Organosilane-functionalized graphene oxide hybrid material: Efficient adsorbent for heavy metal ions in drinking water

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ABSTRACT
Organosilane-functionalized and chemically activated graphene-supported Schiff base ligand were synthesized and characterized with XRD, SEM, EDX, TEM, UV–vis, FT-IR, and TG/DTA techniques. Graphene oxide (GO) obtained with the route of Hummer’s method was reacted with 3-(trimethoxysilyl)propylamine, then, the organosilane functionalized and amine-activated-GO was reacted with 3,5-di-tert-butylsalicylaldehyde obtained the hybrid material containing azomethine group on GO surface. The material was used as an adsorbent in order to remove cobalt(II) and zinc(II) ions in drinking water and standard solutions. The adsorption capacity of the material to cobalt(II) and zinc(II) ions were investigated by using batch method. The effect of pH, contact time, temperature, and concentration on the adsorption capacity of the material was also investigated. The enrichment factors were calculated as 441 and 675 for zinc(II) and cobalt(II), respectively. The recovery performance of the material was determined in 98.65–101.75% and 98.55–104.0% range for zinc(II) and cobalt(II) ions, respectively.

GRAPHICAL ABSTRACT

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Introduction
Waste waters containing heavy metal ions are considered as a serious environmental problem. Zinc is one of the essential elements found in biological systems in the active sites of many type of the enzymes. However, the presence of an excess of zinc in biological systems can be harmful to the environment. There are several symptoms for zinc toxicity including irritability, nausea, loss of appetite and muscular stiffness. The World Health Organization (WHO) reported the recommended level of zinc in drinking water as
5 mg L⁻¹. The trace element ions essential for human health, such as, nickel, cobalt and zinc can show toxic effects at overdoses and cause some different diseases; dermal, nervous system effects, diarrhea, cancer, gastrointestinal disturbances, muscular weakness, hypertension bone, lung damage, liver, kidney effects, bone and blood damage, liver, kidney, and circulatory because of their long biological half-life. Thus, scientists have been focused on the removal of the toxic metal ions from water samples. Some work conditions such as mining, purifying zinc, lead, and cadmium ores, steel production and coal burning and burning of wastes increases the concentration of metal ions to above the defined limits. Several methods have been developed for the removal of zinc from waste and drinking waters. Cobalt is another essential element found in biological systems and found in various forms in the earth’s crust. This metal can also be toxic above the certain concentration and cause health problems including low blood pressure, lung irritation, paralysis, diarrhea, bone defects, and genetic changes in living cells. The methods for the removal of cobalt from waste and drinking waters include precipitation, reverse osmosis, co-precipitation, ion-exchange, membrane, electrolysis, oxidation and adsorption methods.

Solid phase extraction technique with adsorption has been widely studied in wastewater treatment that is based on the physical interaction between metal ions and different types of adsorbents such as nano or macro-solid supported solids. Chemically modified and functionalized magnetite and the silica have been used as metal ions adsorbents in the solid phase extraction of metal ions in the different type of water samples (tap, sea, drinking, well, or pond water). Because of many advantages, chemically functionalized graphene oxide (GO) and GO based hybrid materials (HMs) have been used as sorbents in waste water treatment and in different applications such as new nanomaterials. Graphene-based nanomaterials are considered to be one of the most effective and economical treatment methods for heavy metal ions removal of effluent, river, pond, sea, well and drinking water samples. Because of the fact that oxidized-graphene (GO) can be easily designed and functionalized chemically and the obtained structures have unique physicochemical properties and surface, it is attractive as a multidisciplinary area. The functional groups on the GO surfaces have high surface area and show some potential for the removal of heavy metal ions from aqueous solutions.
In this work, firstly, graphite was oxidized according to Hummer’s method forming GO. After, GO-APTMS was synthesized according to our previous studies with the reaction of GO and 3-(trimethoxysilyl) propylamine (APTMS). The obtained GO-APTMS having free primary amine substituents (–NH₂) was reacted with the 3,5-di-tert-butyl-2-hydroxy-benzenaldehyde to form the material (M). The novel Schiff base ligand supported on organosilane containing GO as a HM was characterized by the EDX, SEM, TEM, XRD, TGA, UV, and FT-IR methods. The synthesized and characterized HM was used as adsorbent for the removal of cobalt(II) and zinc(II) ions from drinking water using batch method. Selectivity and reusability of the graphene based material toward cobalt(II) and zinc(II) metal ions have been investigated.

