

3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

**New nanoadsorbent based on magnetic iron oxide containing
1,4,7,10-tetraazacyclododecane in outer chain ($\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$) for
adsorption and removal of selected heavy metal ions Cd^{2+} , Pb^{2+} , Cu^{2+}**

Amanda Kulpa-Koterwa^a, Jacek Ryl^b, Karolina Górnicka^c, Paweł Niedziałkowski^{a,*}

^a Department of Analytical Chemistry, Faculty of Chemistry, University of Gdansk, Wita Stwosza 63, 80-308 Gdańsk, Poland

^b Division of Electrochemistry and Surface Physical Chemistry, Institute of Nanotechnology and Materials Engineering and Advanced Materials Center, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

^c Faculty of Applied Physics and Mathematics, Advanced Materials Center, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland

*corresponding author: Paweł Niedziałkowski
e-mail address: pawel.niedzialkowski@ug.edu.pl

18 **Abstract**

19 Magnetic Fe₃O₄@SiO₂-cyclen nanoparticles were prepared and used as adsorbent for Cd²⁺,
20 Pb²⁺ and Cu²⁺ from aqueous solution removal process controlled with differential pulse anodic
21 stripping voltammetry (DPASV) and hanging mercury drop electrode (HDME). Nanomaterial
22 was synthesised in three-step process co-precipitation of Fe₃O₄ core, coating with silane and N-
23 (3-(triethoxysilyl)propyl)-1,4,7,10-tetraazacyclododecane-1-carboxamide silane
24 functionalisation. The effectiveness of each step of the synthesis was confirmed using scanning
25 electron microscopy (SEM), high-resolution X-ray photoelectron spectroscopy (XPS), powder
26 X-ray diffraction (pXRD) and fourier-transform infrared spectroscopy (FT-IR) techniques. The
27 Fe₃O₄@SiO₂-cyclen nanoparticles were employed for Cd²⁺, Pb²⁺ and Cu²⁺ ions elimination
28 from individual and mixed solutions by carrying out titration with a suspension of
29 nanocomposites. The binding level for all ions both in the individual solutions and in the
30 mixture was very similar at high levels. For Cd²⁺ and Cu²⁺ ions sorption efficiency level was
31 from 83% to 89%, while for Pb²⁺ ions it was slightly lower at the level over 73%. In all cases,
32 the equilibrium adsorption capacity parameter was over 1 mg/g and reached definitely higher
33 values for individual ions solutions. The research results revealed that Fe₃O₄@SiO₂- cyclen
34 nanoparticles can be a promising adsorbent for magnetic heavy metal ions water treatment
35 agents.

36

37 **Keywords:** functionalised Fe₃O₄ nanoparticles, stripping voltammetry, Cd²⁺, Pb²⁺ and Cu²⁺
38 ions binding, nanoadsorbent, 1,4,7,10-tetraazacyclododecane, heavy metal ions removal

39 **Highlights**

- 40 • Fe₃O₄@SiO₂- cyclen nanoparticles was utilised for the removal of Cd²⁺, Pb²⁺, Cu²⁺.
- 41 • The SEM, XPS, pXRD and FT-IR characterisation of nanoparticles was performed.
- 42 • Ions binding kinetics and efficiency were investigated with DPASV and HDME.
- 43 • Sorption efficiency was calculated and reached a maximum level of nearly 90%.
- 44 • The effectiveness of ions magnetic separation from the aqueous solution was confirmed.

45



46 1. Introduction

47 Over the last few decades, a significant increase has been observed in environmental
48 pollution with heavy metal ions, which is a problem all over the world [1]. The increasing heavy
49 metal ions concentration is generated mainly by technological and operational activities,
50 production processes such as refining, power plants and combined heat and power plants, steel
51 mills, coal and waste combustion, the chemical industry, the use of fertilisers and pesticides,
52 and transport [2]. The presence of heavy metal ions in the environment constitutes a threat due
53 to the possibility of their migration along the rungs of the trophic chain from soil, air, surface
54 waters to plants, animals and in consequence to humans. Exposure to continuously increasing
55 heavy metal ions concentrations lowers the action of biological barriers, which has a negative
56 impact on human health due to their low biodegradability, bioaccumulation tendency, potential
57 carcinogenic effect and mutagenicity [3]. Due to the danger posed by heavy metal ions
58 environment contamination, the recycling of them from aquatic environments has become a
59 very important area of scientific research and industry.

60 Until now, many methods of metal ions remediation from the environment have been
61 used [4,5], particularly methods such as membrane filtration [6], osmosis [7], ion exchange [8],
62 extraction with ionic liquids [9], photocatalysts [10], clays/layered double hydroxides [11],
63 bioremediation [12], biomass and biosorption [13] phytoremediation [14], precipitation and
64 coagulation [15,16] or electrocoagulation [17]. The conventional wastewater treatment
65 technologies involving physical, chemical, and biological methods have their advantages but
66 also disadvantages such as high costs, complex working operation, secondary pollutants
67 production, low selectivity and many others [18]. To overcome these challenges, researchers
68 used adsorption process as an alternative due to its wide working potentials, low price,
69 simplicity in use, process efficiency, selectivity, capacity for material regeneration and
70 pollutants trace concentration removal [19,20]. A wide range of materials have found
71 application as heavy metal ions adsorbents e.g., chitosan and its functionalised forms [21],
72 aerogels and their derivatives [22], based on cellulose [23], metal organic frameworks [24],
73 carbon-based materials [25], polymers [26], dendrimers [27] and many others [28–31].
74 However, among many research groups, various nanoscale adsorbents became very popular
75 due to their high surface area, high mobility in solution, reactivity, good adsorption capacity
76 and in consequence efficiency [32]. A series of nanoparticles and their modification were
77 investigated as heavy metal adsorbents but, in recent years, a particular interest was attached to
78 nanoparticles with magnetic properties, especially magnetite Fe_3O_4 [33,34]. Magnetite

79 nanoparticles occupy a special importance due to the possibility of easy and quick isolation
80 with the use of an external magnetic field [35]. Furthermore, creating core-shell type structures
81 with silica $\text{Fe}_3\text{O}_4@\text{SiO}_2$ provides a good basis for further functionalisation thus for obtaining a
82 material with wide applicability and selectivity [36–38]. There are known plenty of
83 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ modified structures for heavy metal ions adsorption, however, the search for new
84 and selective composites is still topical [39–41]. So far, there is lack of knowledge about crown
85 ethers usage as surface nanocomposites modifiers. Qin et al. designed and synthesised silica gel
86 bound di(aminobenzene)-18-crown-6(SGN18) for zirconium and hafnium adsorption [42]. Aza-
87 crown ethers and derivatives in their heyday were widely used as complexation agents of metal
88 ions in wide range of applications [43,44]. One of the well-known and widely used agent as a
89 metal ions complexation was 1,4,7,10-tetraazacyclododecane [45–49].

90 In view of the fact that previously the authors used $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles
91 containing nitrogen atoms in the outer chain as heavy metal ion adsorbent [50,51], they now
92 decided to combine the excellent complexing properties of 1,4,7,10-tetraazacyclododecane and
93 the possibility of pollutants magnetic isolation. In this work, magnetic core-shell nanoparticles
94 functionalised with 1,4,7,10-tetraazacyclododecane $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen were designed,
95 synthesised and used as heavy metal Cd^{2+} , Pb^{2+} , and Cd^{2+} ions adsorbent for the first time. The
96 newly obtained nanomaterial was characterised at every stage of synthesis using SEM, FT-IR,
97 pXRD and (XPS) methods. Furthermore, the ions binding kinetics studies was performed and
98 the binding capacity of nanoparticles was investigated using the differential pulse anodic
99 stripping voltammetry (DPASV) method coupled with hanging mercury drop electrode (HDM)
100 electrode. It is worth mentioning that the application of electrochemical detection skips
101 conventional techniques' limitations in heavy metal detection and offers the same sensitivity
102 with a lower cost, less complex operational procedures and fast on-site detection [52].
103

104 2. Experimental

105 2.1. Reagents

106 All analytical grade reagents were purchased from the indicated suppliers and used
107 without further purification. All inorganic salts – ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$),
108 ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), potassium chloride KCl (99.9%), cadmium nitrate
109 tetrahydrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%), lead nitrate $\text{Pb}(\text{NO}_3)_2$, and copper nitrate trihydrate
110 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9%) – were purchased from POCh (Poland). The organic solvents,
111 ammonia (25%), tetraethylorthosilicate (98%) (TEOS), triethoxy(3-isocyanatopropyl)silane

112 were purchased from Sigma-Aldrich (Poland). 1,4,7,10-tetraazacyclododecane was bought
113 from Strem Chemicals. Aqueous solutions were prepared using ultra-pure deionised water.

114 2.2. Synthesis of core-shell Fe₃O₄@SiO₂-cyclen nanostructures

115 New functionalised nanocomposites were obtained in the three-steps synthesis process.
116 In the first stage, a magnetic Fe₃O₄ core was received by the co-precipitation method. The
117 mixture of Fe²⁺(FeCl₂·4H₂O) and Fe³⁺ (FeCl₃·6H₂O) in aqueous solution using a three-neck
118 flask was stirred under nitrogen conditions. Then the 25% ammonia solution was dripped into
119 the reaction until the pH reached 11. Then the reaction mixture was heated to 60 °C for 3 hours
120 to complete precipitation of the magnetite. The obtained nanoparticles were separated by a
121 magnet and washed with distilled water several times.

122 The second stage of the synthesis involved the nanomagnetite coating with silica
123 forming Fe₃O₄@SiO₂, which was used for further modification. 16 g of Fe₃O₄ nanoparticles
124 obtained in the previous stage was dispersed in a mixture of 240 mL EtOH and 60 ml H₂O.
125 Then 3 mL of TEOS was added into reaction and the reaction was heated overnight to 50 °C.
126 After this time, the obtained nanoparticles were magnetically collected and washed with
127 distilled water several times.

128 In next stage of synthesis it was necessary to synthesise a modifier of the obtained
129 nanoparticles Fe₃O₄@SiO₂ due to the fact that the silane derivatives containing 1,4,7,10-
130 tetraazacyclododecane are not a commercially available.

131 The reaction of 1,4,7,10-tetraazacyclododecane with triethoxy(3-
132 isocyanatopropyl)silane was performed according to the modified procedure described
133 previously [53] to obtain N-(3-(triethoxysilyl)propyl)-1,4,7,10-tetraazacyclododecane-1-
134 carboxamide.

135 To the solution of 1,4,7,10-tetraazacyclododecane (4.179 g, 24,256 mmol) dissolved in
136 200 ml dichloromethane 6 mL of triethoxy(3-isocyanatopropyl)silane (24,256 mmol) was
137 dropwise added and the reaction was carried out overnight at 40 °C under a reflux condenser.
138 Then the solvent was evaporated under reduced pressure. The obtained colourless oil was dried
139 in a vacuum desiccator over P₂O₅ to obtain 2.159 g of colourless solid with a yield of 21.33%.

