)
649 driven by visible light, *ACS Sustainable Chemistry & Engineering*, 4 (2016) 4055-
650 4063.

651 [35] X. Wang, D. Lizong, Well-dispersed zero-valent iron supported on Fe₃O₄/gC
652 3 N 4 composites via a facile approach with versatile photoredox catalysis, *Journal of*
653 *Nanoparticle Research*, 20 (2018) 1-15.

654 [36] C. Huang, W.-P. Hsieh, J.R. Pan, S.-M. Chang, Characteristic of an innovative
655 TiO₂/Fe₀ composite for treatment of azo dye, *Separation and Purification*
656 *Technology*, 58 (2007) 152-158.

657 [37] K. Kobwittaya, S. Sirivithayapakorn, Photocatalytic reduction of nitrate over
658 Fe-modified TiO₂, *APCBEE procedia*, 10 (2014) 321-325.

659 [38] Y. Liu, J. Wang, Reduction of nitrate by zero valent iron (ZVI)-based materials:
660 A review, *Science of the Total Environment*, 671 (2019) 388-403.

661 [39] O. Sacco, V. Vaiano, W. Navarra, C. Daniel, S. Pragliola, V. Venditto, Catalytic
662 system based on recyclable Fe₀ and ZnS semiconductor for UV-promoted
663 degradation of chlorinated organic compounds, *Separation and Purification*
664 *Technology*, 270 (2021) 118830.

665 [40] D. Friedmann, A General Overview of Heterogeneous Photocatalysis as a
666 Remediation Technology for Wastewaters Containing Pharmaceutical Compounds,
667 *Water*, 14 (2022) 3588.

668 [41] S.K. Loeb, P.J. Alvarez, J.A. Brame, E.L. Cates, W. Choi, J. Crittenden, D.D.
669 Dionysiou, Q. Li, G. Li-Puma, X. Quan, The technology horizon for photocatalytic
670 water treatment: sunrise or sunset?, in, *ACS Publications*, 2018.

671 [42] R. Ata, O. Sacco, V. Vaiano, L. Rizzo, G.Y. Tore, D. Sannino, Visible light
672 active N-doped TiO₂ immobilized on polystyrene as efficient system for wastewater
673 treatment, *Journal of Photochemistry and Photobiology A: Chemistry*, 348 (2017)
674 255-262.

675 [43] V. Vaiano, G. Sarno, O. Sacco, D. Sannino, Degradation of terephthalic acid in
676 a photocatalytic system able to work also at high pressure, *Chemical Engineering*
677 *Journal*, 312 (2017) 10-19.

678 [44] I. Zammit, R.B. Marano, V. Vaiano, E. Cytryn, L. Rizzo, Changes in antibiotic
679 resistance gene levels in soil after irrigation with treated wastewater: a comparison
680 between heterogeneous photocatalysis and chlorination, *Environmental Science &*
681 *Technology*, 54 (2020) 7677-7686.

682 [45] O. Sacco, M. Matarangolo, V. Vaiano, G. Libralato, M. Guida, G. Lofrano, M.
683 Carotenuto, Crystal violet and toxicity removal by adsorption and simultaneous
684 photocatalysis in a continuous flow micro-reactor, *Science of the total environment*,
685 644 (2018) 430-438.

686 [46] D. Minetto, G. Libralato, A.V. Ghirardini, Ecotoxicity of engineered TiO₂
687 nanoparticles to saltwater organisms: an overview, *Environment international*, 66
688 (2014) 18-27.

689 [47] B.M. Rotoli, P. Guidi, B. Bonelli, M. Bernardeschi, M.G. Bianchi, S. Esposito,
690 G. Frenzilli, P. Lucchesi, M. Nigro, V. Scarcelli, Imogolite: an aluminosilicate
691 nanotube endowed with low cytotoxicity and genotoxicity, *Chemical Research in*
692 *Toxicology*, 27 (2014) 1142-1154.

693 [48] V. Addorisio, D. Pirozzi, S. Esposito, F. Sannino, Decontamination of waters
694 polluted with simazine by sorption on mesoporous metal oxides, *Journal of*
695 *hazardous materials*, 196 (2011) 242-247.