**Result and discussion**

**Characterization**

GO was obtained from powder graphite by the route of Hummer’s method. The sheets of GO are strongly hydrophilic and have some chemical and physical interactions between the layers and water molecules. Graphite oxide can be completely exfoliated by simple sonication and by stirring the water/graphite oxide mixture for a long time in order to produce aqueous colloidal suspensions of GO sheets. After this processes, the surface of the obtained GO was chemically modified with 3-(trimethoxysilyl)propylamine (GO-APTMS) having a free amine group (–NH₂) on the surface of GO. Finally, the amine-modified GO-APTMS was reacted with 3,5-di-tert-butylsalicyaldehyde to give the final HM. The synthesized organosilane-functionalized and multifunctional nano-sized material have a good chemisorption.
properties with the complexation of the metal ions in water samples fit Langmuir isotherm.

The proposed reactions and the structures are given in Figure 1.

**FT-IR**

FT-IR spectra of the GO and HM are given in Figure 2. In the FT-IR spectrum of GO, the broad peak at 3452 cm\(^{-1}\) comes from O–H vibrations of the –COOH and –OH groups located on the surface of the GO. The vibration peak at 2926 cm\(^{-1}\) is corresponded to aliphatic C–H stretching modes. The peak at the 1729 cm\(^{-1}\) can be attributed to the carbonyl (C = O) stretching band. In addition, the aromatic C=C vibrations were shown at the 1630 cm\(^{-1}\).

In FT-IR spectra of the obtained GO-APTMS, the vibration band at 3435 cm\(^{-1}\) can be attributed to O–H stretching mode. A weak peak at 1573 cm\(^{-1}\) was the stretch of –NH\(_2\) groups which confirmed the successful grafting of APTMS to GO. The peak at 2930 cm\(^{-1}\) can be attributed to aliphatic C–H vibrations of the methylene in APTMS moiety and aliphatic groups on GO. The bending bands at 1118 and 1053 cm\(^{-1}\) may be assigned to the vibrations of Si–O–Si and Si–O–C, respectively. In the spectrum of the HM, there are two characteristic bands at 1115 and 1048 cm\(^{-1}\). The peak at 1632 cm\(^{-1}\) can be attributed to the azomethine group CH = N.\(^{[6–14,20,28,29,31–34]}\)

**SEM and EDX**

The EDX spectra of GO, GO-APTMS and HM materials are given in Figure S2 (Supplemental Materials). In EDX spectrum of GO (Figure S2), three elements C (70.35%), O (28.68%), and S (0.97%) were calculated in its composition. The very small amount of sulfur gradients in the syntheses may come from sulfuric acid used in the preparation reaction of the GO by Hummer’s method (Figure 3b,c). The elemental compositions of GO-APTMS are 57.03% C, 29.12% O, 7.39% Si, 6.34% N, and 0.12% S calculated in the EDX spectrum of GO-APTMS. According to the EDX spectra of GO-APTMS, it can be said that 3-(trimethoxysilyl)-propylamine was attached on the surface of the GO because of the Si peak present. The compositions of the elements of (HM) are 61.83% C, 24.40% O, 6.94% Si, 6.38% N, and 0.45% S calculated in the EDX spectrum of the material (HM). While the percentages of C and N increase with the Schiff base formation on the functionalized graphene, the percentages of the other elements decreased confirming the modification of the surface.\(^{[6–14,20,28,29,31–34]}\)

The scanning electron microscope (SEM) images of GO and HM materials were given in Figure 4a,b. According to the SEM images, the individual GO sheets were found to have a thickness of 100 μm, that is much larger than the thickness of single layer graphene. This increase in the thickness is due to the introduction of the oxygen-containing functional groups.\(^{[6–14,20,28,29,31–34]}\) It can also be noted that the GO sheets were thicker at the edges. This is because the oxygen-containing functional groups were mainly combined at the edges and the surface of GO. GO sheets were firmly suspended and did not bend according to the SEM images. However, SEM image of HM (Figure 3) reveals the extended sheets of lateral dimensions in the length of 1 μm. On the other hand, SEM image displays two-dimensional crumpled nano-sheets with a few stacked layers.

