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9 **Simultaneous voltammetric determination of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>**  
10 **ions captured by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanostructures of various**  
11 **outer amino chain length**  
12

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30 **Abstract**

31 In the present study, we examined a novel functionalised magnetic nanoparticles  
32  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  as a nano adsorbent for binding of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  ions in an aqueous solution.  
33 First, we obtained the nanoparticles functionalised with various carbon chains containing  
34 different number of amino groups: (3-amino)propyltriethoxysilane ( $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ ),  
35 N-(2-aminoethyl)-3-aminopropyltrimethoxysilane ( $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ ) and  
36  $N^1$ -(3-trimethoxysilylpropyl)diethylenetriamine ( $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ ). In the next step, we  
37 conducted their characterisation using SEM, TEM, FT-IR, and XPS methods.

38 The detection of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  metal ions was performed under optimised  
39 experimental conditions using DPASV and HDME techniques. Using these methods we  
40 conducted the  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  binding comparison in 4.5  $\mu\text{M}$  concentration with 4 mg of  
41  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$ . Obtained results show that the adsorption rate of each ion differs due to the  
42 nanoparticles modification.

43 The highest  $\text{Pb}^{2+}$  binding capacity was achieved using  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  and  
44  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ . The smallest binding capacity was observed for  $\text{Cd}^{2+}$  ions by  
45  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ .

46 The  $\text{Cd}^{2+}$  binding was not observed for both  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$   
47 nanoparticles. Additionally,  $\text{Pb}^{2+}$  was not bound by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ . The research results show  
48 that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles bind copper ions with high selectivity.

49 For the first time we performed the adsorption-desorption experiments using DPASV to  
50 prove the  $\text{Cu}^{2+}$  binding activity of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles. Obtained results indicate that  
51 examined nanoparticles show strong binding capability. Additionally, we obtained 99.9 %  
52 recovery of  $\text{Cu}^{2+}$  ions.

53  
54  
55 **Keywords:**  $\text{Fe}_3\text{O}_4$  nanoparticles; amino-modified  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanostructures; cadmium, lead  
56 and copper ions removal, copper adsorption-desorption experiment  
57  
58

## 59 1. Introduction

60 In the last few decades we observed increasing heavy metal pollution generated by  
61 human activity - manufacturing processes such as refining and use of fertiliser and pesticides.  
62 Heavy metals have caused serious environmental concerns due to their low biodegradability,  
63 bioaccumulation tendency and mutagenicity [1,2]. Many heavy metals are regarded as  
64 carcinogens [3]. Due to the dissemination of lead in the environment and its increasing usage  
65 in industry, its carcinogenicity has been an object of interest of many research projects. Based  
66 on the experimental carcinogenicity results, the International Agency for Research on Cancer  
67 (IARC) commission classified lead and inorganic lead derivatives in 2B group, considered as  
68 possible carcinogenic to humans [4], while cadmium is classified as a human carcinogen [5].  
69 Lead does not cause cancer, but it can contribute to its development [6,7]. Cadmium causes  
70 cancer by multiple mechanism based on, among others, inhibition of DNA damage repair and  
71 oxidative stress [5]. Recycling of heavy metals from wastewater has become essential field of  
72 scientific research and industry.

73 In recent years scientists utilised many metal ion separation and removal methods,  
74 including chemical co-precipitation [8], chemical coagulation process [9], flotation [10,11] and  
75 microflotation [12] techniques, ion removal by membrane filtration [13], osmosis [14],  
76 extraction with ionic liquids [15]. Adsorption methods predominate over traditional separation  
77 techniques due to their simplicity, easy handling and sludge-free operation, regeneration  
78 capacity, and cost-effectiveness [16]. Many metal ion adsorbents are known, including pumice  
79 [17], composite mineral adsorbents [18], pectin-based adsorbents [19], organic frameworks  
80 [20], and carbonaceous materials, such as activated carbon [21], biochar [22], carbon nanotubes  
81 [23], and graphene oxide [24].

82 Nowadays, the most popular agents for wastewater ion removal are the  
83 superparamagnetic modified nanoparticle adsorbents based on iron oxide  $\text{Fe}_3\text{O}_4$  — imprinted  
84 magnetic biosorbent [25], copolymerized polyacrylamide cellulose modified nanomagnetite  
85 [26], sulfone-modified magnetic activated carbon for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{As}^{3+}$  removal [27], and  
86 many magnetic materials used for dye remediation [28–30]. The superparamagnetic  $\text{Fe}_3\text{O}_4$   
87 nanoparticles with functionalised surface adsorbent have been successfully applied to remove  
88 variety of wastewater heavy metal ions, such as copper, zinc, mercury, chromium, lead,  
89 cadmium, manganese, uranium, or silver [31–35]. Among adsorbents utilised to remove both  
90 organic and inorganic wastewater compounds, magnetic nanoparticles with large surface area,  
91 facile maintenance, and high efficiency took a special place due to the simple, convenient, and  
92 fast separation using external magnetic field [36–40]. In comparison with the traditional solvent

93 extraction, these superparamagnetic modified nanoparticle adsorption methods are more  
94 economic, more cost-effective, and environmentally friendly [41]. Many research groups  
95 focused on the amino-functionalised  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell magnetic nanocomposites as a  
96 novel adsorbent for the removal of aqueous pollutants [42,43].

97 Metals like, among others, gadolinium, technetium, iron, manganese, cobalt, gallium,  
98 play a crucial role in medicine. These elements are widely used in diagnostic procedures as, for  
99 example, radioisotope or contrast agents. Additionally, platinum, gold, silver, lithium, zinc,  
100 iron, or bismuth may also be used in a treatment of various diseases [44].

101 Metals can also be extremely toxic and cause life-threatening illnesses [45]. One of the  
102 most frequently occurring disease is Wilson's disease.

103 Wilson's disease is a rare, autosomal recessive, and lethal-without-treatment genetic  
104 disorder caused by the excessive copper storage in various body tissues. In the case of healthy  
105 individuals, we can observe a balance between intestinal absorption of dietary copper and its  
106 hepatic excretion in bile. In Wilson's disease, hepatic copper is neither excreted in bile, nor  
107 incorporated into ceruloplasmin. This abnormality causes the accumulation of copper to toxic  
108 levels and its storage mainly in liver, brain, and cornea. The signs of Wilson's disease are as-  
109 sociated with liver diseases and neurological symptoms. The diagnosis is based on the elevated  
110 urinary and hepatic copper and low ceruloplasmin levels. Management of Wilson's disease in-  
111 volves decreasing the excess levels of copper, chelation therapy, and oral zinc therapy. In some  
112 cases, liver transplantation may be necessary [46].

113 In this work, a series of silica-coated superparamagnetic  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell  
114 nanoparticles with modified surfaces differing in the number of amino groups in outer chains  
115 —  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  — (see, Figure 1) was synthesised. The  
116 characterisation of the obtained structures was performed using SEM, TEM, FT-IR, and XPS  
117 method. Subsequently, the capability of functionalised nanoparticles concerning simultaneous  
118  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  ion binding was studied using electrochemical techniques, such as DPV  
119 in combination with HMDE and preconcentration method. Finally, the adsorption-desorption  
120 experiments using DPASV method were performed for the first time to examine the  $\text{Cu}^{2+}$   
121 binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles in an aqueous solution.

122



## 123 2. Experimental

### 124 2.1. Reagents

125 All reagents, analytical grade, were purchased from the indicated suppliers and used  
126 without further purification. Aqueous solutions were prepared using ultra-pure deionised water.  
127 Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ),  
128 ammonia (25%), tetraethyl orthosilicate (98 %) (TEOS), 3-(aminopropyl)triethoxysilane  
129 (APTES) (99 %), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and  
130  $N^1$ -(3-trimethoxysilylpropyl)diethylenetriamine were purchased from Sigma-Aldrich (Poland).  
131 The organic solvents, potassium chloride KCl (99.9 %), cadmium nitrate tetrahydrate  
132  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99.9 %), lead nitrate  $\text{Pb}(\text{NO}_3)_2$ , and copper nitrate trihydrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$   
133 (99.9 %) were purchased from POCh (Poland).