140 MALDI-TOF MS: m/z 419,29 [M+H]⁺, (MW = 420.31).

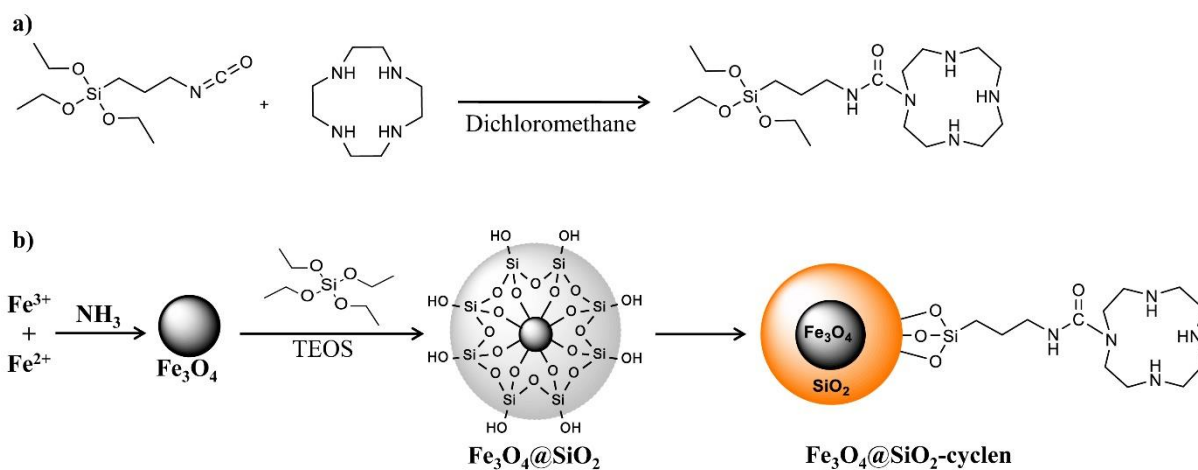
141 IR (KBr) (cm⁻¹): 3291, 2972, 2926, 2886, 2735, 1627, 1536, 1478, 1444, 1391, 1365, 1254,
142 1189, 1165, 1103, 1078, 955, 784.

143 ¹H-NMR (CDCl₃): 0.538-0.572 (t, 2H, (CH₃-CH₂)₃SiO-CH₂-CH₂-CH₂-HN-, J₁ = 7 Hz;
144 J₁ = 10,0 Hz; J₂=8,5 Hz); 1.135-1.165 (dt, 9H, (CH₃-CH₂)₃SiO-CH₂-CH₂-CH₂-HN-, J₁=1 Hz;

145 $J_1 = 1,5 \text{ Hz}$; $J_1 = J_2 = 7.0 \text{ Hz}$); 1.479-1.623 (m, 2H, $(\text{CH}_3\text{-CH}_2)_3\text{SiO-CH}_2\text{-CH}_2\text{-HN-}$);
 146 2.564-3.652 (m, 18H, $(\text{CH}_3\text{-CH}_2)_3\text{SiO-CH}_2\text{-CH}_2\text{-CH}_2\text{-HN- -H-CH}_2\text{-CH}_2\text{-N-}$); 3.734-3.754 (q,
 147 6H, $(\text{CH}_3\text{-CH}_2)_3\text{SiO-CH}_2\text{-CH}_2\text{-CH}_2\text{-HN-}$, $J_1=3 \text{ Hz}$; $J_1 = 4 \text{ Hz}$; $J_3 = J_4 = 3.0 \text{ Hz}$);

148
 149 The third stage consisted of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ modification to obtain $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$.
 150 1.593 g of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ was added to a solution of (3.324 g, 7,928 mmol) N-(3-
 151 (triethoxysilyl)propyl)-1,4,7,10-tetraazacyclododecane-1-carboxamide dissolved in 150 mL
 152 toluene. Then the reaction mixture was stirred for 12 h at 120 °C. After cooling to room
 153 temperature the obtained product was magnetically collected and washed several times with
 154 toluene and then with methanol. The resulting product was air-dried.

155



156
 157
 158 **Figure 1.** Scheme of a) nanoparticles modifier N-(3-(triethoxysilyl)propyl)-1,4,7,10-
 159 tetraazacyclododecane-1-carboxamide and b) functionalised $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$
 160 nanocomposite synthesis.

161 **2.3. The Cd^{2+} , Pb^{2+} and Cu^{2+} ions removal experiments from aqueous solutions by**
 162 **$\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$ binding**

163 The removal experiments of Cd^{2+} , Pb^{2+} and Cu^{2+} ions from aqueous solutions were
 164 performed by titration with $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$ nanoparticles. The ions-binding abilities of
 165 $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$ were studied in the solutions containing both individual ion or the mixture
 166 of Cd^{2+} , Pb^{2+} and Cu^{2+} ions in concentration level $4.5 \cdot 10^{-6} \text{ M}$. Before starting (DPASV)
 167 measurement a 0.25 mg of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-cyclen}$ nanoparticles was added into ion solution at
 168 each titration step and then mixed for 20 minutes All measurements were performed in 0.5 M
 169 KCl pH 6.00.

170 2.4. Methods

171 Fourier Transform Infrared Spectroscopy (FT-IR) spectra were obtained were recorded
172 on a Perkin Elmer Spectrum™ 3 FT-IR spectrometer with the KBr pellet technique.

173 MalDI-ToF mass spectra was performed on autoflex maX Bruker using α -cyano-4-
174 hydroxycinnamic acid (CCA) as a matrix.

175 ^1H NMR spectra were recorded in CDCl_3 on a Bruker Advance III 500 MHz, where
176 tetramethylsilane (TMS) was used as the internal standard. The chemical shifts are reported in
177 ppm, while the signal patterns are given as follows: triplet (t), doublet of triplets (dt), quartet
178 (q) and multiplet (m).

179 The scanning electron microscopy (SEM) images were captured with an FEI Quanta
180 250 FEG (ThermoFisher Scientific) microscope, equipped with a Schottky field emission gun.
181 The microscope was operating at 20 kV accelerating voltage in high vacuum mode.

182 High-resolution X-ray Photoelectron Spectroscopy (XPS) analysis was carried out using
183 Escalab 250Xi multispectroscopy (ThermoFisher Scientific). The spectroscope is equipped
184 with an $\text{AlK}\alpha$ x-ray source; the pass energy through the hemispherical analyser was 20 eV. The
185 measurement was assisted with low-energy electron and low-energy Ar^+ ion bombardment for
186 charge compensation. The measurements were carried out in C 1s, Fe 2p, Si 2p and N 1s core-
187 level binding energy range, where the adventitious C 1s spectra (284.6 eV) was used for final
188 peak calibration. Peak deconvolution was performed using Avantage v5.9921 (ThermoFisher
189 Scientific).

190 The crystalline phases and crystallite size were determined by room-temperature
191 powder x-ray diffraction (pXRD). The pXRD patterns were collected on D2 Phaser (Bruker)
192 diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) with a scanning angle $2\theta = 5\text{--}90^\circ$ and a
193 step size 0.01° . LeBail refinement of the pXRD pattern was performed to determine the lattice
194 parameters, using the DIFFRAC.SUITE TOPAS.

195 All differential pulse anodic stripping voltammetry (DPASV) measurements were
196 performed using an Autolab potentiostat/galvanostat (PGSTAT-128N, Metrohm), equipped
197 with NOVA 2.1.4 software. Three electrode Teflon electrochemical cell was used in all
198 experiments to avoid metal ions sorption on the glass surface. A Static Drop Mercury Electrode
199 (SDME) 663 VA Stand Metrohm was used as a working electrode. The reference electrode was
200 calomel electrode $\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{KCl}_{(\text{saturated})}$ and platinum wire (Pt) were used as the counter
201 electrode.

202 The detection of Cd^{2+} , Pb^{2+} , and Cd^{2+} by DPASV method was performed using the
 203 following conditions: deposition time 90 s, deposition potential -0.9 V, modulation amplitude
 204 0.05 V, modulation time 0.07 s, interval time 1.85 s, and step potential 0.003 V. The
 205 simultaneous Cd^{2+} , Pb^{2+} , and Cd^{2+} ions was performed in a potential range of -0.8 V to -0.04
 206 V, while the individual detection of ions was performed in potential range of -0.8 V to -0.5 V,
 207 -0.6 V to -0.3 V and -0.4 V to -0.04 V for Cd^{2+} , Pb^{2+} , Cu^{2+} detection, respectively.

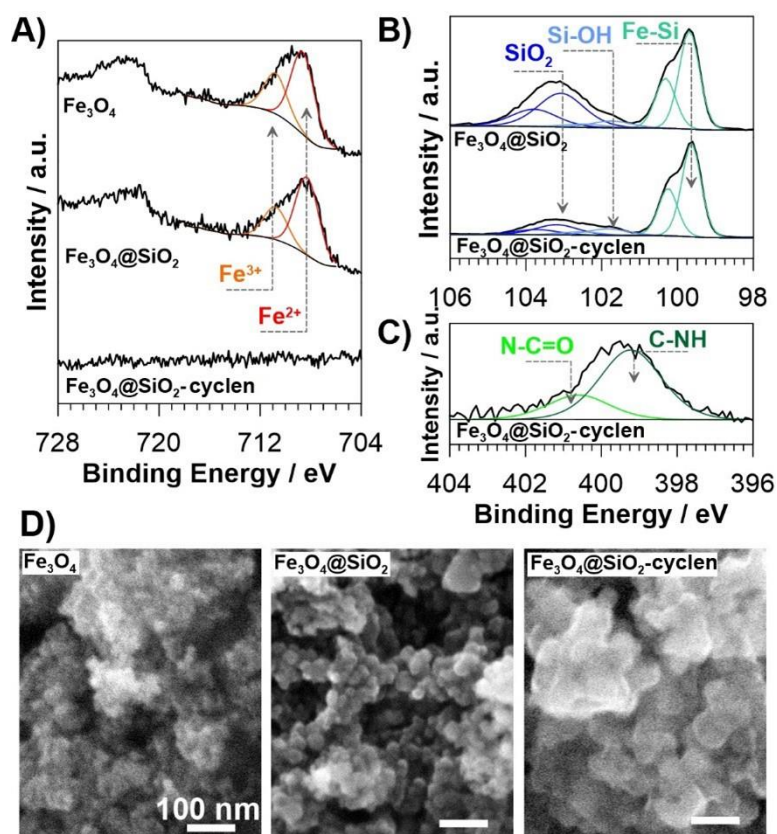
208 The metal ions solutions were prepared in the supporting electrolyte, which was
 209 potassium chloride KCl 0.5 M, pH 6.0 . The $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen nanoparticles suspension in
 210 supporting electrolyte solution before each measurement was freshly prepared by using
 211 ultrasonic bath for 30 minutes.