**XRD and TEM**

The structural changes of GO to HM were observed from X-ray diffraction patterns as in (Figure 4a,b). The sharp diffraction peak at 2θ = 9.45° (d = 0.935 nm) and narrow small peak at 2θ = 44.55° correspond to the spacing of the GO in the plane (Figure 4a). After the synthesis of APTMS-GO, the sharp peak of GO disappeared and a new sharp peak revealed at 2θ = 6.2° (d = 1.42 nm). The other new broader and weaker diffraction peaks appeared at 2θ = 10.95° (d = 0.19 nm) and 22.13° (d = 0.4 nm) indicated that the attachment of the functional silane groups occurred successfully on the surface of GO nano-sheets. In XRD pattern (Figure 4b) of HM, the sharp diffraction peak at 2θ = 10.53° belongs to the GO. The weak peaks at 45.01° and 51.43° can be attributed to the bonded compounds in the HM.

The morphological structures of the materials GO, APTMS-GO and HM were also characterized by transmission electron microscopy (TEM) (Figure 5a–c). The elastic corrugations and the scrolled or folded edges often result in different brightness on the surface of the GO (Figure 5a). The results indicate that GO has a high surface area. The mesoporous structure and low surface area may be due to
the agglomerations of GO sheets during the drying treatment because of the van der Waals forces between each single sheet of GO. In the TEM image (Figure 5b) of APTMS-GO, the black dots on the surface of the GO can be attributed to the amino-silane groups. The TEM image of the HM was taken at 0.2 μm. In the HM (Figure 5c), several black aggregations on the surface of the GO-APTMS may be assigned to the imine group.

**Thermal properties**

Thermal properties of all the materials were analyzed by thermogravimetric (TGA) and differential thermal analyses techniques (DTA) under N₂ atmosphere in the range of 20–900 °C. Thermal curves of the material have been given in Figure S1 (Supplemental Materials). According to our previous study, the adsorbed water molecules desorbed between 50 and 100 °C. The absorbed water molecules and the degradation of some
substituents such as –OH were lost in the range of 100–200°C. After this temperature range, the mass loss of the graphite continues up to 850°C with the degradation of organic backbone. In the TGA curve of the GO, the adsorbed water molecules are move away in 40–50°C range.\cite{31,32}

Organo-silanized substituents and absorbed water were decomposed up to 200°C in the thermal curve of the GO-APTMS. Decomposition of the organic backbone continued up to 900°C. The TG/DTA/DTG curves of the HM (Figure S1) showed that the decomposition process occurs at four steps. At first and second steps, the adsorbed and decomposed water molecules from the substituents such as silanol and oxygen containing structures. At the other steps, the organic parts of the material HM decomposed continued up to 800°C. The thermal stability of the HM is lower than the other graphene derivatives.

**Solid phase extraction**

**Adsorption–desorption and isotherms**
The HM was used as adsorbents for the removal of Zn(II) and Co(II) cations from aqueous solutions. For the adsorption measurements, the aqueous solutions of Zn(II) or Co(II) (25 mg L\(^{-1}\), 25 mL) were mixed with the HM at room temperature as a batch process. At the end of each experiment, HM was filtered, and the metal content was analyzed with ICP-OES. The results were given as the average of the replicates. The effect of pH, concentration, contact time and temperature on the adsorption capacity of the HM were explored. The amount of metal ions adsorbed per unit mass of the HM, maximum absorption capacity \(Q\) (mg g\(^{-1}\)) was determined by the following equation (Equation 1)

\[
Q = \frac{[(C_0 - C) \cdot V]}{m},
\]

where \(C_0\) and \(C\) (mg L\(^{-1}\)) are the liquid-phase concentrations of metals before and after adsorption, respectively. \(V\) is the volume of the solution (L) and \(m\) is the mass of the HM.