134

### 135 2.2. Synthesis of $\text{Fe}_3\text{O}_4$

136  $\text{Fe}_3\text{O}_4$  nanoparticles were obtained by the coprecipitation method in an aqueous solution  
137 according to the procedure described by Panta et al. [47]. The reaction was performed in non-  
138 oxidising conditions maintaining the precise 1 to 2 molar ratio of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in an alkaline  
139 solution. The advantages and disadvantages of the synthesis reducing conditions were  
140 previously described by Kim [48]. The  $\text{Fe}_3\text{O}_4$  nanoparticles were obtained by dissolving  
141 10.81 g (0.04 mol) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 3.98 g (0.02 mol) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 50 mL of deionised  
142 water. Next, argon was passed through the vigorously stirred solution to eliminate oxygen and  
143 then the reaction mixture was heated to 70 °C. When the set temperature was reached, 500 mL  
144 of ammonium hydroxide solution was added dropwise up to pH 11, what resulted in the  
145 formation of  $\text{Fe}_3\text{O}_4$ . Obtained nanoparticles were washed with water to neutralise pH, washed  
146 with methanol, and dried.

147

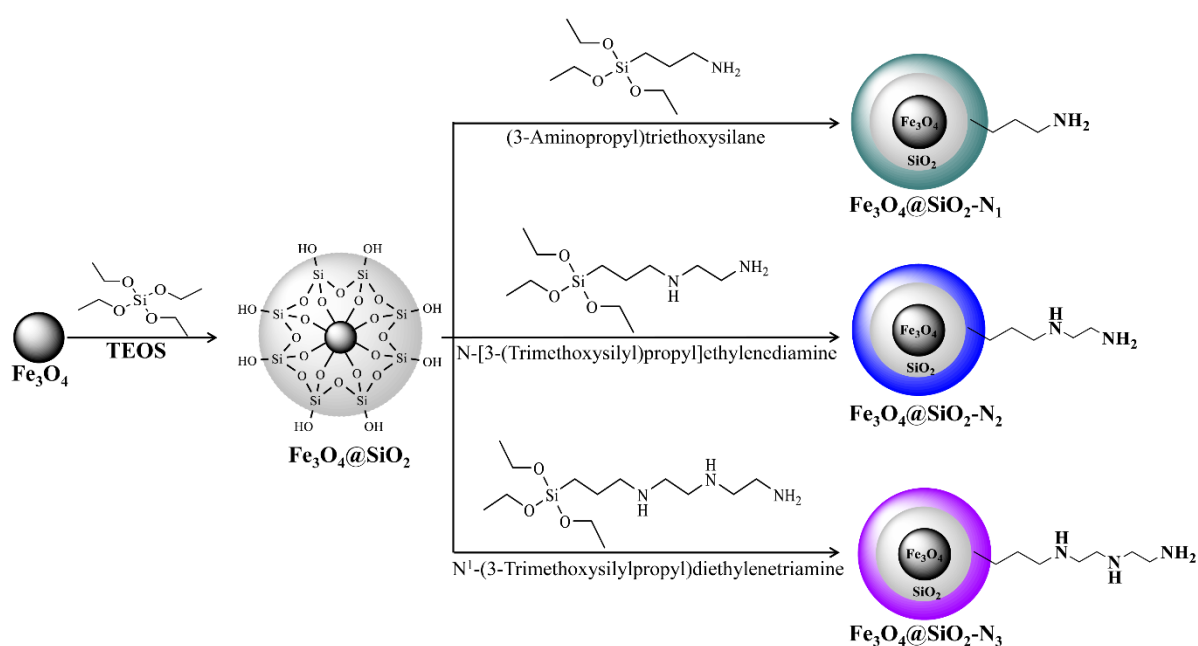
### 148 2.3. Synthesis of core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles

149 Synthesis of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was conducted according to Ströber procedure, which mechanism  
150 and optimisation were widely described in the literature [47,49–52]. 0.1 g of  $\text{Fe}_3\text{O}_4$   
151 nanoparticles was dispersed in the mixture of ethanol and water (60:10, v/v) using an ultrasonic  
152 bath for 15 min. Subsequently, 1 mL of ammonium hydroxide and 2 mL of tetraethyl  
153 orthosilicate (TEOS) were added dropwise to the stirring solution at room temperature. After  
154 24 h, the obtained nanoparticles were washed with water and ethanol and dried in vacuum at  
155 60 °C.

156

## 157 2.4. Modification of core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles by amine derivatives

158 The functionalisation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles by amine derivatives was performed in  
159 anhydrous toluene [53–55] to achieve optimal surface coverage. 4 mL of 3-amino propyl-  
160 triethoxysilane (APTES), N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, or  
161  $N^1$ -(3-trimethoxysilylpropyl) diethylenetriamine was added to 0.5 g of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$   
162 nanoparticles dispersed in 100 mL of anhydrous toluene using ultrasonic bath. Then, the  
163 mixture was mechanically stirred for 12 h at 90 °C. After cooling to room temperature, the  
164 obtained  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  amino derivatives ( $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ , or  
165  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ ) were magnetically collected, washed several times using absolute ethanol,  
166 and dried under vacuum at 50 °C (Figure 1).



167

168 **Figure 1.** Scheme of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles synthesis.

169

## 170 2.5. Methods

171 The images of all  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles were obtained using the scanning  
172 electron microscope (SEM) — JEOL JSM7001F, operating at 9.5 kV — and transmission  
173 electron microscopy (TEM) — Tecnai G2 Spirit BioTWIN FEI, operating at 120 kV. All  
174 nanoparticles samples for TEM imaging were sonicated for 30 min in the absolute ethanol  
175 solution.

176 Fourier Transform Infrared Spectroscopy (FT-IR) spectra were obtained with the KBr  
177 pellet method using Bruker FRA 106 spectrometer.

178 X-Ray Photoelectron Spectroscopy (XPS) was utilised to evaluate the chemical  
179 composition of the investigated nanoparticles. For this purpose, the high-resolution scans were  
180 performed in Fe2p, C1s, O1s, N1s, and Si2p binding energy range. The measurements were  
181 carried out on Escalab 250Xi spectroscope, ThermoFisher Scientific. The monochromatic  $\text{AlK}\alpha$   
182 excitation source was used with a spot diameter of 250  $\mu\text{m}$ . 10 eV pass energy and 0.05 eV  
183 energy step size were utilised. The charge compensation was achieved through the low-energy  
184 electron and low-energy  $\text{Ar}^+$  ions flow, with the final calibration of the XPS spectra for peak  
185 characteristics adventitious carbon C1s at 284.7 eV. The peak deconvolution was carried out  
186 using Avantage software provided by the spectroscope manufacturer.

187 All electrochemical measurements were carried out using Mercury Electrode Metrohm  
188 663 VA Stand integrated with Autolab potentiostat/galvanostat PGSTAT-128N controlled with  
189 NOVA 2.1.4 software. The three-electrode cell contained Static Drop Mercury Electrode  
190 (SDME) as a working electrode. Calomel  $\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{KCl}_{(\text{saturated})}$  and glassy carbon (GC) were  
191 used as the reference and counter electrode, respectively.

192 Differential pulse voltammetry (DPV) was utilised for the detection of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  
193  $\text{Cd}^{2+}$  ions under optimised experimental conditions: deposition potential -0.9 V, deposition time  
194 90 s, modulation amplitude 0.05 V, modulation time 0.07 s, interval time 1.85 s, and step  
195 potential 0.005 V. All measurements were conducted in Teflon cell to avoid a sorption of metal  
196 ions on the glass surface.