212

213 3. Results and discussion

214 3.1. XPS and SEM analysis

215 The high-resolution XPS analysis was performed to evaluate the efficiency of
 216 consecutive Fe_3O_4 nanoparticles functionalisation steps. The XPS spectra of each studied
 217 sample are presented in Fig. 2.



218

219 **Figure 2.** High-resolution XPS analysis of the studied Fe₃O₄, Fe₃O₄@SiO₂ and
 220 Fe₃O₄@SiO₂-cyclen samples in the binding energy range of: A) Fe 2p, B) Si 2p and C) N 1s
 221 peak with spectral deconvolution. D) SEM micrographs of studied materials. The scale bar
 222 marks 100 nm.

223 Figure 2A shows iron chemistry. The spectra obtained for the Fe₃O₄ sample may be
 224 deconvoluted into two Fe 2p_{3/2} features, peaking at 708.6 and 710.8 eV, which is characteristic
 225 of Fe²⁺ and Fe³⁺ in Fe₃O₄, respectively [54]. The calculated Fe²⁺:Fe³⁺ ratio is 2:1. Importantly,
 226 upon the formation of Fe₃O₄@SiO₂ core-shell structure, the peak position as well as the
 227 Fe²⁺:Fe³⁺ ratio remains unchanged, testifying to unchanged iron chemistry and structure within
 228 the nanoparticles. Nevertheless, the Fe 2p spectra intensity weakens upon the NP coverage with
 229 an SiO₂ shell, and eventually becomes indistinguishable for Fe₃O₄@SiO₂-cyclen, due to the
 230 limited depth of the XPS signal origin (approx. 3-5 nm).

231 The Si 2p spectra shows more complex character, with not less than three deconvolution
 232 peak doublets to be distinguished in Figure 2B. The characteristic component at 103.2 eV is
 233 attributed to SiO₂ while the second, smaller component negatively shifted at 0.9 eV may
 234 correspond to Si-OH bonds [55]. The third, notable component with Si 2p_{3/2} at 99.8 eV may
 235 have multiple origins, including Si-Fe bonds [56] or even Si-C bonds [57]. Adventitious carbon
 236 contribution in Fe₃O₄@SiO₂ NP powder is a relevant source for Si-C. After further modification
 237 with N-(3-(triethoxysilyl)propyl)-1,4,7,10-tetraazacyclododecane-1-carboxamide the share of
 238 99.8 eV feature rises by 35%. This modification is assisted with two time decreases of the SiO₂
 239 share, again due to the restricted depth of the XPS analysis. The detailed information are
 240 presented in **Table 1**.

241
 242 **Table 1.** The chemical composition (in at.%) using XPS analysis by peak deconvolution.

Sample	Fe 2p		Si 2p			N 1s	
	Fe ²⁺	Fe ³⁺	SiO ₂	Si-OH	Si-(Fe/C)	NH-C	NC=O
BE / eV	708.6	710.8	103.2	102.3	99.8	399.3	400.6
Fe ₃ O ₄	67.1	32.9	--	--	--	--	--
Fe ₃ O ₄ @SiO ₂	1.3	0.6	40.2	6.9	50.0	--	--
Fe ₃ O ₄ @SiO ₂ -cyclen	--	--	16.4	9.7	67.4	4.8	1.7

243

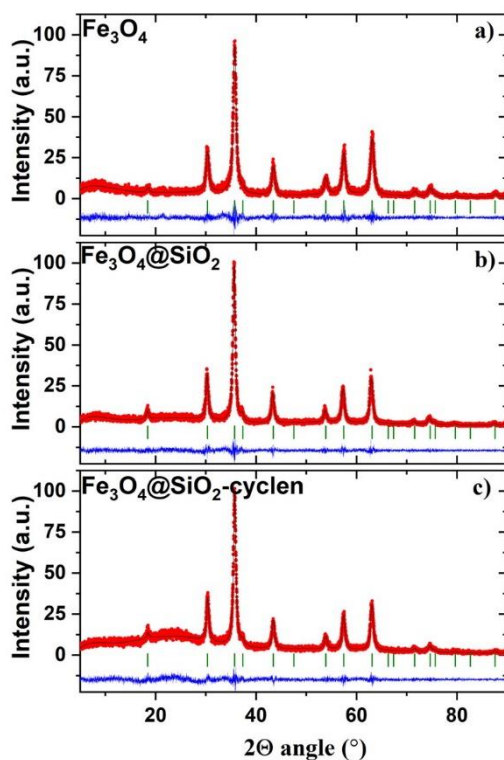
244 While the N-(3-(triethoxysilyl)propyl)-1,4,7,10-tetraazacyclododecane-1-carboxamide
245 compounds do not introduce C 1s features that can be easily differentiated from the surface-
246 adsorbed adventitious carbon under air exposure, the successful Fe₃O₄@SiO₂-cyclen synthesis
247 may be confirmed tracking N 1s spectral shape. As seen in Figure 2C this peak was
248 deconvoluted using two separate components. The first, and more notable, at 399.3 eV is
249 characteristic of NH-C bonds [58], while the latter, at 400.6 eV, was assigned to NC=O [59].

250 The morphology of each studied nanomaterial was revealed by SEM micrographs as
251 seen in Figure 2D. The size of the Fe₃O₄ nanoparticles is below 20 nm, thus making it
252 impossible for accurate estimation. Such small particle size is reported as sufficient to achieve
253 superparamagnetism in Fe₃O₄ NPs [60]. Further encapsulation in SiO₂ by TEOS allows for full
254 NP contours to be recognised and increasing the average size to approx. 34 ± 5 nm. This result
255 suggests the SiO₂ thickness to exceed 5 nm, testifying for nearly the entire removal of the high
256 resolution Fe 2p signal. The final functionalisation notably enlarges the Fe₃O₄@SiO₂-cyclen
257 dimensions, which now reach 50 to as much as 100 nm. The less regular size introduced by
258 Sil- Prop- cyclen is the probable explanation behind a significant share of Si still to be
259 recognised by XPS.

260

261 **3.2. pXRD analysis**

262 The pXRD analysis was used to investigate the crystallinity nature, and size of crystallites of
263 bare Fe₃O₄ nanoparticles and after each functionalisation steps. The XRD patterns of a) bare
264 Fe₃O₄, b) silica-coated Fe₃O₄@SiO₂, and c) functionalised Fe₃O₄@SiO₂-cyclen nanoparticles
265 together with the LeBail refinement (solid red line) are presented in Figure 3. A difference
266 plot (between experimental and fitted data) and the Bragg positions are also shown in Figure
267 3.



268

269 **Figure 3.** Powder x-ray diffraction pattern (pXRD) (red points) together with the LeBail
 270 refinement profile (solid black line) for a) bare Fe_3O_4 , b) silica coated $\text{Fe}_3\text{O}_4@SiO_2$ and c)
 271 functionalized $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen. The green vertical bars indicate the expected Bragg peak
 272 positions for Fe_3O_4 (JCPDS card PDF 00-065-0731).

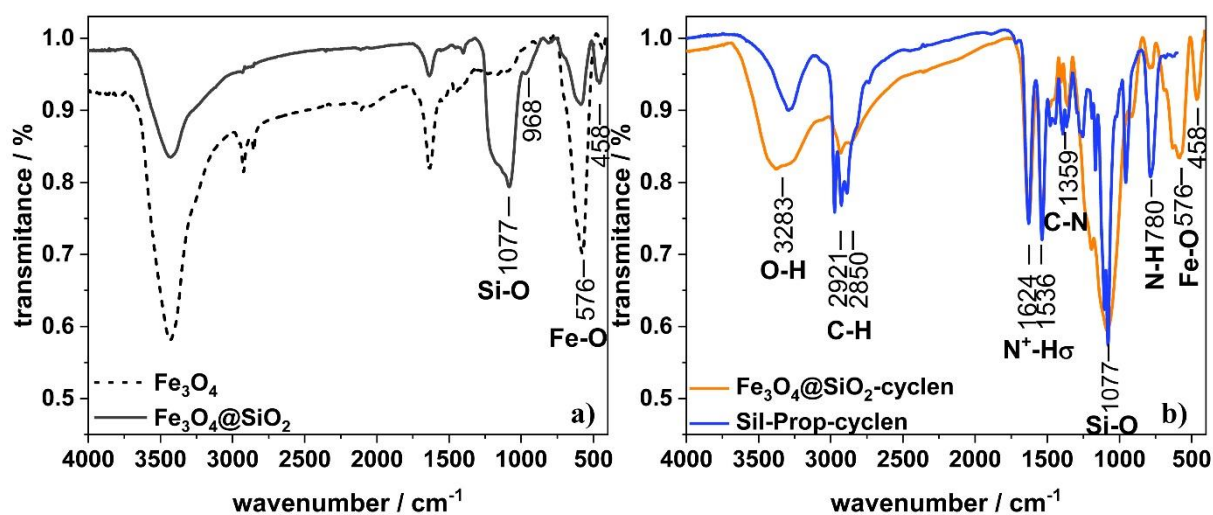
273

274 Our pXRD analysis confirms that for each studied sample all the diffraction peaks
 275 correspond to the cubic crystal structure (space group $Fd-3m$, no. 227). Estimated lattice
 276 parameters for the Fe_3O_4 phase do not differ much and are $a = 8.329(1) \text{ \AA}$ for bare Fe_3O_4 , $a =$
 277 $8.3521(6) \text{ \AA}$ for $\text{Fe}_3\text{O}_4@SiO_2$, and $a = 8.3462(6) \text{ \AA}$ for $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen nanoparticles. The
 278 average crystallite size of the Fe_3O_4 phase was estimated from the Scherrer formula based on
 279 the line broadening at half the maximum intensity of the reflection (220). The estimated
 280 crystallite sizes are 14, 19 and 18 nm for Fe_3O_4 , $\text{Fe}_3\text{O}_4@SiO_2$, and $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen samples,
 281 respectively. The obtained results are in agreement with SEM micrographs.

282

283 3.3. FT-IR spectroscopy analysis

284 FT-IR analysis was performed to identify the appropriate functional groups present in
 285 the Fe_3O_4 nanoparticles at each functionalisation steps.



286

287 **Figure 4.** FT-IR spectra for a) bare Fe_3O_4 , silica coated $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and b) functionalised
 288 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen nanoparticles, modifier silane N-(3-(triethoxysilyl)propyl)-1,4,7,10-
 289 tetraazacyclododecane-1-carboxamide (Sil-Prop-cyclen).