**Effect of pH**
The maximum adsorptions were provided at pH 9 for Zn(II) (24.624 mg g\(^{-1}\)) and Co(II) (23.766 mg g\(^{-1}\)). During the adsorption process, the oxygen-containing functional groups on
the surface of the HM are formed anionic layer with H\(^+\) ions releasing in the solution. The adsorption of Zn(II) and Co(II) is gradually subjected to ion exchange with the hydrogen cation on the surface of the HM when pH is increased.\(^{[40]}\) The effect of pH on the adsorption is shown in Figure 6.

**Effect of contact time**

The effect of the reaction time on the adsorption capacity of the HM was also investigated at pH 9 in the 0–120 min range. The dependence on time is shown in Figure 7. For both Co(II) and Zn(II), the adsorption rate is extremely high for the first 10 min with the adsorption of 21.26 and 23.12 mg g\(^{-1}\), respectively. The adsorption capacity of HM for Co(II) reaches a maximum at 50 min with 20.37 mg g\(^{-1}\) and remains constant. The maximum absorption occurs at 70 min with 24.76 mg g\(^{-1}\) for Zn(II). The adsorption equilibrium is mainly due to high geometrical affinity between heavy metal ions and functional HM. The slightly faster adsorption of Co(II) may be better coordination interactions between HM and metal ion.

**Effect of the initial metal concentration on the adsorption capacity**

Effect of the initial metal concentration on the adsorption capacity was investigated at pH 9 for a period of 50 min for Co(II) and 70 min for Zn(II) (Figure 8). The adsorption capacity of HM presents an increasing trend with concentration increasing. The maximum adsorption occurs at 691.00 ppm for Zn(II) and 623.79 ppm for Co(II) and remains almost constant above these concentrations. The concentration increase results in a slightly better adsorption for Zn(II).

**Effect of temperature**

The effect of temperature on the adsorption capacity was investigated in the 0–60°C range (Figure 9). Until 25°C, the
sharp adsorption increase was observed for Zn(II) and Co(II) ions. The maximum adsorptions were obtained at 24.92 and 24.37/C14/C for Zn(II) and Co(II), respectively. In the 20–60/C14/C range, there is no considerable change in the adsorption capacity of HM.

Reusability of the adsorbent
The regeneration process is very important in industry.[6–14,20,30,41] The reusability of the HM was investigated 10 times. The obtained results are given in Figure 10. After each experiment, the adsorbed metal ions were removed from HM by using HNO3 (4 M) as the desorption agent. According to the adsorption capacity of the HM decreased because of the metal ion-ligand and metal ion-anion complexation on the surface of HM in adsorption media as seen in Figure S3 (Supplemental Materials). In the FT-IR spectrum, the decrease of the adsorption of the metal ion after the seventh cycle can be explained by the fact that new metal ion-ligand and metal ion-anion stretches are observed as a band about 700 cm⁻¹. The seven cycles showed that the reusability of the synthesized HM was very applicable in the solid phase extraction of Co(II) and Zn(II) ions in water samples.[6–14,20,30,41]

Analysis of real samples and analytical performance of the method
The standard addition methods were used for the removal of Co(II) and Zn(II) ions from drinking water samples by the HM. The internal standard addition method by spiking the samples with Co(II) and Zn(II) ions in the fixed concentrations were used. The obtained results were given in Table 1. The recovery performance of was obtained as 98.65–101.75% for Zn(II) adsorption while 98.55–104.0% for Co(II). The analytical performance data for the pre-concentration studies for Co(II) and Zn(II) ions are listed in Table 2. The obtained data indicate that the Co(II) and Zn(II) ions can be detected as low concentration as 2.13 and 3.43 ng mL⁻¹, respectively. The precision of the method was found as 1.9% for Zn(II) and 3.8% for Co(II). In the pre-concentration studies, a linear curve was observed in the range of 0.7–26.0 ng mL⁻¹ for Zn(II) and 0.5–22 ng mL⁻¹ for Co(II). The enrichment factor was found to be 441 for Zn(II) and 675 for Co(II).