197 The ion detection was performed in a potential range of -0.8 V to 0.0 V. The solutions  
198 of metal ions were prepared using potassium chloride KCl, pH 6.5 as the supporting electrolyte.  
199  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles were prepared by dispersion using the ultrasonic bath for 30 min  
200 before each measurement.

201  
202  
203

## 204 **2.6. Determination of removal efficiency**

205 The adsorption-desorption experiment was conducted to examine the efficiency of  $\text{Cu}^{2+}$   
206 removal from an aqueous solution. The ion desorption process was investigated in 0.1 M HCl  
207 solution which was used as a desorbing agent. 5.08 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  was used to capture  
208 copper ions present in 10 mL of 4.3  $\mu\text{M}$   $\text{Cu}^{2+}$  solution. The solution was then left for 40 min at  
209 room temperature with shaking. Subsequently, all nanoparticles were collected magnetically  
210 and the supernatant was removed. Then, 10 mL of 0.1 M HCl was added to  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$   
211 nanoparticles with adsorbed  $\text{Cu}^{2+}$  and mixed with a stream of argon. The measurement of  
212 desorbed  $\text{Cu}^{2+}$  concentration was performed immediately using DPASV technique. The removal  
213 efficiency was calculated by the determination of the obtained voltammograms peak area for  
214 the standard solution and after desorption in 0.1 M HCl.

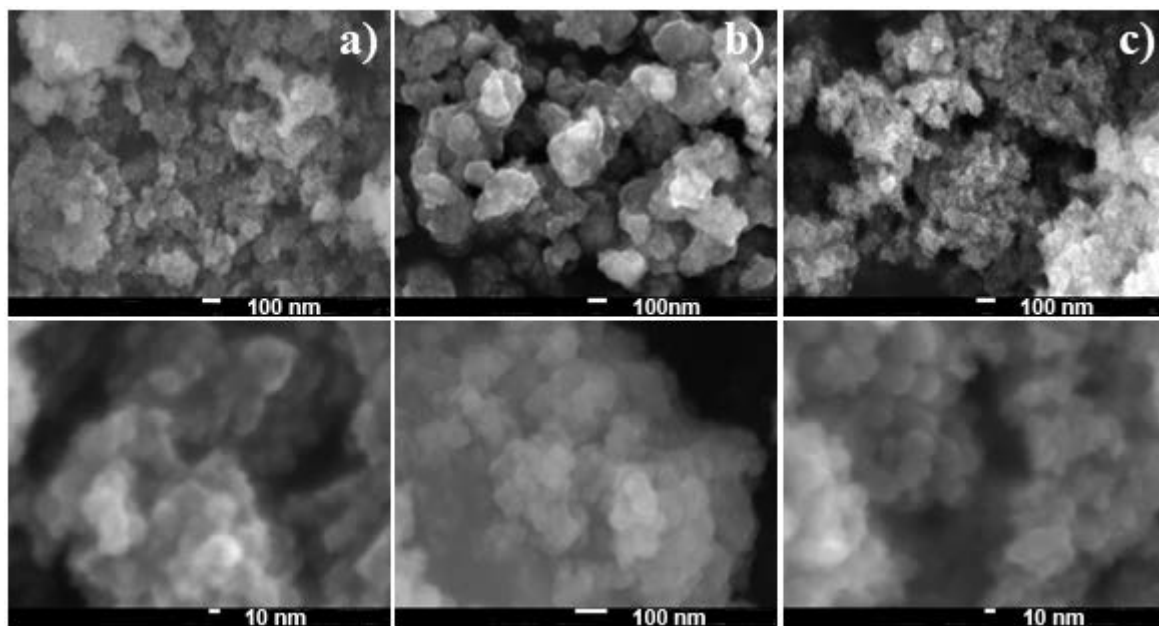
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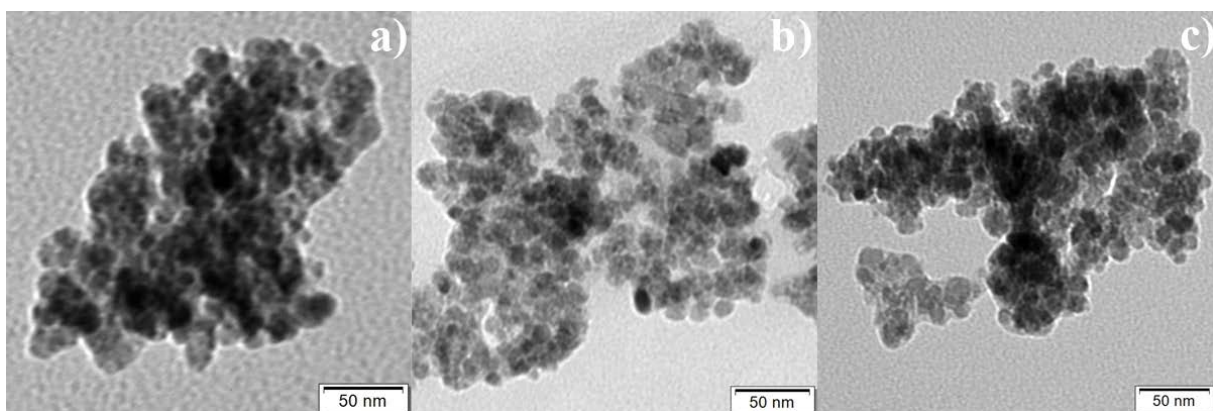
216 **3. Results and discussion**

217 **3.1. SEM and TEM — Morphology analysis**

218 In the first step, the obtained  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles were characterised using  
219 Scanning Electron Microscopy and Transmission Electron Microscopy (Figure 2). SEM and  
220 TEM images of magnetite nanoparticles modified with different length of amino chains showed  
221 that the nanostructures received by co-precipitation method are highly homogeneous in shape  
222 and size. Figure 3 confirms the presence of small and quasi-spherical core-shell structures. The  
223 average size of all  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles was approximately 30 – 50 nm. All of the  
224 examined nanoparticles were in the agglomerated state due to their natural tendency to form  
225 agglomerates based on their magnetic nature.



226 **Figure 2.** SEM images of: column a)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ , column b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ ,  
227 and column c)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ .  
228



229 **Figure 3.** TEM images of: a)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ , b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ , and c)  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ .  
230  
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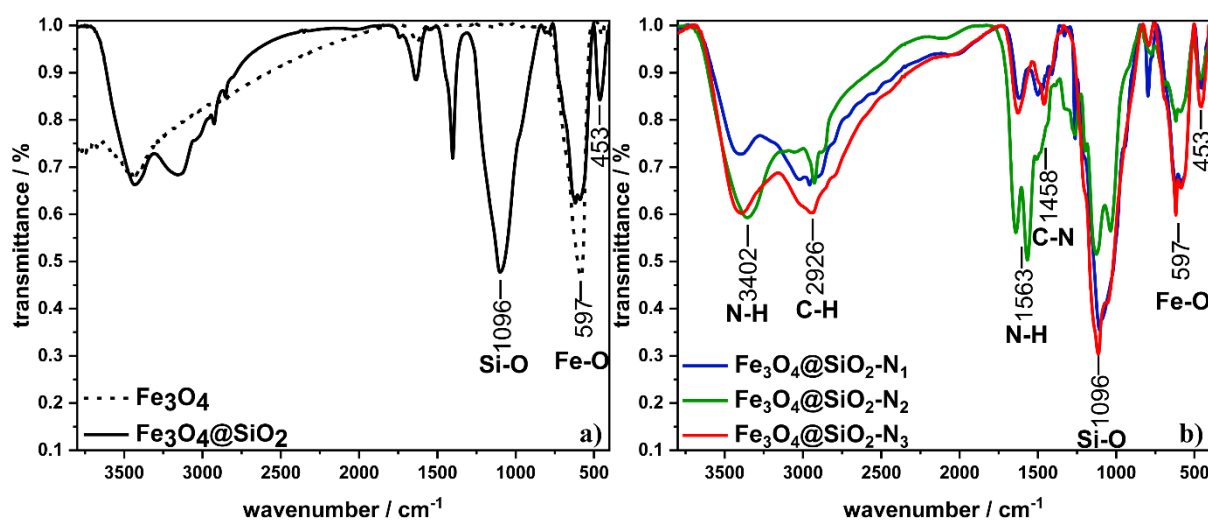
### 3.2. FT-IR spectroscopy analysis