290 The Fe_3O_4 spectrum (Figure 4 a) shows strong stretching vibration Fe–O band at 576
 291 cm^{-1} typical for iron oxide [61]. Also observed was the reduction in the Fe–O band intensity for
 292 coated nanoparticles with silica and functional group. The band intensity decrease confirms the
 293 success in the surface functionalisation process [50]. After silica coating of nanomagnetite the
 294 intense Si–O band appeared at 1077 cm^{-1} . It is associated with stretching vibrations of Si–O–Si
 295 and O–Si–O on the surface of the magnetic core at 968 cm^{-1} and 1077 cm^{-1} , respectively [62,63].
 296 The broad strong band at 3433 cm^{-1} is related to the overlapping of O–H stretching bond, which
 297 proves hydroxyl groups formation on the magnetite surface [64]. Figure 4 b blue line shows
 298 spectra for nanoparticles modifier N-(3-(triethoxysilyl)propyl)-1,4,7,10-
 299 tetraazacyclododecane-1-carboxamide for comparison. A 780 cm^{-1} weak band and a two headed
 300 band about 1536 cm^{-1} and 1624 cm^{-1} characteristic for N–H vibrations are observed.
 301 Furthermore, there are bands that appeared at 1359 cm^{-1} and about 2900 cm^{-1} corresponding to
 302 C–N and N–H stretching vibrations, respectively. The same characteristic bands for the
 303 spectrum for the functionalised nanoparticles $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen (Figure 4 b orange line) are
 304 observed, which proves the success of the nanomaterials synthesis process. In addition, there is
 305 a bandwidth extension at 3283 cm^{-1} which probably corresponds to overlapping O–H and N–H
 306 bands. On the basis of SEM, XPS and FT-IR analysis it can be concluded that the functionalised
 307 core-shell nanoparticles formation was conducted successfully.

308

309

310 **3.3. Electrochemical analysis**

311 In this work, the independent and simultaneous determination of Cd²⁺, Pb²⁺ and Cu²⁺
312 ions was performed under optimised experimental conditions using the DPASV method and
313 HDM electrode. 1,4,7,10-tetraazacyclododecane functionalised magnetite nanoparticles
314 Fe₃O₄@SiO₂-cyclen were investigated as a new heavy metal ions adsorbent. To examine the
315 ions-binding abilities of Fe₃O₄@SiO₂-cyclen, a series of measurements were performed in the
316 solutions containing Cd²⁺, Pb²⁺ and Cu²⁺ ions in concentration level 4.5·10⁻⁶ M. All
317 electrochemical experiments were performed in 0.5 M KCl pH 6.00. The pH was adjusted to
318 avoid the formation of other metal ion species, mainly hydroxides, in the solution aside from
319 the free ion [65–67]. The selection of pH and an influence of electrolyte was previously
320 described by the authors in review paper [68]. There was three well-defined peaks observed at
321 anodic stripping voltammograms at –0.65 V, –0.44 V and –0.20 V confirming the presence of
322 Cd²⁺, Pb²⁺ and Cu²⁺ ion, respectively. Current intensities were multiplied by the dilution factor
323 expressed by the equation (1):

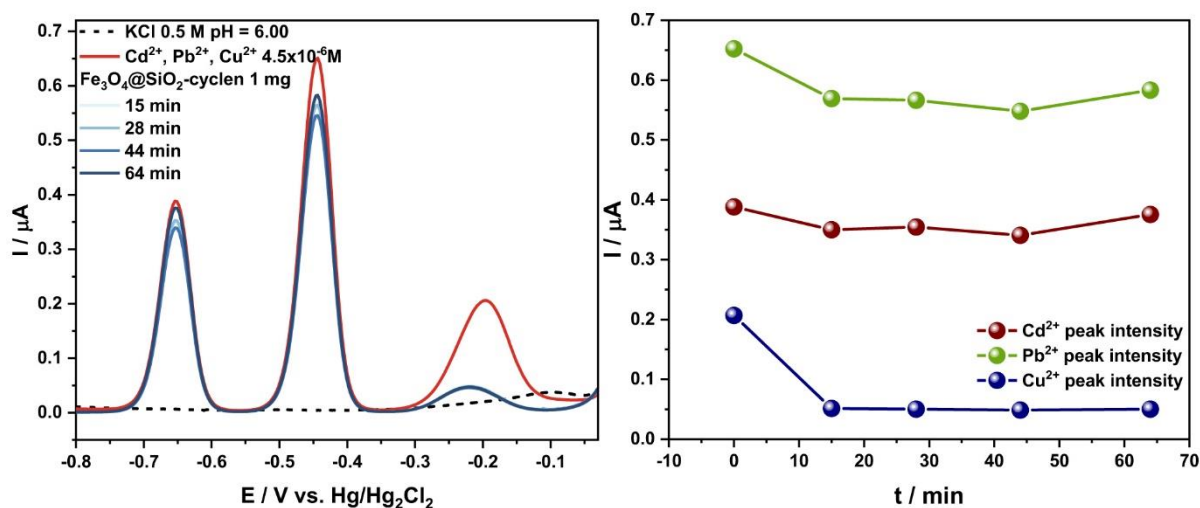
$$324 \quad DF = \frac{V_0 + V_s}{V_0} \quad (1)$$

325 where V₀ is initial volume and V_s is the volume of added nanoparticles suspension in a
326 particular portion.

327 **3.3.1. Cd²⁺, Pb²⁺, Cu²⁺ ions binding by Fe₃O₄@SiO₂-cyclen - kinetics examination**

328 First, kinetic studies were performed to determine the effectual time to establish the
329 equilibrium in the solution after adding the nanoparticles portion. All voltammograms were
330 recorded immediately after adding 1 mg of Fe₃O₄@SiO₂-cyclen nanoparticles to the ion
331 solution and after every 5 minutes of having mixed the solution. In the graph is shown the actual
332 time that the nanoparticles stayed in the solution due to the length of the DPASV measurement
333 (Figure 5).





334

335 **Figure 5.** Simultaneous differential pulse anodic stripping voltammograms for examination of
 336 kinetics Cd²⁺, Pb²⁺ and Cu²⁺ (4.5·10⁻⁶M) ions binding – changes of peak intensities over time
 337 after addition of 1 mg Fe₃O₄@SiO₂-cyclen nanoparticles.

338 After adding one portion of nanoparticles to the ion solution, a decrease in the peak
 339 intensity in the case of only the Cu²⁺ ion was observed. It can be stated that the addition 1 mg
 340 of nanoparticles does not affect Cd²⁺ and Pb²⁺ ions binding. It can be assumed that the slight
 341 peaks intensity changes are within the limit of the measurement error. On the basis of the
 342 experiment it can be concluded that the equilibrium in the solution is established no more than
 343 15 minutes after adding the portion of nanoparticles. A different phenomenon is observed in
 344 the case of an experiment in independent Cd²⁺, Pb²⁺ and Cu²⁺ ion solutions (Figure S1. in the
 345 Supporting Information file). In such a case, one observes a decrease in the peaks intensity over
 346 time for both the Cd²⁺ and Cu²⁺ ion after adding 0.5 mg Fe₃O₄@SiO₂- cyclen nanoparticles.
 347 Functionalised nanomagnetite show no tendency to Pb²⁺ ions binding and it is certainly not
 348 influenced by the time of their presence in the solution. It can be assumed that in the case of
 349 Cd²⁺ and Cu²⁺ ions the equilibrium in the solution is established after about 50 minutes after
 350 adding the nanoparticles. After analysing the kinetics of ion binding by Fe₃O₄@SiO₂- cyclen
 351 nanoparticles, both in individual ion solutions and simultaneous analysis, it was found that the
 352 optimal time for adding the nanoparticles portion to the solution to the measurement is 20
 353 minutes after mixing. Also, the conducted kinetics experiment suggests that the ion binding
 354 level may be influenced by the amount of added nanoparticles. Consequently, the observed

355 dependencies lead to the study of the Fe₃O₄@SiO₂- cyclen nanoparticles binding capacity by
356 titration of the Cd²⁺, Pb²⁺ and Cu²⁺ ions solution.

357

358 **3.3.2. Determination of Fe₃O₄@SiO₂-cyclen binding ability in Cd²⁺, Pb²⁺ and Cu²⁺ ions** 359 **solutions**