When compared the adsorption efficiency capacity (mmol g⁻¹) of our synthesized organosilane-functionalized azomethine-graphene to the nanomaterials in the literature, the synthesized is one of the best adsorbents for Zn(II) and Co(II) ions (Table 3) with over “1” adsorption efficiency capacity (mmol g⁻¹).[8,42–45]

Langmuir isotherms
The adsorption isotherms were used to investigate the interaction types between the adsorbents and metal ions. Possible interaction between the HM and the metal ions [Zn(II) or Co(II)] is in the form of coordinated-covalent bonding. Therefore, it fits with Langmuir adsorption model. The model suggests that the molecules or ions are adsorbed at a fixed number of well-defined sites. During the batch experiments, the Langmuir adsorption isotherm was used to evaluate adsorption properties. Equation (2) expresses the Langmuir adsorption isotherm:

\[ Q = \frac{Q_{\text{max}} b}{C_{\text{eq}} + b} \]

where \( Q \) is the adsorbed amount of Zn(II) or Co(II) (mg/g), \( C_{\text{eq}} \) the equilibrium Zn(II)/Co(II) concentration (mg/mL), \( b \) the Langmuir constant (mL/mg), and \( Q_{\text{max}} \) is the maximum desorption capacity (mg/g). Figure 11 and Table 4 illustrate the equilibrium constants of Langmuir isotherm. The correlation coefficients of Langmuir isotherm (\( R^2 \)) were determined as 0.9841 for Zn(II) and 0.998 for Co(II). The experimental and theoretical maximum adsorption values show a good correlation between each other (Table 4).

Conclusions
The imine-graphene HM was prepared and characterized by the FT-IR, XRD, EDX, SEM, TEM, and UV–vis techniques. Thermal properties of HM were investigated by TGA/DTA.
methods in the 25–1000 °C temperature range. The HM was used as adsorbent for the removal of Co(II) and Zn(II) from aqueous solutions using the batch process. The several parameters such as pH, contact time, temperature, and concentration were applied to optimize the adsorption capacity of the HM. The enrichment factor was found as 441 for Zn(II) and 675 for Co(II). The recovery performance of was obtained as 98.65–101.75% for Zn(II) adsorption while 98.55–104.0% for Co(II). The adsorption results suggest that the HM can have a potential usage as an adsorbent material for the detection and removal of Co(II) and Zn(II) ions because of the fact that the organosilane-functionalized HM have the potential active donors for the coordination to the metal ions easily. In addition, the HM can be used again and again up to seven times in the solid phase extraction of Co(II) and Zn(II) ions in drinking water samples. It can be said that the material is also thermally and the chemically stable in the solid phase extraction and recycling experiments. However, the cost of the synthesis can be high at first usages in the industry.

Experimental

General

Graphite powder was supplied from Sigma-Aldrich (St. Louis, USA). H2SO4 and KMnO4 were purchased from Sigma-Aldrich (Germany). H2O2, HCl and NaOH were purchased from Merck. Absolute ethanol and methanol were obtained from Sigma-Aldrich. 3-(Trimethoxysilyl)propylamine was obtained from Sigma-Aldrich (Germany). H2O2, HCl and NaOH were purchased from Merck 119806 CertiPUR® for Zn(II) and Sigma Aldrich 49564 TraceCERT® for Co(II) were used certified solutions.

Instrumental

Infrared spectra were obtained using KBr disk (4000–400 cm⁻¹) on a Perkin Elmer Spectrum 100 FT-IR. The electronic spectra in the 200–900 nm range were obtained on a Perkin Elmer Lambda 45 spectrophotometer. The thermal studies of the compounds were performed on a Perkin Elmer STA 6000 simultaneous Thermal Analyzer under nitrogen atmosphere at a heating rate of 10 °C/min. The quantity of the Co(II) and Zn(II) ions obtained from the aqueous solutions was determined by Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Brand Optima 2100 DV). All experimental conditions were kept the same for all samples. X-ray diffraction (XRD) patterns of the GO, APTES-GO, and HM were conducted by using a Philips X’Pert Pro X-ray diffractometer (XRD), with Cu-Kz radiation. Scanning range was 0–60° and taken as 2θ. The surface morphology and EDX analysis of the nanocomposite ligands and the complexes were analyzed using Zeiss Evo LS10 SEM attached with Bruker Quantax EDS. Hanna HI 2211-05 desktop pH meter was used for pH adjustments of the solutions. GO sheets, silanization derivative, and hybrid structures were analyzed using a high resolution images in transmission electron microscopy mode (HRTEM) Jeol JEM 2100F TEM, which has a point resolution of 0.18 nm at 200 kV and room temperature. The TEM analyses included amplitude-contrast bright field (BF) images and HRTEM images.