The FT-IR spectra were obtained to compare the spectroscopic differences and to validate the presence of functional groups on the nanomagnetite surface. Figure 4 a) shows the FT-IR spectra for pure  $\text{Fe}_3\text{O}_4$  nanoparticles and silica-coated  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  as a reference and for nanoparticles functionalised by amino groups  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-N}_1$ ,  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-N}_2$ , and  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-N}_3$ . For all samples, two characteristic bands were shown at wavenumbers  $453 \text{ cm}^{-1}$  and  $597 \text{ cm}^{-1}$  from metal-oxygen stretching at  $\text{Fe}^{3+}$  site [56–58]. In all IR spectra, the decrease in the intensity of the Fe-O band for nanoparticles coated with silica and amino groups was observed. The decrease in the band intensity confirms that the nanoparticles surface was successfully functionalised [59]. Spectra for silica-coated nanoparticles showed a broad, strong band near  $1096 \text{ cm}^{-1}$  region assigned to symmetric and asymmetric Si-O-Si stretching vibrations caused by the coating of silica shells on the magnetite surface [60].

On the spectra of all amino-modified nanoparticles (Figure 4 b) a new band appeared in the region of  $1563 \text{ cm}^{-1}$  and  $3402 \text{ cm}^{-1}$  attributed to N-H stretching vibrations of amino groups. These bands confirm the successful amino-functionalisation of the silica layer on  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  nanoparticles and the presence of terminal  $-\text{NH}_2$  [61,62].

Additionally, a weak band at  $1458 \text{ cm}^{-1}$  attributed to the C-N stretch vibration was noticed [63]. The absorption bands at about  $2930 \text{ cm}^{-1}$  and  $2850 \text{ cm}^{-1}$  are the result of C-H stretching vibrations in the carbon chain [64].

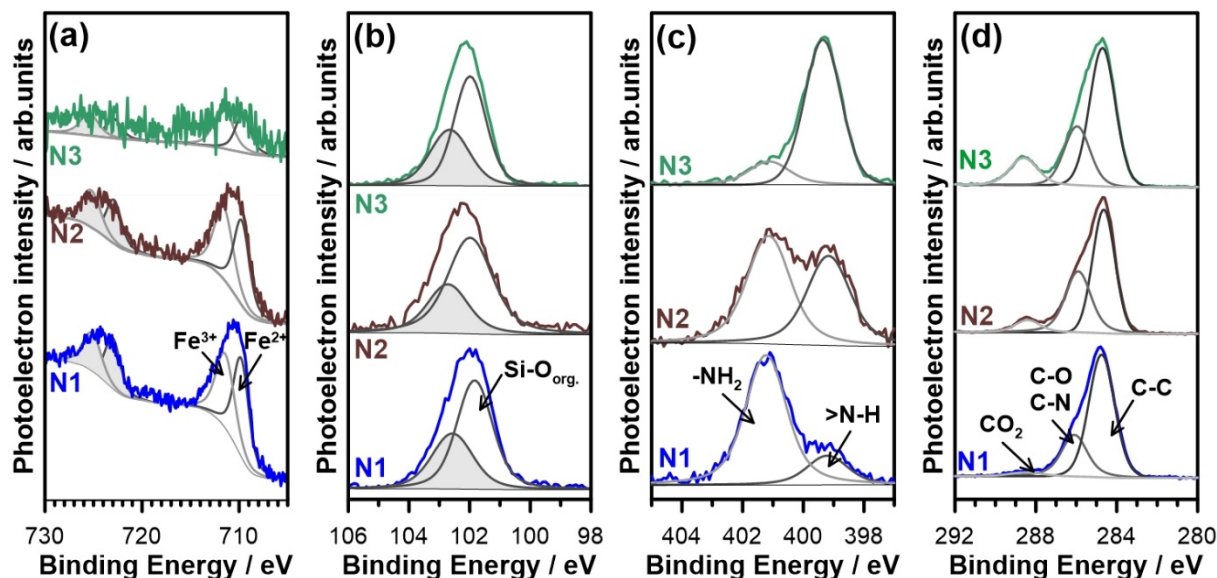
These FT-IR spectra confirmed the formation of a silica shell on the surface of  $\text{Fe}_3\text{O}_4$  and the amino-functionalisation of the  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  core-shell nanostructures.



**Figure 4.** FT-IR spectra for non-functionalised a)  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  and b) functionalised  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-N}_1$ ,  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-N}_2$ , and  $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-N}_3$  nanoparticles.

### 257 3.3. XPS analysis

258 Moreover, we performed the XPS analyses for all obtained samples to confirm the  
 259 structure of formed core-shell nanoparticles. The results of the high-resolution XPS analysis  
 260 are collectively presented in Figure 5 and Table 1 for each of the analysed samples.



261 Figure 5. High-resolution XPS spectra obtained for each investigated nanoparticle  
 262  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ , and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  within the analysed binding energy  
 263 range: (a)  $\text{Fe}2p$ , (b)  $\text{Si}2p$ , (c)  $\text{N}1s$ , and (d)  $\text{C}1s$  with superimposed deconvolution according to  
 264 the model described below. The grey areas represent the  $\text{Fe}2p_{1/2}$  and  $\text{Si}2p_{1/2}$  peaks in  $\text{Fe}2p$  and  
 265  $\text{Si}2p$  peak doublets, respectively.  
 266

267  
 268 The deconvolution in  $\text{Fe}2p$  binding energy (BE) range can be carried out with two spin-  
 269 orbit doublets, characteristic for both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Furthermore,  $\text{Fe}2p$  signal for  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$   
 270 was barely detected [65–67]. The peak position remains unaltered for each studied  
 271 compound, proving that modification of the organic chain does not influence the inner shell  
 272 structure. Similar to the case of  $\text{Fe}_3\text{O}_4$ , the amount of silica is at its peak for  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$   
 273 functionalisation. Moreover, the significant differences were not observed between  
 274  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  samples in this case, what may imply that the thickness  
 275 of the organic amino shell is similar for both of these nanoparticles.

276 The shape of recorded  $\text{N}1s$  spectra reveal major differences between the analysed  
 277 samples. Each of the nanoparticles contains nitrogen in two different chemical states, while  
 278 their quantity differs significantly. Two deconvolution spectra used in the proposed model peak  
 279 at 399.2 and 401.2 eV. The peak at higher BE's, dominant in the case of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$   
 280 sample, should represent the terminal amino- $\text{NH}_2$  functional groups in the compound. The

281 presence of >N-H tertiary amino groups in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> nanoparticles  
282 is reflected in *N1s* spectra with the increasing contribution of the component, located at lower  
283 binding energy range. Here, the share of terminal amino groups is reduced to 45 % for  
284 Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> and to 18 % for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> samples. The aforementioned model finds a  
285 good correlation with the literature findings. The presence of N-H groups in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub>  
286 can be associated with the adsorption of CO<sub>2</sub> from the ambient atmosphere [68–70].