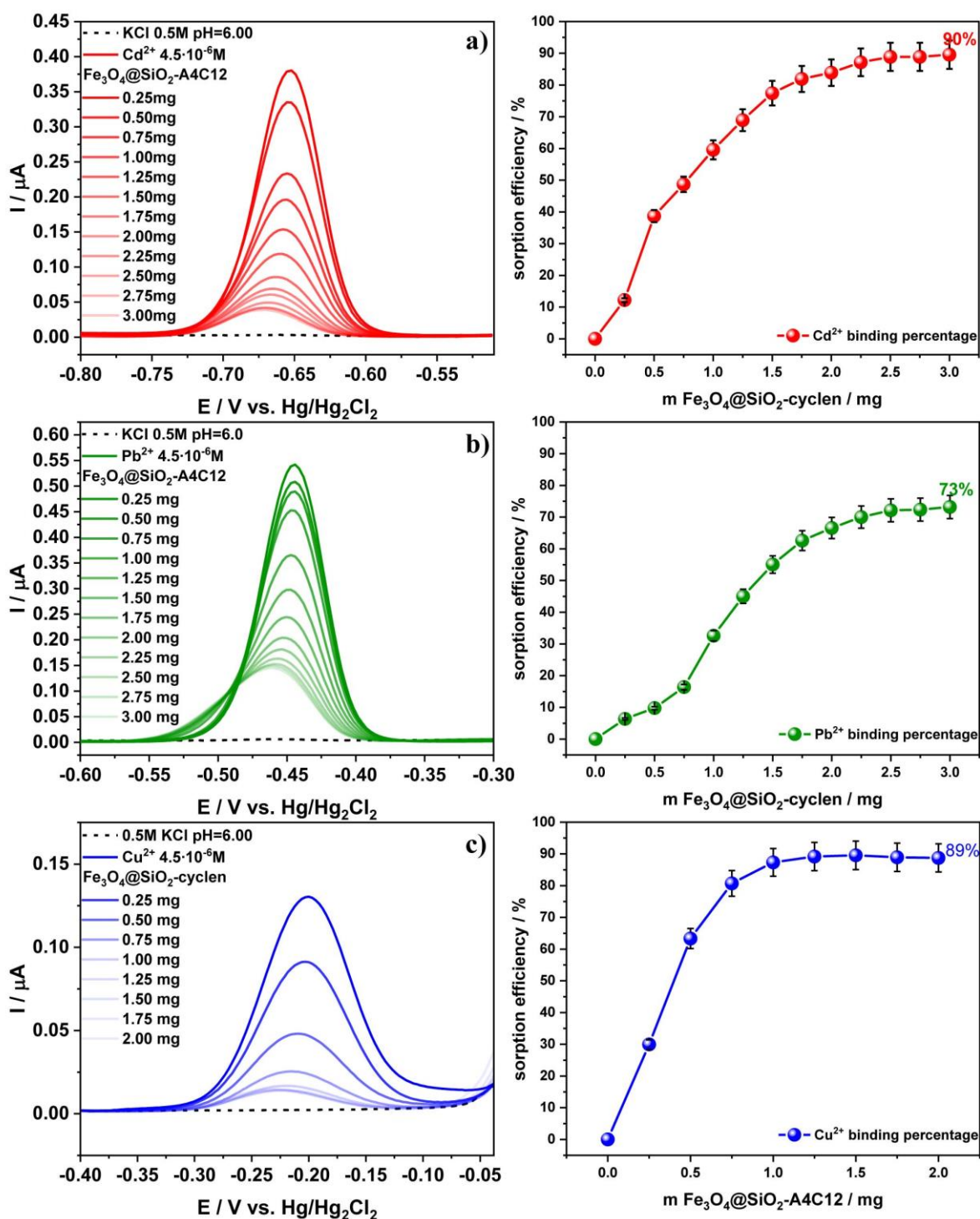
360 In order to determine the ion Cd²⁺, Pb²⁺ and Cu²⁺ binding capacity of
361 Fe₃O₄@SiO₂- cyclen nanoparticles, both in individual solutions and in the mixture, titration
362 with nanoparticles was performed. Used as the measurement analytical method was a two-stage
363 DPASV analysis involving pre-concentration and metal ions stripping. In the first stage, the
364 negative potential of -0.9 V was applied to Cd²⁺, Pb²⁺ and Cu²⁺ ions electrodeposition on the
365 working electrode. Subsequently, the faradic current obtained by oxidation was recorded during
366 the potential sweep toward the positive potential direction from -0,8 V to -0.5 V, from -0,6 V
367 to -0.3 V, from -0,4 V to -0.04 V and from -0.8 V to 0.0 V, for Cd²⁺, Pb²⁺, Cu²⁺ and
368 simultaneous ions detection, respectively. A 0.25 mg portion of Fe₃O₄@SiO₂- cyclen
369 nanoparticles was added into ion solution at each titration step and mixed for 20 minutes before
370 starting the DPASV measurement. The mixing time was determined by the equilibrium
371 establishment experiment in time. Peaks intensity changes during the addition of further
372 nanoparticles portions were recalculated into sorption efficiency R_% (%) at every measuring
373 step based on the formula (2) [69]:

374

$$R_{\%} = \frac{(C_0 - C_f)}{C_0} \cdot 100\% \quad (2)$$

375 where C₀ (mg/L) is initial ion Me²⁺ concentration in the solution, C_f (C_e) (mg/L) is the final ion
376 concentration remaining in the solution [69].





377

378 **Figure 6.** Individual differential pulse anodic stripping voltammograms and calculated sorption
 379 efficiency for a) Cd²⁺, b) Pb²⁺ and c) Cu²⁺ ions binding by Fe₃O₄@SiO₂-cyclen nanoparticles.

380

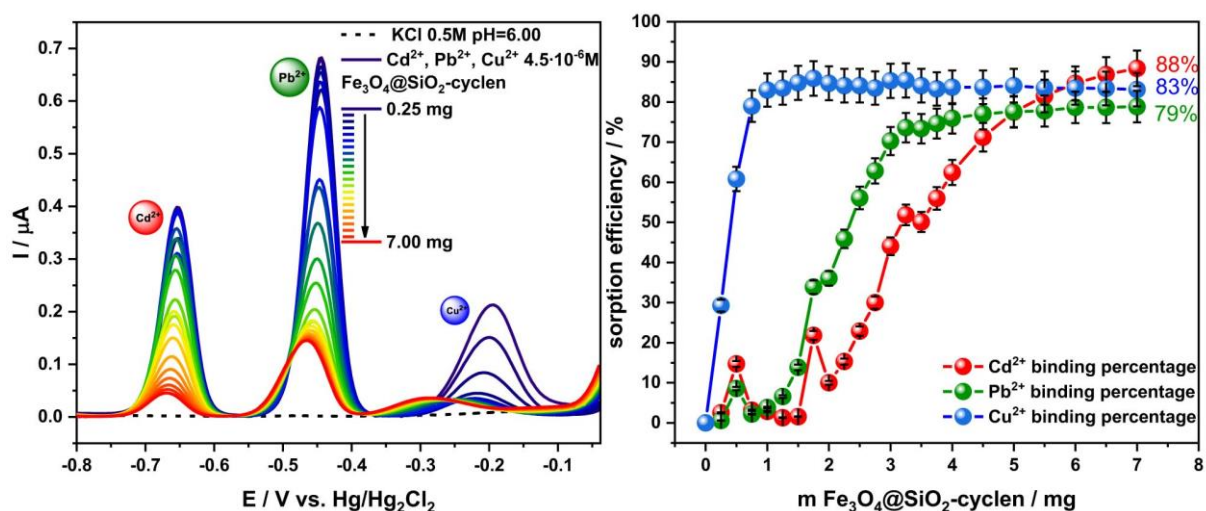
381 Figure 6 shows an individual Cd²⁺, Pb²⁺ and Cu²⁺ ions titration using
 382 Fe₃O₄@SiO₂-cyclen nanoparticles in portion of 0.25 mg added in every titration step.

383 Figure 6 a) shows Cd²⁺ ions binding capacity. While adding successive nanoparticles portions,



384 the peak intensity decreases, thus the sorption efficiency increases. After adding about 2–2.5 mg
 385 of nanoparticles, the equilibrium is established and the next portions do not affect the peak
 386 intensity reduction. The sorption effectiveness reaches about 90% and remains at this level
 387 despite nanoparticles excess. A very similar phenomenon was observed during the titration of
 388 the Pb^{2+} ion (Figure 6b). Initially, the peak intensity decreases with each subsequent
 389 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen portion so that after the addition of about 2–2.5 mg of nanoparticles, it
 390 reaches equilibrium. The titration ending determines the Pb^{2+} ion sorption efficiency at a level
 391 of 73%. The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen nanoparticles behaviour was very different in the Cu^{2+}
 392 solution. Similar as in the case of Cd^{2+} and Pb^{2+} ions titrations, a decrease in peak intensity
 393 during titration was observed. However, a much smaller amount of nanoparticles was needed
 394 to establish equilibrium in the solution. An equilibrium establishing was observed after the
 395 addition of about 1 mg of nanoparticles. The addition of excess nanoparticles did not increase
 396 the sorption efficiency, and its level reached about 89%.

397 Afterwards, to compare, all three ions were titrated simultaneously by
 398 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen nanoparticles starting with 0.25 mg for the first portion and 0.5 mg in the
 399 final steps (Figure 7).



400
 401 **Figure 7.** Simultaneous differential pulse anodic stripping voltammograms and calculated
 402 sorption efficiency for Cd^{2+} , Pb^{2+} , Cu^{2+} ions binding by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen nanoparticles.

403 In the initial titration steps, only a decrease in the intensity of the Cu^{2+} peak was
 404 observed. After adding about 1–1.5 mg of nanoparticles, the percentage of Cu^{2+} binding
 405 remained unchanged at a level of 83%. Then, after the Cu^{2+} binding equilibrium establishing,
 406 changes in the intensity of the Cd^{2+} and Pb^{2+} peaks were observed. As more
 407 $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen portions are added, the intensity of the Cd^{2+} and Pb^{2+} peaks was reduced

408 and the binding efficiency increased. The Pb^{2+} binding equilibrium was established after adding
409 about 3–3.5 mg of nanoparticles to the ions solution and the sorption efficiency reached 79%.
410 As the last equilibrium was Cd^{2+} binding established after the addition stage of ion binding
411 remains at a comparable level, however, it requires different amount of nanoparticles.

412 The exact calculated sorption efficiency parameters for individual (from Figure 6) and
413 simultaneous (from Figure 7) is presented in Table 2. The sorption efficiency $R_{\%}$ calculated on
414 the basis of the conducted DPASV experiments show that for Cd^{2+} this ion was detected at
415 similar levels of 89-88% regardless as an individual ion in solution or in a mixture of studied
416 ions. In the case of Pb^{2+} , the sorption level was higher for the simultaneous solution, while for
417 Cu^{2+} sorption value was higher in the single-component. Nevertheless, the sorption efficiency
418 are at very high levels for all analysed solutions, which confirms high efficiency of ions binding
419 by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -cyclen nanoparticles.

420

421 **Table 2.** Sorption efficiency parameters for individual and simultaneous Cd^{2+} , Pb^{2+} and Cu^{2+}
422 ions binding by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ - cyclen nanoparticles.

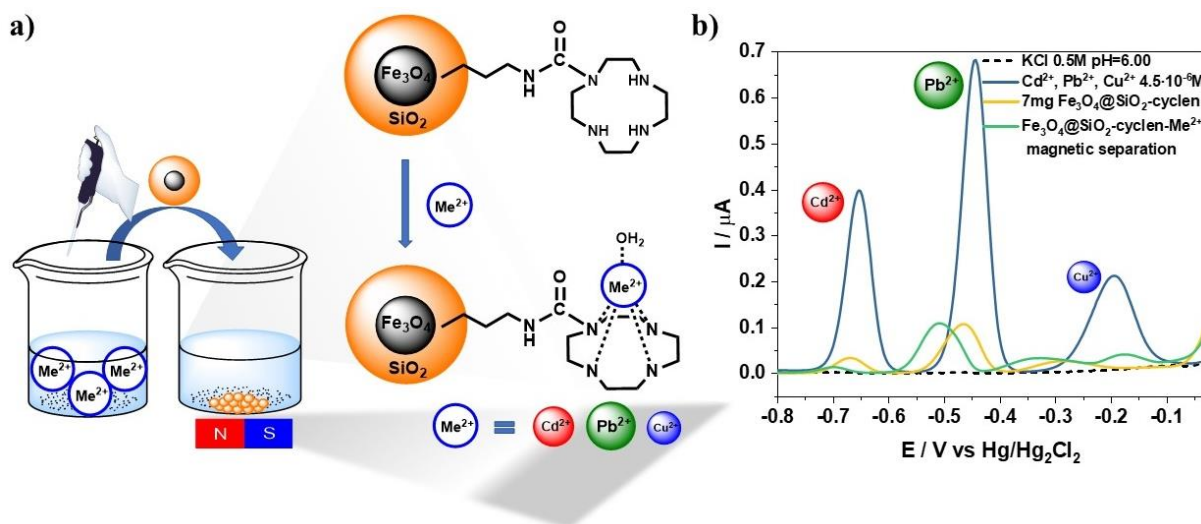
	Individual	Simultaneous
	$R_{\%}$	$R_{\%}$
Cd^{2+}	89.55%	88.37%
Pb^{2+}	73.20%	78.85%
Cu^{2+}	88.75%	83.08%

423

424 3.3.3. Magnetic separation of adsorbed Cd^{2+} , Pb^{2+} and Cu^{2+}

425 Finally, the separation effectiveness of nanoparticles with adsorbed heavy metal ions by
426 external magnetic field was investigated. First, the necessary amount of nanoparticles to bind
427 Cd^{2+} , Pb^{2+} , Cu^{2+} ions solution was added to them. After that, the reduction in the metal ions
428 peaks intensity at the DPAS voltammograms was observed (from blue line to yellow line). Then
429 the nanoparticles contained in the solution were isolated with the use of a magnet and the
430 solution was separated and subjected to DPASV measurement. The obtained voltammogram,
431 apart from slightly negatively shifted potentials, shows no deviation from that obtained directly
432 after the adsorption process. This phenomenon indicates the separation of all bound ions along
433 with the nanoparticles from the solution (Figure 8).