Preparation of GO-APTMS

GO has been synthesized by the route of Hummer’s method.[25] GO-APTMS was also synthesized according to our previous study; the obtained GO (1 g) and 3-(trimethoxysilyl)propylamine (1 g) in ethanol (50 mL) were mixed and the reaction solution was refluxed for 48 h. The reaction mixture was then cooled to room temperature and the obtained product GO-APTMS was dried at room temperature.[31,32]

Preparation of the HM

The GO-APTMS (1 g) and 3,5-di-tert-butylsalicylaldehyde (1 g) in ethanol (50 mL) were mixed and refluxed for 30 h. The reaction mixture was cooled to the room temperature and filtered under vacuum. The synthesized material (HM) was washed with ethanol in order to remove the unreacted chemicals and impurities. The obtained HM was dried in air.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Grout, J. A.; Levings, C. D. Effects of Acid Mine Drainage from an Abandoned Copper Mine, Britannia Mines, Howe Sound, British Columbia, Canada, on Transplanted Blue Mussels Mytilus edulis. Mar. Environ. Res. 2001, 51, 265–288. DOI: 10.1016/S0141-1136(00)00104-5.
[2] Lin, C.; Wu, Y.; Lu, W.; Chen, A.; Liu, Y. Water Chemistry and Ecotoxicity of an Acid Mine Drainage-Affected Stream in Subtropical China during a Major Flood Event. J. Hazard. Mater. 2007, 142, 199–207. DOI: 10.1016/j.jhazmat.2006.08.006.
[3] Tang, X.; Li, Z.; Chen, Y. Adsorption Behavior of Zn(II) on Calcinated Chinese Loess. J. Hazard. Mater. 2009, 161, 824–834. DOI: 10.1016/j.jhazmat.2008.04.059.
[4] National Research Council (US) Safe Drinking Water Committee. Drinking Water and Health: Volume 1. National Academies Press: Washington, DC, 1977.
[5] World Health Organization. Guidelines for Drinking-Water Quality. Geneva: World Health Organization, 1993.
[6] Das, S.; Chatterjee, S.; Mondal, S.; Modak, A.; Chandra, B. K.; Das, S.; Nessim, G. D.; Majee, A.; Bhaumik, A. Thiadiazole Containing N- and S-Rich Highly Ordered Periodic Mesoporous Organosilica for Efficient Removal of Hg(II) from Polluted Water. Chem. Commun. 2020, 56, 3963–3966. DOI: 10.1039/D0CC00407C.
[7] Modak, A.; Bhanja, P.; Selvaraj, M.; Bhaumik, A. Functionalized Porous Organic Materials as Efficient Media for the Adsorptive Removal of Hg(II) Ions. Environ. Sci. Nano 2020, 7, 2887–2923. DOI: 10.1039/D0EN00714E.
[8] Mahmoud, M. E.; Saad, E. A.; Soliman, M. A.; Abdelwahab, M. S. Removal of Radioactive Cobalt/Zinc and Some Heavy Metals
from Water Using Diethylentriamine/2-Pyridinecarboxaldehyde Supported on NZVI. *Microchim. J.* 2019, 145, 1102–1111. DOI: 10.1016/j.microc.2018.12.032.

[9] Lentini, G.; Milanì, G.; Habibtemi, S. Comment on “In Situ Derivatization of (RS)-Mexitelen and Enantiopereparation Using Micellar Liquid Chromatography: A Green Approach.” *ACS Sustain. Chem. Eng.* 2019, 7, 6424–6425. DOI: 10.1021/acssuschemeng.8b06684.