696 [49] F. Tescione, O. Tammara, A. Bifulco, G. Del Monaco, S. Esposito, M. Pansini,
697 B. Silvestri, A. Costantini, Silica meets tannic acid: Designing green nanoplatfoms
698 for environment preservation, *Molecules*, 27 (2022) 1944.

699 [50] T. McMurray, P. Dunlop, J. Byrne, The photocatalytic degradation of atrazine
700 on nanoparticulate TiO₂ films, *Journal of Photochemistry and Photobiology A:*
701 *Chemistry*, 182 (2006) 43-51.

702 [51] M. Karavasilis, M. Theodoropoulou, C. Tsakiroglou, Degradation of the
703 persistent organic pollutant-lindane in fixed-bed photoreactor packed with
704 immobilized Zinc Oxide and Iron oxide-doped Zinc Oxide photocatalysts, in: *IOP*
705 *Conference Series: Earth and Environmental Science*, IOP Publishing, 2022, pp.
706 012082.

707 [52] V. Venditto, M. Pellegrino, R. Califano, G. Guerra, C. Daniel, L. Ambrosio, A.
708 Borriello, Monolithic polymeric aerogels with VOCs sorbent nanoporous crystalline
709 and water sorbent amorphous phases, *ACS applied materials & interfaces*, 7 (2015)
710 1318-1326.

711 [53] C. Daniel, M. Pellegrino, V. Venditto, S. Aurucci, G. Guerra, Nanoporous-
712 crystalline poly (2, 6-dimethyl-1, 4-phenylene) oxide (PPO) aerogels, *Polymer*, 105
713 (2016) 96-103.

714 [54] G. Balasubramanian, D.D. Dionysiou, M.T. Suidan, I. Baudin, J.-M. Lané,
715 Evaluating the activities of immobilized TiO₂ powder films for the photocatalytic
716 degradation of organic contaminants in water, *Applied Catalysis B: Environmental*,
717 47 (2004) 73-84.

718 [55] S. Suárez, J.M. Coronado, R. Portela, J.C. Martín, M. Yates, P. Avila, B.
719 Sánchez, On the preparation of TiO₂- sepiolite hybrid materials for the
720 photocatalytic degradation of TCE: influence of TiO₂ distribution in the
721 mineralization, *Environmental science & technology*, 42 (2008) 5892-5896.

722 [56] O. Sacco, V. Vaiano, M. Matarangolo, ZnO supported on zeolite pellets as
723 efficient catalytic system for the removal of caffeine by adsorption and
724 photocatalysis, *Separation and Purification Technology*, 193 (2018) 303-310.

725 [57] S. Singh, H. Mahalingam, P.K. Singh, Polymer-supported titanium dioxide
726 photocatalysts for environmental remediation: A review, *Applied Catalysis A:*
727 *General*, 462 (2013) 178-195.

728 [58] M.J. Silva, J. Gomes, P. Ferreira, R.C. Martins, An overview of polymer-
729 supported catalysts for wastewater treatment through light-driven processes, *Water*,
730 14 (2022) 825.

731 [59] W. Navarra, O. Sacco, C. Daniel, V. Venditto, V. Vaiano, D.A.L. Vignati, C.
732 Bojic, G. Libralato, G. Lofrano, M. Carotenuto, Photocatalytic degradation of
733 atrazine by an N-doped TiO₂/polymer composite: catalytic efficiency and toxicity
734 evaluation, *Journal of Environmental Chemical Engineering*, 10 (2022) 108167.

735 [60] S. Pragliola, R. De Vita, P. Longo, Aqueous emulsion polymerization of styrene
736 and substituted styrenes using titanocene compounds, *Polymer*, 54 (2013) 1583-
737 1587.

738 [61] C. Daniel, S. Longo, R. Ricciardi, E. Reverchon, G. Guerra, Monolithic
739 nanoporous crystalline aerogels, *Macromolecular rapid communications*, 34 (2013)
740 1194-1207.