434

435 **Figure 8.** a) Scheme of magnetic Me^{2+} ions binding and magnetic separation experiment. Ion
 436 binding model by aza-crown based on Subat et al. [46]. b) Simultaneous differential pulse
 437 anodic stripping voltammograms: of Cd^{2+} , Pb^{2+} , Cu^{2+} ions (blue line), after adsorption by 7 mg
 438 $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen nanoparticles (yellow line) and after magnetic isolation nanoparticles with
 439 adsorbed ions (green line).

440

441 4. Conclusions

442 In this work, new core-shell nanostructures were synthesised containing a magnetic
 443 Fe_3O_4 core and silane shell functionalised with 1,4,7,10-tetraazacyclododecane were
 444 synthesised and characterised and their binding capacity was investigated. The results of
 445 nanomaterial characteristics using SEM, XPS, pXRD and FT-IR confirmed the success of the
 446 three-stage synthesis process.

447 Moreover, $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen nanoparticles binding kinetics and the sorption
 448 efficiency of Cd^{2+} , Pb^{2+} and Cu^{2+} was investigated both in individual ions solutions and in an
 449 ions mixture. Electrochemical studies proved that nanoparticles can be effectively used as
 450 adsorbents in environment heavy metal ions pollution management, which can be easily
 451 collected using an external magnetic field.

452 The research showed that nanoparticles have a binding tendency to all selected ions
 453 Cd^{2+} , Pb^{2+} and Cu^{2+} in their individual solutions and their sorption efficiency remains at 90%,
 454 73% and 89%, respectively. It is worth mentioning that the smallest amount of nanoparticles
 455 was needed to bind the Cu^{2+} . Simultaneous Cd^{2+} , Pb^{2+} and Cu^{2+} determination also indicates
 456 the ability of $\text{Fe}_3\text{O}_4@SiO_2$ -cyclen to bind of all ions. However, a clear order of ion binding was

457 observed in the mixture during the addition of further nanoparticles portions. First, Cu^{2+} ions
458 were bound, then Pb^{2+} and Cd^{2+} the sorption efficiency remains at 83%, 79% and 88% level,
459 respectively. This phenomenon can be explained by the complexation constants value of these
460 ions by 1,4,7,10-tetraazacyclododecane. The fastest Cu^{2+} binding can be explained by the
461 highest value of the complexation constant 23.9, 24.8 according to Antunes et al. [70], whereas
462 the complexation constants of Pb^{2+} and Cd^{2+} are 15.9 and 14.3, respectively [70]. Additionally,
463 the level of ion binding depends on the amount of added nanoparticles. On this basis, it can be
464 concluded that the presence of cyclen functional groups on the surface of nanoparticles gives
465 them the ability to bind ions. Furthermore, the Cd^{2+} , Pb^{2+} , Cu^{2+} ions adsorption and magnetic
466 separation experiment confirms the effectiveness of ion binding and purification of water
467 environments. On the basis of this work, it can be assumed that the new nanomaterials based
468 on Fe_3O_4 and functionalised with N-(3-(triethoxysilyl)propyl)-1,4,7,10-tetraazacyclododecane-
469 1-carboxamide can be successfully used as a universal Cd^{2+} , Pb^{2+} , Cu^{2+} ions magnetic
470 adsorbent.

471

472 **Acknowledgements**

473 This work was created thanks to the University of Gdansk within the project supporting
474 young scientists and PhD students (grant No. BMN 539-T050-B019-22).

475 **CRedit authorship contribution statement**

476 **Amanda Kulpa-Koterwa:** Methodology, Formal analysis, Investigation, Data Curation,
477 Writing - Original Draft, Writing - Review & Editing, Visualization, Funding acquisition **Jacek**
478 **Ryl:** Investigation, Data Curation, Writing - Original Draft, **Karolina Górnicka:** Investigation,
479 Data Curation, Writing - Original Draft **Paweł Niedziałkowski:** Conceptualization, Resources,
480 Writing - Original Draft, Writing - Review & Editing, Supervision

481 **Declaration of competing interest**

482 The authors declare that they have no known competing financial interests or personal
483 relationships that could have appeared to influence the work reported in this paper.

484



485 **References**

- 486 [1] S.S. Kolluru, S. Agarwal, S. Sireesha, I. Sreedhar, S.R. Kale, Heavy metal removal from
 487 wastewater using nanomaterials-process and engineering aspects, *Process Safety and*
 488 *Environmental Protection*. 150 (2021) 323–355.
 489 <https://doi.org/10.1016/j.psep.2021.04.025>.
- 490 [2] T.K. Das, A. Poater, Review on the Use of Heavy Metal Deposits from Water Treatment
 491 Waste towards Catalytic Chemical Syntheses, *Int J Mol Sci*. 22 (2021) 13383.
 492 <https://doi.org/10.3390/ijms222413383>.
- 493 [3] J. Briffa, E. Sinagra, R. Blundell, Heavy metal pollution in the environment and their
 494 toxicological effects on humans, *Heliyon*. 6 (2020) e04691.
 495 <https://doi.org/10.1016/j.heliyon.2020.e04691>.
- 496 [4] R.K. Gautam, S.K. Sharma, S. Mahiya, M.C. Chattopadhyaya, CHAPTER 1
 497 Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and
 498 Technologies for Remediation, (2014) 1–24. [https://doi.org/10.1039/9781782620174-](https://doi.org/10.1039/9781782620174-00001)
 499 [00001](https://doi.org/10.1039/9781782620174-00001).
- 500 [5] R. Shrestha, S. Ban, S. Devkota, S. Sharma, R. Joshi, A.P. Tiwari, H.Y. Kim, M.K.
 501 Joshi, Technological trends in heavy metals removal from industrial wastewater: A
 502 review, *Journal of Environmental Chemical Engineering*. 9 (2021) 105688.
 503 <https://doi.org/10.1016/j.jece.2021.105688>.
- 504 [6] D.-Q. Cao, X. Song, X.-M. Fang, W.-Y. Yang, X.-D. Hao, E. Iritani, N. Katagiri,
 505 Membrane filtration-based recovery of extracellular polymer substances from excess
 506 sludge and analysis of their heavy metal ion adsorption properties, *Chemical*
 507 *Engineering Journal*. 354 (2018) 866–874. <https://doi.org/10.1016/j.cej.2018.08.121>.
- 508 [7] A. Saeedi-Jurkuyeh, A.J. Jafari, R.R. Kalantary, A. Esrafil, A novel synthetic thin-film
 509 nanocomposite forward osmosis membrane modified by graphene oxide and
 510 polyethylene glycol for heavy metals removal from aqueous solutions, *Reactive and*
 511 *Functional Polymers*. 146 (2020) 104397.
 512 <https://doi.org/10.1016/j.reactfunctpolym.2019.104397>.
- 513 [8] Y. Ibrahim, E. Abdulkarem, V. Naddeo, F. Banat, S.W. Hasan, Synthesis of super
 514 hydrophilic cellulose-alpha zirconium phosphate ion exchange membrane via surface
 515 coating for the removal of heavy metals from wastewater, *Science of The Total*
 516 *Environment*. 690 (2019) 167–180. <https://doi.org/10.1016/j.scitotenv.2019.07.009>.
- 517 [9] S. Platzer, M. Kar, R. Leyma, S. Chib, A. Roller, F. Jirsa, R. Krachler, D.R. MacFarlane,
 518 W. Kandioller, B.K. Keppler, Task-specific thioglycolate ionic liquids for heavy metal
 519 extraction: Synthesis, extraction efficacies and recycling properties, *Journal of*
 520 *Hazardous Materials*. 324 (2017) 241–249.
 521 <https://doi.org/10.1016/j.jhazmat.2016.10.054>.
- 522 [10] Y. Deng, C. Feng, L. Tang, G. Zeng, Z. Chen, M. Zhang, Chapter 5 - Nanohybrid
 523 Photocatalysts for Heavy Metal Pollutant Control, in: L. Tang, Y. Deng, J. Wang, J.
 524 Wang, G. Zeng (Eds.), *Nanohybrid and Nanoporous Materials for Aquatic Pollution*
 525 *Control*, Elsevier, 2019: pp. 125–153. [https://doi.org/10.1016/B978-0-12-814154-](https://doi.org/10.1016/B978-0-12-814154-0.00005-0)
 526 [0.00005-0](https://doi.org/10.1016/B978-0-12-814154-0.00005-0).
- 527 [11] X. Guan, X. Yuan, Y. Zhao, H. Wang, H. Wang, J. Bai, Y. Li, Application of
 528 functionalized layered double hydroxides for heavy metal removal: A review, *Science of*
 529 *The Total Environment*. (2022) 155693. <https://doi.org/10.1016/j.scitotenv.2022.155693>.
- 530 [12] C. Yan, Z. Qu, J. Wang, L. Cao, Q. Han, Microalgal bioremediation of heavy metal
 531 pollution in water: Recent advances, challenges, and prospects, *Chemosphere*. 286
 532 (2022) 131870. <https://doi.org/10.1016/j.chemosphere.2021.131870>.
- 533 [13] J. He, J.P. Chen, A comprehensive review on biosorption of heavy metals by algal
 534 biomass: Materials, performances, chemistry, and modeling simulation tools,