[10] Pokpas, K.; Jahed, N.; Baker, P. G.; Iwuoha, E. I. Complexation-Based Detection of Nickel(II) at a Graphene-Chelate Probe in the Presence of Cobalt and Zinc by Adsorptive Stripping Voltammetry. *Sensors* 2017, 17, 1711–1722. DOI: 10.3390/s17081711.

[11] Keramat, A.; Zare-Dorabei, R. Ultrasonic-Assisted Dispersive Magnetic Solid Phase Extraction for Preconcentration and Determination of Trace Amount of Hg(II) Ions from Food Samples and Aqueous Solutions by Magnetic Graphene Oxide (Fe₃O₄@GO/2-PTSC): Central Composite Design Optimization. *Ultrason. Sonochem.* 2017, 38, 421–429. DOI: 10.1016/j.ultsonch.2017.03.039.

[12] Zare-Dorabei, R.; Ferdowsi, S. M.; Barzin, A.; Tadjari, A. Highly Efficient Simultaneous Ultrasonic-Assisted Adsorption of Pb(II), Cd(II), Ni(II), and Cu(II) Ions from Aqueous Solutions by Graphene Oxide Modified with 2,2′-dipyridylamine: Central composite design optimization. *Ultrason. Sonochem.* 2016, 32, 265–276. DOI: 10.1016/j.ultsonch.2016.03.020.

[13] Tadjari, A.; Moazen Ferdowsi, S.; Zare-Dorabei, R.; Barzin, A. Highly Efficient Ultrasonic-Assisted Removal of Hg(II) Ions on Graphene Oxide Modified with 2-Pyridinecarboxaldehyde Thiosemicarbazone: Adsorption Isotherms and Kinetics Studies. *Ultrason. Sonochem.* 2016, 33, 118–128. DOI: 10.1016/j.ultsonch.2016.04.030.

[14] Ozay, O.; Ozay, H. Novel Hexacentered Phosphazene Compound as Selective Fe²⁺ Ions Sensor with High Quantum Yield: Synthesis and Application. *Phosphorus Sulfur Silicon Relat. Elem.* 2019, 194, 221–228. DOI: 10.1080/10426507.2018.1539491.

[15] Netzer, A.; Hughes, D. E. Adsorption of Copper, Lead and Cobalt by Activated Carbon. *Water Res.* 1984, 18, 927–933. (84)90241-0. DOI: 10.1016/0043-1354.

[16] Tavlarides, L. L.; Bae, J. H.; Lee, C. K. Solvent Extraction, Membranes, and Ion Exchange in Hydrometallurgical Dilute Solutions. *Cobalt by Activated Carbon.* 2009, 18, 2788. DOI: 10.1016/j.ultsonch.2016.03.020.

[17] Krause, B.; Sandenbergh, R. F. Optimization of Cobalt Removal from an Aqueous Sulfate Zinc Leach Solution for Zinc Electrowinning. *Hydrometallurgy* 2015, 155, 132–140. DOI: 10.1016/j.hydromet.2015.05.001.

[18] Mizerá, J.; Mizerová, G.; Machovič, V.; Berecký, L. Sorption of Cerium, Cobalt and Europium on Low-Rank Coal and Chitosan. *Water Res.* 2007, 41, 620–626. DOI: 10.1016/j.watres.2006.11.008.

[19] Oliva, J.; De Pablo, J.; Cortina, J. L.; Cama, J.; Ayora, C. Removal of Cadmium, Copper, Nickel, Cobalt and Mercury from Water by Apatite II® Column Experiments. *J. Hazard. Mater.* 2011, 194, 312–323. DOI: 10.1016/j.jhazmat.2011.07.104.

[20] Della’Era, A.; Pasqualli, M.; Lupi, C.; Zaza, F. Purification of Nickel or Cobalt Ion Containing Effluents by Electrolysis on Reticulated Vitreous Carbon Cathode. *Hydrometallurgy* 2014, 150, 1–8. DOI: 10.1016/j.hydromet.2014.09.001.