287 The presence of Si-O bonds with the organic chain was confirmed by a strong peak  
288 doublet at 101.7 eV. Similar values were previously reported for silicone groups in silanes and  
289 other organic, silicon-containing compounds [58,71]. Finally, the *C1s* peak region was analysed  
290 and deconvoluted in three different chemical states. The most significant component, detected  
291 at 284.7 eV, should be ascribed to C-C and C-H bonds in the functionalisation molecules  
292 forming the shell of the nanoparticles. Its total share in the analysed signal ranges between 33.3  
293 and 36.8 at.%. Importantly, the presence of the component mentioned above may be caused by  
294 adventitious carbon from the air exposure [72]. The second notable component lies at 286.2 eV,  
295 an energy range typical for C-N bonds in amines and C-O bonds [73,74]. The share of the  
296 organic chain (measured as a sum of C-C and C-N components) is naturally the most prominent  
297 for the shortest amino chains with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub> molecule functionalisation. However, the  
298 significant differences were not observed between Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub>  
299 samples, what is similar to the earlier conclusion regarding *Si2p* component. Finally, the last  
300 *C1s* peak emerges for both Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> samples, at energies  
301 exceeding 288 eV. This component is most often ascribed to carbon dioxide, which is probably  
302 adsorbed onto the nanoparticles surface [75]. Surface defects as well as structure modifications  
303 of the examined compounds influence the CO<sub>2</sub> adsorption [76,77]. Since its contribution is the  
304 highest for the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> sample, it is suggested that its presence is connected with  
305 changes within >NH groups.

306 These analyses are confirmed in the distribution of various components in *O1s* spectra,  
307 which were deconvoluted in three peaks, connected with iron oxides (529.9 eV), silica, and  
308 possible C-O interaction (531.7 eV) and C=O bonds (533.5 eV). The Fe<sub>3</sub>O<sub>4</sub> signal is the  
309 strongest for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub> sample and is up to four times weaker for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub>,  
310 where, on the other hand, the signal from C=O bonds is more prominent. The two times higher  
311 contribution from silica in the *O1s* of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub> sample was also confirmed, strongly  
312 supporting the hypothesis regarding the smaller functionalisation thickness of these  
313 nanoparticles.

314

315 **Table 1.** Surface chemical composition of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub>, and  
 316 Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> samples based on the deconvoluted high-resolution XPS spectra.

BE / eV	<i>Fe2p</i>		<i>Si2p</i>	<i>N1s</i>		<i>C1s</i>			<i>O1s</i>		
	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Si-O	>NH	-NH <sub>2</sub>	C-C	CN	C=O	Fe-O	Si-O	C=O
	709.8	711.4	101.7	399.2	401.2	284.7	286.1	288.5	529.9	531.7	533.5
N <sub>1</sub>	1.1	1.0	13.0	1.3	5.7	33.3	12.8	1.3	4.0	25.3	1.2
N <sub>2</sub>	0.7	0.7	7.9	2.8	3.4	34.2	22.0	4.4	2.6	16.9	4.3
N <sub>3</sub>	0.1	0.1	7.9	8.2	1.7	36.8	16.1	8.0	0.9	17.0	3.1

317

318

### 3.4. Simultaneous electrochemical determination of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>

The individual and simultaneous determination of Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Pb<sup>2+</sup> applying amino-functionalised Fe<sub>3</sub>O<sub>4</sub>@Carbon microspheres were previously measured by Bai et al. [78] using modified glassy carbon electrode.

In this work, the simultaneous detection of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> was carried out under optimised experimental conditions using DPASV technique and HDM electrode. The main advantage of these electrodes, besides its surface reproducibility and fast measurement, [79] is the analysis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>n</sub> nanoparticles to assess their capability for binding the metal ions without electrode modification. We investigated three types of nanoparticles differing in the number of amino groups in the outer carbon chain — Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub> with one amino group, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> with two amino groups, and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> with three amino groups.

To achieve this goal, all measurements were conducted under laboratory conditions to reduce the risk of environmental mercury contamination. Mercury from HDME can be reused after proper treatment. Two-stage DPASV analysis involved pre-concentration and metal ions stripping. First, the Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> ions were electrodeposited onto the working electrode by application of the negative potential (-0.9 V). Subsequently, the faradic current obtained by oxidation was recorded during the potential sweep toward the anodic direction (-0.8 V to 0.0 V).

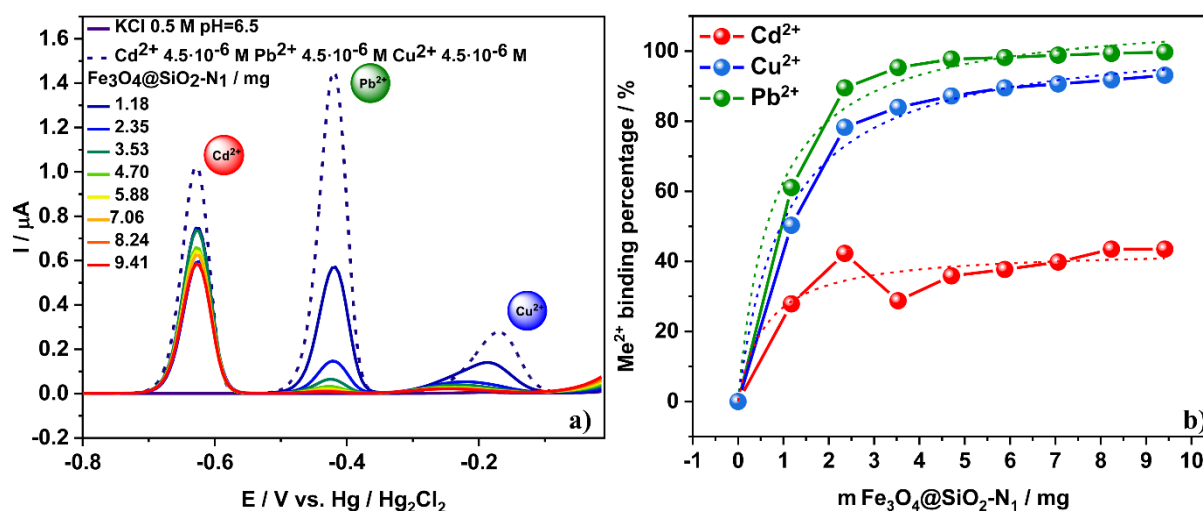
To examine the selected ion binding abilities of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub>, series of measurements were performed in the solution containing Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>, 4.5 μM concentration. All electrochemical experiments were performed in 0.5 M KCl pH = 6.5 due to the formation of hydroxides of utilised metals at pH higher than 7 [58]. Furthermore, the adsorption of metal ions depends on the charge located on the nanocomposite surface and the number of functional groups [80].

Three well-defined peaks at -0.63 V, -0.42 V, and -0.17 V in anodic stripping voltammograms confirm the presence of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> in the solution, respectively (see, Figure 6). During the next portions of nanoparticles addition, a decrease in the intensity of the ions peaks was observed. The rate of peaks intensity change depended on the determined ion and used nanoparticles type. In all presented voltammograms, the dilution factor was expressed by the formula:  $DF = \frac{V_0 + V_s}{V_0}$ , where V<sub>0</sub> is the initial volume and V<sub>s</sub> is the step volume applied.

Figure 6 a) presents the voltammograms obtained during the titration of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub>. The metal ion peaks intensity decreased during the addition of the next portions of nanoparticles in an amount of 1.18 mg to 9.41 mg, conducted in eight steps.

351 The obtained results directly indicate that the initial linear current peak (blue intermittent line)  
352 decreases for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions of each nanoparticles portion.