741 [62] V. Vaiano, O. Sacco, D. Sannino, P. Ciambelli, S. Longo, V. Venditto, G.
742 Guerra, N-doped TiO₂/s-PS aerogels for photocatalytic degradation of organic dyes
743 in wastewater under visible light irradiation, *Journal of Chemical Technology &*
744 *Biotechnology*, 89 (2014) 1175-1181.

745 [63] A. Mancuso, V. Vaiano, P. Antico, O. Sacco, V. Venditto, Photoreactive
746 polymer composite for selective oxidation of benzene to phenol, *Catalysis Today*,
747 413 (2023) 113914.

748 [64] W. Navarra, O. Sacco, V. Venditto, V. Vaiano, Selective Photocatalytic
749 Reduction of Nitrobenzene to Aniline Using TiO₂ Embedded in sPS Aerogel,
750 *Polymers*, 15 (2023) 359.

751 [65] O. Sacco, V. Vaiano, C. Daniel, W. Navarra, V. Venditto, Highly robust and
752 selective system for water pollutants removal: How to transform a traditional
753 photocatalyst into a highly robust and selective system for water pollutants removal,
754 *Nanomaterials*, 9 (2019) 1509.

755 [66] O. Sacco, V. Vaiano, C. Daniel, W. Navarra, V. Venditto, Removal of phenol in
756 aqueous media by N-doped TiO₂ based photocatalytic aerogels, *Materials Science in*
757 *Semiconductor Processing*, 80 (2018) 104-110.

758 [67] V. Vaiano, O. Sacco, D. Sannino, Enhanced photocatalytic degradation of
759 organic pollutants in wastewater using photocatalysts coupled with luminescent
760 materials, *Chemical Engineering Transactions*, 60 (2017) 211-216.

761 [68] O. Sacco, V. Vaiano, D. Sannino, R. Picca, N. Cioffi, Ag modified ZnS for
762 photocatalytic water pollutants degradation: Influence of metal loading and
763 preparation method, *Journal of colloid and interface science*, 537 (2019) 671-681.

764 [69] G. Bagnasco, C. Cammarano, M. Turco, S. Esposito, A. Aronne, P. Pernice,
765 TPR/TPO characterization of cobalt-silicon mixed oxide nanocomposites prepared
766 by sol-gel, *Thermochimica acta*, 471 (2008) 51-54.

767 [70] L. Albarano, S. Serafini, M. Toscanesi, M. Trifuoggi, V. Zupo, M. Costantini,
768 D.A. Vignati, M. Guida, G. Libralato, Genotoxicity Set Up in *Artemia franciscana*
769 *Nauplii* and Adults Exposed to Phenanthrene, Naphthalene, Fluoranthene, and Benzo
770 (k) fluoranthene, *Water*, 14 (2022) 1594.

771 [71] L. Albarano, M. Toscanesi, M. Trifuoggi, M. Guida, G. Lofrano, G. Libralato,
772 In situ microcosm remediation of polyaromatic hydrocarbons: influence and
773 effectiveness of Nano-Zero Valent Iron and activated carbon, *Environmental Science*
774 *and Pollution Research*, 30 (2023) 3235-3251.

775 [72] M. Pansini, G. Dell'Agli, A. Marocco, P.A. Netti, E. Battista, V. Lettera, P.
776 Vergara, P. Allia, B. Bonelli, P. Tiberto, Preparation and characterization of
777 magnetic and porous metal-ceramic nanocomposites from a zeolite precursor and
778 their application for DNA separation, *Journal of Biomedical Nanotechnology*, 13
779 (2017) 337-348.

780 [73] E. Dutková, P. Baláž, P. Pourghahramani, S. Velumani, J. Ascencio, N.
781 Kostova, Properties of mechanochemically synthesized ZnS nanoparticles, *Journal of*
782 *Nanoscience and Nanotechnology*, 9 (2009) 6600-6605.

783 [74] W. Jozwiak, E. Kaczmarek, T. Maniecki, W. Ignaczak, W. Maniukiewicz,
784 Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres,
785 *Applied Catalysis A: General*, 326 (2007) 17-27.