[21] Krause, B.; Sandenbergh, R. F. Optimization of Cobalt Removal from an Aqueous Sulfate Zinc Leach Solution for Zinc Electrowinning. *Hydrometallurgy* 2015, 155, 132–140. DOI: 10.1016/j.hydromet.2015.05.001.

[22] Mizerá, J.; Mizerová, G.; Machovič, V.; Berecký, L. Sorption of Cerium, Cobalt and Europium on Low-Rank Coal and Chitosan. *Water Res.* 2007, 41, 620–626. DOI: 10.1016/j.watres.2006.11.008.

[23] Oliva, J.; De Pablo, J.; Cortina, J. L.; Cama, J.; Ayora, C. Removal of Cadmium, Copper, Nickel, Cobalt and Mercury from Water by Apatite II® Column Experiments. *J. Hazard. Mater.* 2011, 194, 312–323. DOI: 10.1016/j.jhazmat.2011.07.104.

[24] Della’Era, A.; Pasqualli, M.; Lupi, C.; Zaza, F. Purification of Nickel or Cobalt Ion Containing Effluents by Electrolysis on Reticulated Vitreous Carbon Cathode. *Hydrometallurgy* 2014, 150, 1–8. DOI: 10.1016/j.hydromet.2014.09.001.

[25] Krause, B.; Sandenbergh, R. F. Optimization of Cobalt Removal from an Aqueous Sulfate Zinc Leach Solution for Zinc Electrowinning. *Hydrometallurgy* 2015, 155, 132–140. DOI: 10.1016/j.hydromet.2015.05.001.
[39] Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 1958, 80, 1339–1339. DOI: 10.1021/ja01539a017.

[40] Wu, S.; Zhao, X.; Li, Y.; Du, Q.; Sun, J.; Wang, Y.; Wang, X.; Xia, Y.; Wang, Z.; Xia, L. Adsorption Properties of Doxorubicin Hydrochloride onto Graphene Oxide: Equilibrium, Kinetic and Thermodynamic Studies. *Materials.* 2013, 6, 2026–2042. DOI: 10.3390/ma6052026.

[41] Uruş, S.; Purtaş, S.; Ceyhan, G.; Tümer, F. Solid Phase Extraction of Pb(II), Cu(II), Cd(II) and Cr(III) with Syringe Technique Using Novel Silica-Supported Bis(Diazoimine) Ligands. *Chem. Eng. J.* 2013, 220, 420–430. DOI: 10.1016/j.cej.2013.01.037.

[42] Mahmoud, M. E.; Saad, E. A.; Soliman, M. A.; Abdelwahab, M. S. Encapsulation of Nano Zerovalent Iron with Ethylenediamine and Diethylenetriamine for Removing Cobalt and Zinc and Their Radionuclides from Water. *J. Environ. Chem. Eng.* 2017, 5, 5157–5168. DOI: 10.1016/j.jece.2017.09.044.

[43] Mahmoud, M. E.; Saad, E. A.; Soliman, M. A.; Abdelwahab, M. S. Synthesis and Surface Protection of Nano Zerovalent Iron (NZVI) with 3-Aminopropyltrimethoxysilane for Water Remediation of Cobalt and Zinc and Their Radioactive Isotopes. *RSC Adv.* 2016, 6, 66242–66251. DOI: 10.1039/C6RA11049E.

[44] Zhang, C. Z.; Yuan, Y.; Guo, Z. Experimental Study on Functional Graphene Oxide Containing Many Primary Amino Groups Fast-Adsorbing Heavy Metal Ions and Adsorption Mechanism. *Sep. Sci. Technol.* 2018, 53, 1666–1677. DOI: 10.1080/01496395.2018.1436071.

[45] Park, C. M.; Wang, D.; Han, J.; Heo, J.; Su, C. Evaluation of the Colloidal Stability and Adsorption Performance of Reduced Graphene Oxide-Elemental Silver/Magnetite Nanohybrids for Selected Toxic Heavy Metals in Aqueous Solutions. *Appl. Surf. Sci.* 2019, 471, 8–17. DOI: 10.1016/j.apsusc.2018.11.240.