353 The intensity of  $\text{Cd}^{2+}$  peak decreased by a half and remained at this stable level. After  
354 the addition of 7.06 mg of nanoparticles, the equilibrium was established and the next portion  
355 of nanoparticles caused no changes in the current peak intensity. The  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  binding  
356 percentage was calculated (Figure 6 b) for  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  and reached 99.7 % and 92.8 %,  
357 respectively. However, the binding percentage for  $\text{Cd}^{2+}$  remained stable at the level of 40 %.  
358 These results indicate that  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  nanoparticles express high sensitivity towards  $\text{Pb}^{2+}$   
359 and  $\text{Cu}^{2+}$ , what is observed by binding of these ions in nearly 100 %.



360  
361 **Figure 6.** a) Anodic stripping voltammograms and b) percentage of  $\text{Cd}^{2+}$  (4.5 μM),  
362  $\text{Pb}^{2+}$  (4.5 μM) and  $\text{Cu}^{2+}$  (4.5 μM) binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  nanoparticles.

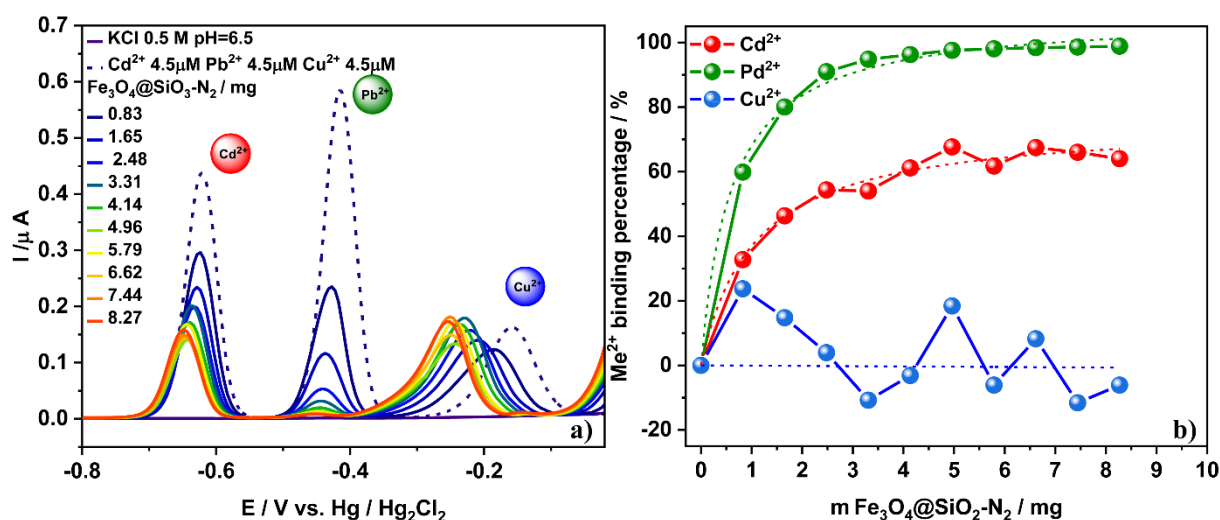
363  
364 In the next step, we conducted the simultaneous experiments using  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$   
365 to evaluate the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  nanoparticles binding capacity. The titration of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  
366  $\text{Cu}^{2+}$  was carried out in five steps using various amounts of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  nanoparticles —  
367 0.83 mg to 8.27 mg (Figure 7a).

368 Surprisingly, besides a decrease in the peak intensity observed during  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$   
369 titration, we also detected a slight shift in the peaks towards lower potentials. Figure 7a shows  
370 the voltammograms where a complete disappearance of  $\text{Pb}^{2+}$  peak and decrease in the  $\text{Cd}^{2+}$   
371 peak intensity were observed.

372 In the case of  $\text{Cu}^{2+}$  titration (Figure 7a), the effect of the signal decreasing is observed  
373 only in the first two steps, following a comparable signal level afterwards, shifted toward  
374 negative potentials. This phenomenon is probably associated with the adsorption of

375 nanoparticles and their complexes to the mercury drop [81]. The irregular changes in the peak  
 376 intensity clearly indicate that the equilibrium is not establishing.

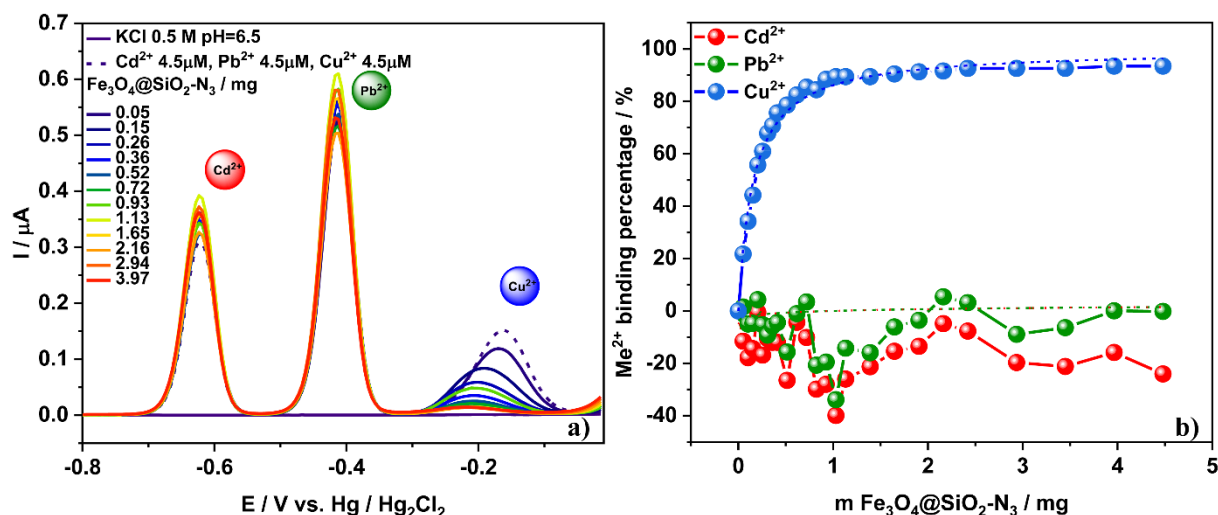
377 After addition of 3.31 mg  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  no significant changes in the voltammogram  
 378 were observed. Figure 7b shows the binding percentage for  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  nanoparticles. The  
 379 percentage of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ion binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  was established at 98.5 % and  
 380 66.6%, respectively. It is worth to notice that there was no ion binding observed for  $\text{Cu}^{2+}$ . The  
 381 percentage of  $\text{Cu}^{2+}$  binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  remains at 0 % even if nanoparticles were added  
 382 in an excess. An average of obtained results and slight differences in  $\text{Cu}^{2+}$  peak intensity were  
 383 regarded as measurement errors.



384  
 385 **Figure 7.** a) Anodic stripping voltammograms and b) percentage of  $\text{Cd}^{2+}$  (4.5  $\mu\text{M}$ ),  
 386  $\text{Pb}^{2+}$  (4.5  $\mu\text{M}$ ), and  $\text{Cu}^{2+}$  (4.5  $\mu\text{M}$ ) binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  nanoparticles.

387  
 388 The voltammograms presented in Figure 8a reveal the  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  titration by  
 389  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  in twelve steps in the nanoparticles amount range of 0.05 mg to 3.97 mg. The  
 390 addition of the next nanoparticles portions led only to the disappearance of the  $\text{Cu}^{2+}$  peak. The  
 391  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  slight peak intensity changes were considered to be in the range of measurement  
 392 error. For  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles, the  $\text{Cu}^{2+}$  binding percentage reached 92.5 %, while  
 393 0 % binding percentage was observed for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions (Figure 8 b).