- 535 Bioresource Technology. 160 (2014) 67–78.
536 <https://doi.org/10.1016/j.biortech.2014.01.068>.
- 537 [14] L. Yang, J. Wang, Y. Yang, S. Li, T. Wang, P. Oleksak, Z. Chrienova, Q. Wu, E.
538 Nepovimova, X. Zhang, K. Kuca, Phytoremediation of heavy metal pollution: Hotspots
539 and future prospects, *Ecotoxicology and Environmental Safety*. 234 (2022) 113403.
540 <https://doi.org/10.1016/j.ecoenv.2022.113403>.
- 541 [15] Q. Chen, Y. Yao, X. Li, J. Lu, J. Zhou, Z. Huang, Comparison of heavy metal removals
542 from aqueous solutions by chemical precipitation and characteristics of precipitates,
543 *Journal of Water Process Engineering*. 26 (2018) 289–300.
544 <https://doi.org/10.1016/j.jwpe.2018.11.003>.
- 545 [16] A.J. Bora, R.K. Dutta, Removal of metals (Pb, Cd, Cu, Cr, Ni, and Co) from drinking
546 water by oxidation-coagulation-adsorption at optimized pH, *Journal of Water Process
547 Engineering*. 31 (2019) 100839. <https://doi.org/10.1016/j.jwpe.2019.100839>.
- 548 [17] A. Jain, S. Rai, R. Srinivas, R.I. Al-Raoush, Bioinspired modeling and biogeography-
549 based optimization of electrocoagulation parameters for enhanced heavy metal removal,
550 *Journal of Cleaner Production*. 338 (2022) 130622.
551 <https://doi.org/10.1016/j.jclepro.2022.130622>.
- 552 [18] S. Shukla, R. Khan, A. Daverey, Synthesis and characterization of magnetic
553 nanoparticles, and their applications in wastewater treatment: A review, *Environmental
554 Technology & Innovation*. 24 (2021) 101924. <https://doi.org/10.1016/j.eti.2021.101924>.
- 555 [19] R.M. Ali, H.A. Hamad, M.M. Hussein, G.F. Malash, Potential of using green adsorbent
556 of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm,
557 thermodynamic, mechanism and economic analysis, *Ecological Engineering*. 91 (2016)
558 317–332. <https://doi.org/10.1016/j.ecoleng.2016.03.015>.
- 559 [20] D. Saritha, A concise review on the removal of heavy metals from wastewater using
560 adsorbents, *Materials Today: Proceedings*. 63 (2022) 3973–3977.
561 <https://doi.org/10.1016/j.matpr.2022.04.579>.
- 562 [21] U. Haripriyan, K.P. Gopinath, J. Arun, Chitosan based nano adsorbents and its types for
563 heavy metal removal: A mini review, *Materials Letters*. 312 (2022) 131670.
564 <https://doi.org/10.1016/j.matlet.2022.131670>.
- 565 [22] I. Ihsanullah, M. Sajid, S. Khan, M. Bilal, Aerogel-based adsorbents as emerging
566 materials for the removal of heavy metals from water: Progress, challenges, and
567 prospects, *Separation and Purification Technology*. 291 (2022) 120923.
568 <https://doi.org/10.1016/j.seppur.2022.120923>.
- 569 [23] Y. Yue, Y. Liu, W. Zhang, J. Guo, Y. Gong, Y. Yu, Amidoxime functionalized low-cost
570 cellulose-based adsorbent derived from waste cigarette filters for efficient heavy metal
571 removal, *Journal of Environmental Chemical Engineering*. 10 (2022) 107846.
572 <https://doi.org/10.1016/j.jece.2022.107846>.
- 573 [24] H. Zhang, X. Hu, T. Li, Y. Zhang, H. Xu, Y. Sun, X. Gu, C. Gu, J. Luo, B. Gao, MIL
574 series of metal organic frameworks (MOFs) as novel adsorbents for heavy metals in
575 water: A review, *Journal of Hazardous Materials*. 429 (2022) 128271.
576 <https://doi.org/10.1016/j.jhazmat.2022.128271>.
- 577 [25] C. Duan, T. Ma, J. Wang, Y. Zhou, Removal of heavy metals from aqueous solution
578 using carbon-based adsorbents: A review, *Journal of Water Process Engineering*. 37
579 (2020) 101339. <https://doi.org/10.1016/j.jwpe.2020.101339>.
- 580 [26] S. Cho, J.-H. Kim, K.S. Yang, M. Chang, Facile preparation of amino-functionalized
581 polymeric microcapsules as efficient adsorbent for heavy metal ions removal, *Chemical
582 Engineering Journal*. 425 (2021) 130645. <https://doi.org/10.1016/j.cej.2021.130645>.
- 583 [27] E. Vunain, A. Mishra, B. Mamba, Dendrimers, mesoporous silicas and chitosan-based
584 nanosorbents for the removal of heavy-metal ions: A review, *International Journal of*

- 585 Biological Macromolecules. 86 (2016) 570–586.
586 <https://doi.org/10.1016/j.ijbiomac.2016.02.005>.
- 587 [28] M.M. Al-Mahadeen, A.G. Jiries, S.A. Al-Trawneh, S.F. Alshahateet, A.S. Eldouhaibi, S.
588 Sagadevan, Kinetics and equilibrium studies for the removal of heavy metal ions from
589 aqueous solution using the synthesized C-4-bromophenylcalix[4]resorcinarene
590 adsorbent, Chemical Physics Letters. 783 (2021) 139053.
591 <https://doi.org/10.1016/j.cplett.2021.139053>.
- 592 [29] Z. Cheng, J. Yang, L. Li, Y. Chen, X. Wang, Flocculation inspired combination of
593 layered double hydroxides and fulvic acid to form a novel composite adsorbent for the
594 simultaneous adsorption of anionic dye and heavy metals, Journal of Colloid and
595 Interface Science. 618 (2022) 386–398. <https://doi.org/10.1016/j.jcis.2022.03.097>.
- 596 [30] R. Torkaman, F. Maleki, M. Gholami, M. Torab-Mostaedi, M. Asadollahzadeh,
597 Assessing the radiation-induced graft polymeric adsorbents with emphasis on heavy
598 metals removing: A systematic literature review, Journal of Water Process Engineering.
599 44 (2021) 102371. <https://doi.org/10.1016/j.jwpe.2021.102371>.
- 600 [31] V. Vinayagam, S. Murugan, R. Kumaresan, M. Narayanan, M. Sillanpää, D.-V.N. Vo,
601 O.S. Kushwaha, Protein nanofibrils as versatile and sustainable adsorbents for an
602 effective removal of heavy metals from wastewater: A review, Chemosphere. 301 (2022)
603 134635. <https://doi.org/10.1016/j.chemosphere.2022.134635>.
- 604 [32] J. R., B. Gurunathan, S. K., S. Varjani, H.H. Ngo, E. Gnansounou, Advancements in
605 heavy metals removal from effluents employing nano-adsorbents: Way towards cleaner
606 production, Environmental Research. 203 (2022) 111815.
607 <https://doi.org/10.1016/j.envres.2021.111815>.
- 608 [33] R. Bhatia, R. Singh, A review on nanotechnological application of magnetic iron
609 oxides for heavy metal removal, Journal of Water Process Engineering. 31 (2019)
610 100845. <https://doi.org/10.1016/j.jwpe.2019.100845>.
- 611 [34] A. Latif, D. Sheng, K. Sun, Y. Si, M. Azeem, A. Abbas, M. Bilal, Remediation of heavy
612 metals polluted environment using Fe-based nanoparticles: Mechanisms, influencing
613 factors, and environmental implications, Environmental Pollution. 264 (2020) 114728.
614 <https://doi.org/10.1016/j.envpol.2020.114728>.
- 615 [35] F. Ghorbani, S. Kamari, Core-shell magnetic nanocomposite of Fe₃O₄@SiO₂@NH₂ as
616 an efficient and highly recyclable adsorbent of methyl red dye from aqueous
617 environments, Environmental Technology & Innovation. 14 (2019) 100333.
618 <https://doi.org/10.1016/j.eti.2019.100333>.
- 619 [36] S. Patil, R. Tandon, N. Tandon, A current research on silica coated ferrite nanoparticle
620 and their application: Review, Current Research in Green and Sustainable Chemistry. 4
621 (2021) 100063. <https://doi.org/10.1016/j.crgsc.2021.100063>.
- 622 [37] L. Wang, X. Huang, C. Wang, X. Tian, X. Chang, Y. Ren, S. Yu, Applications of
623 surface functionalized Fe₃O₄ NPs-based detection methods in food safety, Food
624 Chemistry. 342 (2021) 128343. <https://doi.org/10.1016/j.foodchem.2020.128343>.
- 625 [38] S. Jin, B.C. Park, W.S. Ham, L. Pan, Y.K. Kim, Effect of the magnetic core size of
626 amino-functionalized Fe₃O₄-mesoporous SiO₂ core-shell nanoparticles on the removal
627 of heavy metal ions, Colloids and Surfaces A: Physicochemical and Engineering
628 Aspects. 531 (2017) 133–140. <https://doi.org/10.1016/j.colsurfa.2017.07.086>.
- 629 [39] Y. Harinath, D.H.K. Reddy, L.S. Sharma, K. Seshaiyah, Development of hyperbranched
630 polymer encapsulated magnetic adsorbent (Fe₃O₄@SiO₂-NH₂-PAA) and its
631 application for decontamination of heavy metal ions, Journal of Environmental Chemical
632 Engineering. 5 (2017) 4994–5001. <https://doi.org/10.1016/j.jece.2017.09.031>.
- 633 [40] N. Naini, H. Sid Kalal, M.R. Almasian, D. Niknafs, M. Taghiof, H. Hoveidi, Phosphine-
634 functionalized Fe₃O₄/SiO₂/composites as efficient magnetic nanoadsorbents for the