786 [75] D. Denzler, M. Olschewski, K. Sattler, Luminescence studies of localized gap
787 states in colloidal ZnS nanocrystals, *Journal of applied physics*, 84 (1998) 2841-
788 2845.

789 [76] K.N. Devi, T.S. Chanu, L.A. Chanu, W.J. Singh, K.J. Singh, Operational
790 parameters and major active species responsible for the photodegradation of
791 malachite green dye by ZnO/ZnS core-shell nanocomposite photocatalyst, *Journal of*
792 *Materials Research*, 38 (2023) 473-483.

793 [77] S. Horoz, O. Sahin, Investigations of structural, optical, and photovoltaic
794 properties of Fe-alloyed ZnS quantum dots, *Journal of Materials Science: Materials*
795 *in Electronics*, 28 (2017) 9559-9565.

- 796 [78] S. Kumar, N. Verma, Structural, optical and magnetic investigations on Fe-
797 doped ZnS nanoparticles, *Journal of Materials Science: Materials in Electronics*, 26
798 (2015) 2754-2759.
- 799 [79] W. He, H. Jia, J. Cai, X. Han, Z. Zheng, W.G. Wamer, J.-J. Yin, Production of
800 reactive oxygen species and electrons from photoexcited ZnO and ZnS nanoparticles:
801 a comparative study for unraveling their distinct photocatalytic activities, *The*
802 *Journal of Physical Chemistry C*, 120 (2016) 3187-3195.
- 803 [80] L. Isac, A. Enesca, Recent Developments in ZnS-Based Nanostructures
804 Photocatalysts for Wastewater Treatment, *International Journal of Molecular*
805 *Sciences*, 23 (2022) 15668.
- 806 [81] L.O. Conte, S. Cotillas, A. Sánchez-Yepes, D. Lorenzo, A. Santos, LED visible
807 light assisted photochemical oxidation of HCHs in aqueous phases polluted with
808 DNAPL, *Process Safety and Environmental Protection*, 168 (2022) 434-442.
- 809 [82] S. Khan, X. He, J.A. Khan, H.M. Khan, D.L. Boccelli, D.D. Dionysiou, Kinetics
810 and mechanism of sulfate radical-and hydroxyl radical-induced degradation of highly
811 chlorinated pesticide lindane in UV/peroxymonosulfate system, *Chemical*
812 *engineering journal*, 318 (2017) 135-142.
- 813 [83] B. Gunawardana, N. Singhal, P. Swedlund, Degradation of chlorinated phenols
814 by zero valent iron and bimetallics of iron: a review, *Environmental Engineering*
815 *Research*, 16 (2011) 187-203.
- 816 [84] C. Daniel, D. Sannino, G. Guerra, Syndiotactic polystyrene aerogels: adsorption
817 in amorphous pores and absorption in crystalline nanocavities, *Chemistry of*
818 *Materials*, 20 (2008) 577-582.
- 819 [85] A. Mancuso, O. Sacco, V. Venditto, W. Navarra, P. Antico, C. Daniel, V.
820 Vaiano, Selective Absorption of Aromatic Compounds by Syndiotactic Polystyrene
821 Aerogels, in: *Macromolecular Symposia*, Wiley Online Library, 2023, pp. 2200062.
- 822 [86] C. Chang, F. Lian, L. Zhu, Simultaneous adsorption and degradation of γ -HCH
823 by nZVI/Cu bimetallic nanoparticles with activated carbon support, *Environmental*
824 *pollution*, 159 (2011) 2507-2514.
- 825 [87] Z. Wang, W. Huang, Dechlorination of γ -hexachlorocyclohexane by zero-valent
826 metallic iron, *Journal of Hazardous Materials*, 166 (2009) 992-997.
- 827 [88] N. Radić, B. Grbić, S. Stojadinović, M. Ilić, O. Došen, P. Stefanov, TiO₂-CeO₂
828 composite coatings for photocatalytic degradation of chloropesticide and organic
829 dye, *Journal of Materials Science: Materials in Electronics*, 33 (2022) 5073-5086.

830
831

832