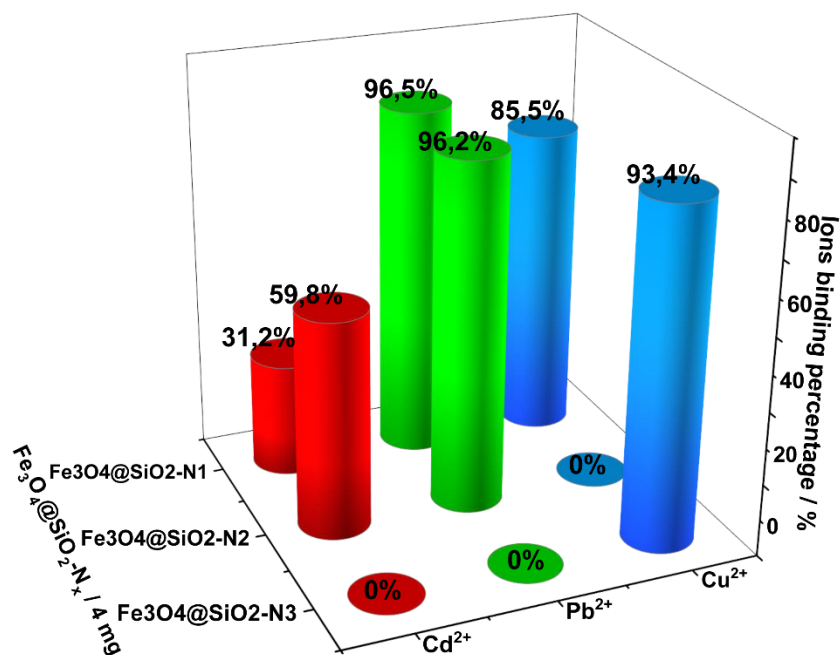


394  
 395 **Figure 8.** a) Anodic stripping voltammograms and b) percentage of  $\text{Cd}^{2+}$  (4.5  $\mu\text{M}$ ),  
 396  $\text{Pb}^{2+}$  (4.5  $\mu\text{M}$ ), and  $\text{Cu}^{2+}$  (4.5  $\mu\text{M}$ ) binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles.

397  
 398 Figure 9 presents the comparison of ion binding percentage for each  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$   
 399 nanoparticle. The binding percentage was recounted for 4 mg of nanoparticles added to the ion  
 400 solution. The highest observed binding percentage for  $\text{Pb}^{2+}$  was over 96%, both for  
 401  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ . The slightly smaller binding percentage was observed  
 402 for  $\text{Cu}^{2+}$  binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  resulting in 93.4 % and 85.5 %, respectively.

404 Furthermore, there was no  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  binding observed for  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ ,  
 405  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ , and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ , respectively. These results directly indicate that the  
 406  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles bind  $\text{Cu}^{2+}$  with high selectivity.

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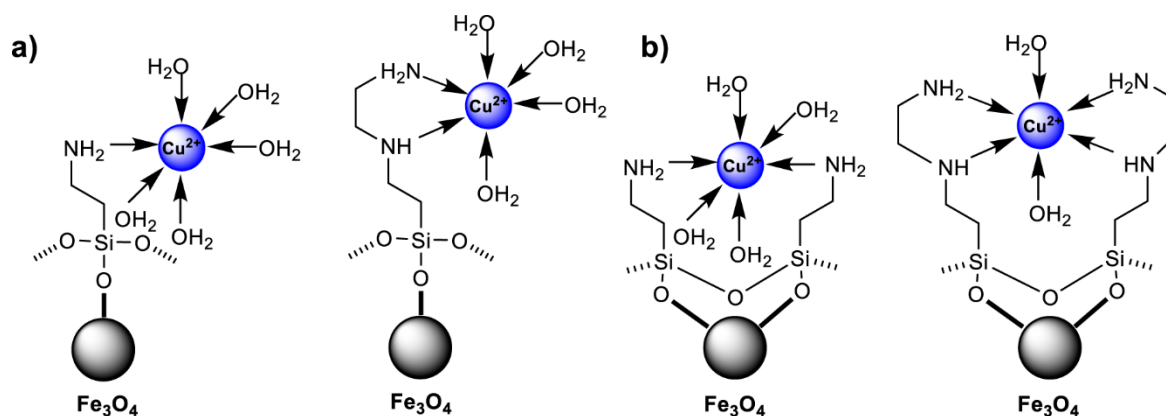
**Figure 9.** Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> ions binding percentage for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> nanoparticles

414 On the basis of the structural characteristics of Cu (II) diamine complexes supported on  
415 silica gel and the distribution of these forms as a function of the pH solution described by  
416 Nowicki [82], the proposed structure of copper complex formation by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>n</sub> is pre-  
417 sented in Figure 10. It seems that formation of complexes with metal ions with 1:1 and 1:2  
418 stoichiometry is the key factor in the complexation of ions by amines in the hybrid material  
419 (Figure 10).

420 The number of donor nitrogen atoms in the structure of the complexes, the size of the  
421 ions, the density of the charge of metal ions, and the number of water molecules that hydrate  
422 both the complexes and ligands significantly determine the stoichiometry and the process of  
423 complex formation by the hybrid material [83].

424 The differences in the binding selectivity for the examined metal ions by  
425 Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>n</sub> is probably related to the presence of intramolecular hydrogen bonds occurring  
426 both in the external and internal parts of the functional layer. The observation that  
427 Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>1</sub> binds Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>2</sub> binds Cd<sup>2+</sup>, Pb<sup>2+</sup>, and  
428 Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-N<sub>3</sub> binds only Cu<sup>2+</sup> results from these interactions. The aqua and amino com-  
429 plexes form between metal ions and amines with the deposition directly on a hybrid material.  
430 Subsequently, free electron pairs in this material, which come to varying degrees from nitrogen

431 atoms of amines, determine the manner and selectivity of the ion binding with the studied ma-  
432 terial.



433  
434 **Figure 10.** Proposed structure of the two-type complexes a) 1:1 and b) 1:2  $\text{Fe}_3\text{O}_4@SiO_2-N_n$   
435 nanoparticles and ion metal interactions.

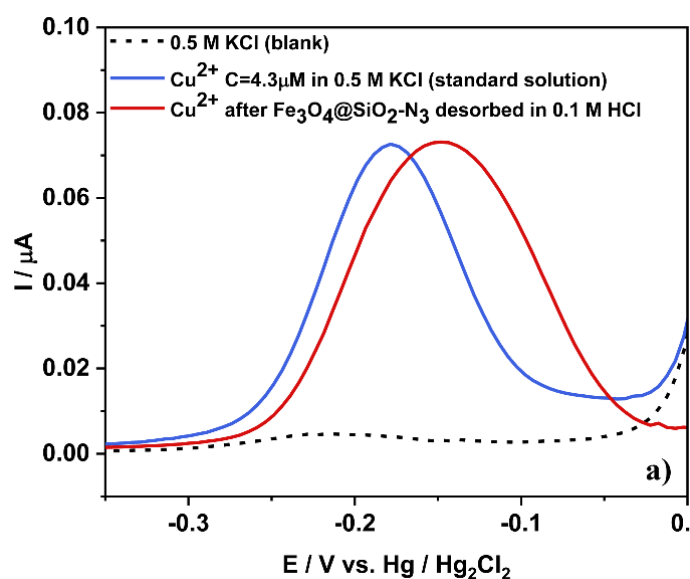
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### 437 3.5. $\text{Cu}^{2+}$ adsorption-desorption experiment using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ nanoparticles