- 635 removal of palladium ions from aqueous solution: Kinetic, thermodynamic and isotherm
636 studies, *Materials Chemistry and Physics*. 287 (2022) 126242.
637 <https://doi.org/10.1016/j.matchemphys.2022.126242>.
- 638 [41] E. Ragheb, M. Shamsipur, F. Jalali, F. Mousavi, Modified magnetic-metal organic
639 framework as a green and efficient adsorbent for removal of heavy metals, *Journal of*
640 *Environmental Chemical Engineering*. 10 (2022) 107297.
641 <https://doi.org/10.1016/j.jece.2022.107297>.
- 642 [42] W. Qin, S. Xu, G. Xu, Q. Xie, C. Wang, Z. Xu, Preparation of silica gel bound crown
643 ether and its extraction performance towards zirconium and hafnium, *Chemical*
644 *Engineering Journal*. 225 (2013) 528–534. <https://doi.org/10.1016/j.cej.2013.03.127>.
- 645 [43] M. Subat, K. Woinaroschy, S. Anthofer, B. Malterer, B. König, 1,4,7,10-
646 Tetraazacyclododecane Metal Complexes as Potent Promoters of Carboxyester
647 Hydrolysis under Physiological Conditions, *Inorg. Chem.* 46 (2007) 4336–4356.
648 <https://doi.org/10.1021/ic070101z>.
- 649 [44] J.M. Park, O.J. Shon, H. Hong, J.S. Kim, Y. Kim, H.B. Lim, Development of a
650 microchip metal ion sensor using dinitro-azocalix[4]azacrown, *Microchemical Journal*.
651 80 (2005) 139–144. <https://doi.org/10.1016/j.microc.2004.07.017>.
- 652 [45] B. König, M. Pelka, M. Subat, I. Dix, P.G. Jones, Urea Derivatives of 1,4,7,10-
653 Tetraazacyclododecane – Synthesis and Binding Properties, *European Journal of*
654 *Organic Chemistry*. 2001 (2001) 1943–1949. [https://doi.org/10.1002/1099-](https://doi.org/10.1002/1099-0690(200105)2001:10<1943::AID-EJOC1943>3.0.CO;2-O)
655 [0690\(200105\)2001:10<1943::AID-EJOC1943>3.0.CO;2-O](https://doi.org/10.1002/1099-0690(200105)2001:10<1943::AID-EJOC1943>3.0.CO;2-O).
- 656 [46] M. Subat, K. Woinaroschy, C. Gerstl, B. Sarkar, W. Kaim, B. König, 1,4,7,10-
657 Tetraazacyclododecane Metal Complexes as Potent Promoters of Phosphodiester
658 Hydrolysis under Physiological Conditions, *Inorg. Chem.* 47 (2008) 4661–4668.
659 <https://doi.org/10.1021/ic702413q>.
- 660 [47] M. Regueiro-Figueroa, E. Ruscák, L. Fra, G. Tircsó, I. Tóth, A. de Blas, T. Rodríguez-
661 Blas, C. Platas-Iglesias, D. Esteban-Gómez, Highly Stable Complexes of Divalent Metal
662 Ions (Mg²⁺, Ca²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Pb²⁺) with a DOTA-Like Ligand Containing
663 a Picolinate Pendant, *European Journal of Inorganic Chemistry*. 2014 (2014) 6165–6173.
664 <https://doi.org/10.1002/ejic.201402693>.
- 665 [48] P. Antunes, P.M. Campello, R. Delgado, M.G.B. Drew, V. Félix, I. Santos, Metal
666 complexes of a tetraazacyclopentane: solution and molecular modelling studies, *Dalton*
667 *Trans.* (2003) 1852–1860. <https://doi.org/10.1039/B301033C>.
- 668 [49] P. Niedziałkowski, D. Zarzeczńska, T. Ossowski, Synthesis and Characterization of
669 1,4,7,10-Tetraazacyclododecane Derivatives and Their Metal Complexes, *Polish Journal*
670 *of Chemistry*. Vol. 82 (2008) 1175–1197.
- 671 [50] A. Kulpa, J. Ryl, G. Skowierzak, A. Koterwa, G. Schroeder, T. Ossowski, P.
672 Niedziałkowski, Comparison of Cadmium Cd²⁺ and Lead Pb²⁺ Binding by
673 Fe₂O₃@SiO₂-EDTA Nanoparticles – Binding Stability and Kinetic Studies,
674 *Electroanalysis*. 32 (2020) 588–597. <https://doi.org/10.1002/elan.201900616>.
- 675 [51] A. Kulpa, J. Ryl, G. Schroeder, A. Koterwa, J. Sein Anand, T. Ossowski, P.
676 Niedziałkowski, Simultaneous voltammetric determination of Cd²⁺, Pb²⁺, and Cu²⁺
677 ions captured by Fe₃O₄@SiO₂ core-shell nanostructures of various outer amino chain
678 length, *Journal of Molecular Liquids*. 314 (2020) 113677.
679 <https://doi.org/10.1016/j.molliq.2020.113677>.
- 680 [52] S. Sawan, R. Maalouf, A. Errachid, N. Jaffrezic-Renault, Metal and metal oxide
681 nanoparticles in the voltammetric detection of heavy metals: A review, *TrAC Trends in*
682 *Analytical Chemistry*. 131 (2020) 116014. <https://doi.org/10.1016/j.trac.2020.116014>.

- 683 [53] T. Matsuoka, S. Yamamoto, O. Moriya, M. Kashio, T. Sugizaki, Synthesis of
684 thermoresponsive polysilsesquioxane with methoxyethylamide group and crown ether,
685 Polym J. 42 (2010) 313–318. <https://doi.org/10.1038/pj.2010.7>.
- 686 [54] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.St.C. Smart,
687 Resolving surface chemical states in XPS analysis of first row transition metals, oxides
688 and hydroxides: Cr, Mn, Fe, Co and Ni, Applied Surface Science. 257 (2011) 2717–
689 2730. <https://doi.org/10.1016/j.apsusc.2010.10.051>.
- 690 [55] Š. Meškiniš, A. Vasiliauskas, M. Andrulevičius, D. Peckus, S. Tamulevičius, K.
691 Viskontas, Diamond Like Carbon Films Containing Si: Structure and Nonlinear Optical
692 Properties, Materials. 13 (2020) 1003. <https://doi.org/10.3390/ma13041003>.
- 693 [56] F. Sirotti, M. De Santis, G. Rossi, Synchrotron-radiation photoemission and x-ray
694 absorption of Fe silicides, Phys. Rev. B. 48 (1993) 8299–8306.
695 <https://doi.org/10.1103/PhysRevB.48.8299>.
- 696 [57] R. Bywalez, H. Karacuban, H. Nienhaus, C. Schulz, H. Wiggers, Stabilization of mid-
697 sized silicon nanoparticles by functionalization with acrylic acid, Nanoscale Research
698 Letters. 7 (2012) 76. <https://doi.org/10.1186/1556-276X-7-76>.
- 699 [58] A. Mohtasebi, T. Chowdhury, L.H.H. Hsu, M.C. Biesinger, P. Kruse, Interfacial Charge
700 Transfer between Phenyl-Capped Aniline Tetramer Films and Iron Oxide Surfaces, J.
701 Phys. Chem. C. 120 (2016) 29248–29263. <https://doi.org/10.1021/acs.jpcc.6b09950>.
- 702 [59] A. Tanver, M.-H. Huang, Y. Luo, Energetic interpenetrating polymer network (EIPN):
703 enhanced thermo-mechanical properties of NCO-fMWCNTs/HTPB PU and alkyne-
704 fMWCNTs/acyl-GAP based nanocomposite and its propellants, RSC Adv. 6 (2016)
705 49101–49112. <https://doi.org/10.1039/C6RA07742K>.
- 706 [60] Q. Li, C.W. Kartikowati, S. Horie, T. Ogi, T. Iwaki, K. Okuyama, Correlation between
707 particle size/domain structure and magnetic properties of highly crystalline Fe₃O₄
708 nanoparticles, Sci Rep. 7 (2017) 9894. <https://doi.org/10.1038/s41598-017-09897-5>.
- 709 [61] F. Shalali, S. Cheraghi, M.A. Taher, A sensitive electrochemical sensor amplified with
710 ionic liquid and N-CQD/Fe₃O₄ nanoparticles for detection of raloxifene in the presence
711 of tamoxifen as two essentials anticancer drugs, Materials Chemistry and Physics. 278
712 (2022) 125658. <https://doi.org/10.1016/j.matchemphys.2021.125658>.
- 713 [62] T. Yousofi, A. Rahmati, Fe₃O₄@SiO₂-BU core-shell as a new nanomagnetic gelator for
714 oil recovery from water, Polyhedron. 180 (2020) 114363.
715 <https://doi.org/10.1016/j.poly.2020.114363>.
- 716 [63] T. Akbarpour, J. Yousefi Seyf, A. Khazaei, N. Sarmasti, Synthesis of Pyrano [2,3-c]
717 Pyrazole Derivatives Using a Novel Ionic-Liquid Based Nano-Magnetic Catalyst (Fe₃
718 O₄@SiO₂@(CH₂)₃NH@CC@Imidazole@SO₃H + Cl⁻), Polycyclic Aromatic
719 Compounds. (2021) 1–21. <https://doi.org/10.1080/10406638.2021.1873152>.
- 720 [64] D. Chen, T. Awut, B. Liu, Y. Ma, T. Wang, I. Nurulla, Functionalized magnetic Fe₃O₄
721 nanoparticles for removal of heavy metal ions from aqueous solutions, E-Polymers. 16
722 (2016) 313–322. <https://doi.org/10.1515/epoly-2016-0043>.
- 723 [65] Q. Kong, C. Wei, S. Preis, Y. Hu, F. Wang, Facile preparation of nitrogen and sulfur co-
724 doped graphene-based aerogel for simultaneous removal of Cd²⁺ and organic dyes,
725 Environ Sci Pollut Res Int. 25 (2018) 21164–21175. <https://doi.org/10.1007/s11356-018-2195-8>.
- 726 [66] T. Chen, H. Li, H. Wang, X. Zou, H. Liu, D. Chen, Y. Zhou, Removal of Pb(II) from
727 Aqueous Solutions by Periclase/Calcite Nanocomposites, Water Air Soil Pollut. 230
728 (2019) 299. <https://doi.org/10.1007/s11270-019-4354-z>.
- 729 [67] J. Liu, D. Luo, L. Huang, Y. Wang, S. Wen, Copper adsorption reaction rate and ion
730 exchange ratio during the copper activation of sphalerite, Physicochem. Probl. Miner.
731 Process. 54 (2017) 377–385. <https://doi.org/10.5277/ppmp1832>.
- 732

- 733 [68] A. Kulpa-Koterwa, T. Ossowski, P. Niedziałkowski, Functionalized Fe₃O₄
734 Nanoparticles as Glassy Carbon Electrode Modifiers for Heavy Metal Ions
735 Detection—A Mini Review, *Materials*. 14 (2021) 7725.
736 <https://doi.org/10.3390/ma14247725>.
- 737 [69] C. Zeng, P. Liu, Z. Xiao, Y. Li, L. Song, Z. Cao, D. Wu, Y.-F. Zhang, Highly Selective
738 Adsorption and Recovery of Palladium from Spent Catalyst Wastewater by 1,4,7,10-
739 Tetraazacyclododecane-Modified Mesoporous Silica, *ACS Sustainable Chem. Eng.* 10
740 (2022) 1103–1114. <https://doi.org/10.1021/acssuschemeng.1c05915>.
- 741 [70] P. Antunes, P.M. Campello, R. Delgado, M.G.B. Drew, V. Félix, I. Santos, Metal
742 complexes of a tetraazacyclophane: solution and molecular modelling studies, *Dalton*
743 *Trans.* (2003) 1852–1860. <https://doi.org/10.1039/B301033C>.
744