438

439 Based on the high selectivity of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  for  $\text{Cu}^{2+}$  which was observed using  
440 electrochemical method, we decided to evaluate the adsorption-desorption properties only of  
441 this studied nanoparticle. It is worth to notice that, according to the authors' knowledge, this  
442 experiment using DPASV was performed for the first time. The procedure of  $\text{Cu}^{2+}$  adsorption  
443 was described in the experimental section. 5.08 mg of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  was used to bind  
444 43 nmol of  $\text{Cu}^{2+}$  in 0.5 M KCl solution. The adsorption process for nanoparticles containing an  
445 amino group is usually performed from a couple of minutes to hours [84–86,43]. In this work,  
446 the adsorption process was performed within 40 min incubation time at room temperature, with  
447 shaking. The desorption process was performed in 0.1 M HCl to obtain acidic pH and  
448 protonation of amino groups leading to the  $\text{Cu}^{2+}$  ions desorption. The desorption process was  
449 conducted using DPASV method directly after the addition of HCl. According to the previous  
450 research, the hydrochloric acid was selected as an optimal desorption agent [61,84]. In other  
451 study the desorption time ranged from 5 min to 40 min [43,85]. We, however, established the  
452 desorption time which was shorter than 5 minutes. Figure 11 shows the voltammograms  
453 obtained for standard  $\text{Cu}^{2+}$  solution and after the nanoparticles regeneration. The peak shift is  
454 the consequence of different pH of the solution. The calculated  $\text{Cu}^{2+}$  removal efficiency was  
455 99.9 %.

456



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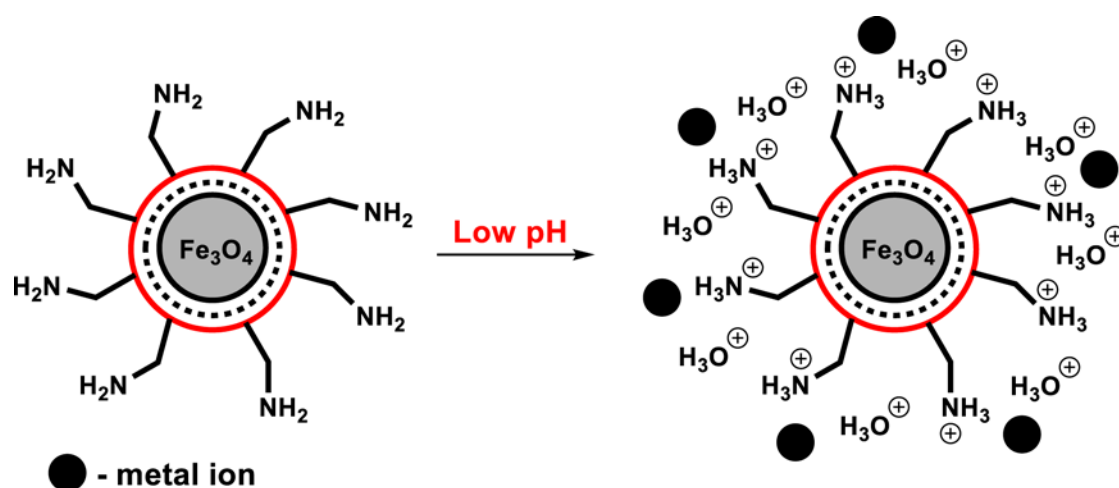
458 **Figure 11.** Comparison of anodic stripping voltammograms of 0.5 M KCl electrolyte (blank),

459  $\text{Cu}^{2+}$  standard solution  $C = 4.3 \mu\text{M}$ ,  $\text{Cu}^{2+}$  after  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  nanoparticles regeneration.

460

461 Proper selection of pH range, which effects the behaviour of the nanoparticles, the form  
 462 of determined metal ion, and its solubility, is the most important factor for the examination of  
 463 the adsorption and desorption process efficiency [86]. The form of  $\text{Cu}^{2+}$  depends on the pH  
 464 value of the solution.  $\text{Cu}^{2+}$  species occur at  $\text{pH} < 7$  [84,87]. At  $\text{pH} > 7$  different derivative  
 465 products of  $\text{Cu}^{2+}$  hydrolysis —  $\text{Cu}_2(\text{OH})_2^{2+}$ ,  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_3^-$ ,  $\text{Cu}(\text{OH})_4^-$  — exist  
 466 in the solution [88]. The  $\text{Cu}^{2+}$  quantity drops with the increasing pH value, what leads to the  
 467 precipitation of various hydrolysis forms of  $\text{Cu}^{2+}$ . Due to this phenomenon, the adsorption  
 468 process was performed at pH 6.5.

469 The adsorption and desorption process occurring for the studied nanoparticles is the  
 470 consequence of the acid-base interactions. In an aqueous solution both  $\text{H}_3\text{O}^+$  and metal ions  
 471 undergo the adsorption processes onto amino groups present in  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles  
 472 (Figure 12). Low pH value causes the increase of  $\text{H}_3\text{O}^+$  species in a solution and the protonation  
 473 of amino groups present on the nanoparticles surface. This, in consequence, leads to the  
 474 decrease in the metal ion concentration due to the nanoparticle adsorption (Figure 12). On the  
 475 other hand, high pH value is associated with the elevated number of hydroxyl groups in the  
 476 solution, what causes the amino groups deprotonation (Figure 12). In consequence, the  
 477 deprotonated amino groups increased the capability of the nanoparticles to bind metal ions [86].  
 478



479  
 480 **Figure 12.** Scheme of the proposed adsorption and desorption mechanism for  
 481 the  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles — metal ions interaction.  
 482

#### 483 4. Conclusions

484 In present work we examined a series of functionalised magnetite nanoparticles  
485  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  as a novel  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  nano-adsorbent in KCl aqueous solution.

486 First, we synthesised the nanoparticles coated preliminary with  $\text{SiO}_2$  using TEOS and  
487 then with various carbon chains containing a different number of amino groups —  
488  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ , and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ . FT-IR and XPS spectra confirmed the  
489 presence of characteristic functional groups on the nanoparticles surface. Additionally, SEM  
490 and TEM analysis were utilised to confirm the homogenous spherical 30 to 50 nm  
491 nanostructures.

492 These three types of obtained nanoparticles were used as  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  metal ion  
493 adsorbents. Metal ion binding ability of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  was measured using DPASV method  
494 in combination with HDME in 0.5 M KCl solution.

495 To compare binding capacity in 4.5  $\mu\text{M}$   $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  solutions, the binding  
496 percentage was recalculated for 4 mg of used nanoparticles. Obtained results show that the  
497 adsorption rate is different for each ion depending on the nanoparticles type. The ion binding  
498 capacity and selectivity depends on the interactions occurring between the outer carbon amino  
499 chains and the metal ion.

500 The highest binding percentage — 96 % — was observed for  $\text{Pb}^{2+}$  binding for both  
501  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$ . Furthermore, slightly lower binding level of nearly 93 %  
502 was observed for  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$   $\text{Cu}^{2+}$ . The middle value of the binding percentage — 85% —  
503 was observed for  $\text{Cu}^{2+}$  binding by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$ . The lowest binding percentage was found  
504 in the case of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_1$  for  $\text{Cd}^{2+}$  at the level of 60% and 31%,  
505 respectively. Moreover, the binding was not observed for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$   
506 and for  $\text{Pb}^{2+}$  by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ . The obtained results show that the nanoparticles with three  
507 amino groups in the outer chain —  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$  — bind  $\text{Cu}^{2+}$  with high selectivity.

508 Furthermore, we used the adsorption and desorption experiment to analyse the  $\text{Cu}^{2+}$   
509 binding selectivity of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_3$ . The obtained results directly indicate that the recovery  
510 of  $\text{Cu}^{2+}$  from the aqueous solution is very high and reached 99.9%.

511 Examined series of amino functionalised  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-N}_n$  nanoparticles are promising  
512 metal ion nano-adsorbents due to their high ion capacity, easy separation using magnetic field,  
513 and renewability based on the pH value control.

514

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## 521 **6. References**

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