

**Solid-phase extraction and fluorimetric determination of Zn(II) in natural water using novel adsorbent based on silica modified with polyhexamethylene guanidine and Ferron**

Svetlana L. Didukh-Shadrina, Olga V. Buyko\*, Vladimir N. Losev

*Scientific Research Engineering Center “Kristall”, Siberian Federal University, pr. Svobodnyi, 79, 660041 Krasnoyarsk, Russian Federation*

Corresponding author: Olga V. Buyko e-mail: obuyko@sfu-kras.ru

# **Solid-phase extraction and fluorimetric determination of Zn(II) in natural water using novel adsorbent based on silica modified with polyhexamethylene guanidine and Ferron**

Novel silica-based adsorbent layer-by-layer modified with polyhexamethylene guanidine and 7-iodine-8-hydroxyquinoline-5-sulfonic acid (Ferron) was used for preconcentration and adsorption-fluorimetric determination of Zn(II). A simple and express method for adsorbent preparation is described in the present work. The prepared adsorbent extracts Zn(II) from solutions with pH of 5.0–7.0, with the formation of a luminescent complex  $\lambda_{\text{lum}} = 500 \text{ nm}$  ( $\lambda_{\text{ex}} = 380 \text{ nm}$ ) on the surface. An adsorption-fluorimetric method was developed for determination of Zn(II) in natural water using adsorbent sequentially modified with polyhexamethylene guanidine and Ferron; detection limit was  $4 \mu\text{g L}^{-1}$ . The procedure was used for the analysis of water from rivers and artesian wells of the Krasnoyarsk Krai (Russia).

Keywords: adsorption; modified silica; luminescent determination; Zn(II)

## **1. Introduction**

Industrial development, the active use of automobile transport leads to large emissions of hazardous pollutants into the environment. Zinc is a widespread pollutant. It is released into the environment through several industrial activities, such as, mining, livestock farms [1], battery production, and its use in drugs, wood, sun blocks, deodorants [2]. Zn(II), as a rule, accumulates in the tissues of the body, causing various diseases and disorders, such as skin irritation, gastrointestinal disorders, respiratory diseases, anemia, etc. [3]. The permissible limits of Zn(II) in drinking water are:  $1 \text{ mg L}^{-1}$  in Russia,  $5.00 \text{ mg L}^{-1}$  according to the US Environmental Protection Agency (USEPA) and  $3.00 \text{ mg L}^{-1}$  according to the recommendations of World Health Organization (WHO) [4-5].

Zinc(II) occurs in natural water at the trace level, so solid-phase extraction (SPE) is widely used for its determination. For these purposes, various adsorbents are proposed: anion exchange resins modified with sulfonated chelating agents [6], silica gel chemically modified with 8-hydroxyquinoline [7], controlled pore glass with immobilized 8-quinolinol [8], cellulose modified with 8-hydroxyquinoline-5-sulfonic

acid [9]. Most studies are devoted to the use of adsorption materials for preconcentration of analytes, followed by elution and determination in solution using atomic spectroscopy [6–8] or mass spectrometry [10].

Various quinoline derivatives are widely used for the fluorimetric determination of Zn(II): 8-quinolyl derivatives substituted with anionic dissociative group at the hydroxyl [11], Ferron [12], 4-methyl-2-((2-(quinolin-2-yl)hydrazono)methyl)phenol [13].

But a convenient and inexpensive way is to determine the microcomponent not in the solution, but in the phase of the adsorbent using diffuse reflectance spectroscopy or fluorescence. This allows to achieve preconcentration of the analyte, its separation from the accompanying elements, as well as the reducing of the relative detection limits. Graphene oxide functionalized with 8-hydroxyquinoline groups [14] was proposed as a fluorescent nanosensor for the determination of Zn(II) in an aqueous media. In our work, we used silica, sequentially non-covalently modified with polyhexamethylene guanidine (PHMG) and 7-iodine-8-hydroxyquinoline-5-sulfonic acid (Ferron) (SiO<sub>2</sub>-PHMG-Ferron) or 8-hydroxyquinoline-5-sulfonic acid (HQS) (SiO<sub>2</sub>-PHMG-HQS). The advantage of the new adsorbent is a simple synthesis. Adsorbents based on inorganic oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>) [14-18] have a number of advantages: colorlessness, absence of proper luminescence, non-swelling, and thermal stability. The proposed adsorbents were synthesized in an aqueous media; the fixing of reagents on the surface of silica occurs due to the formation of electrostatic and hydrogen bonds. Sulfo derivatives of 8-hydroxyquinoline are proposed to be used as the outer layer. These reagents are available, and they have sulfo groups that allows electrostatic fixation of the reagents on the positively charged surface of SiO<sub>2</sub>-PHMG.

SiO<sub>2</sub>-PHMG-Ferron was used for solid-phase extraction of Zn(II) from natural waters and its fluorimetric determination directly in the phase of the adsorbent.

## **2. Experimental**

### **2.1. Reagents**

Stock solution of Zn(II) with the concentration of 1 g L<sup>-1</sup> was prepared by dissolving of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O purchased from Sigma-Aldrich in 2M HNO<sub>3</sub>. Solutions with lower concentrations were prepared by dilution of stock solution with acid solution of appropriate concentration.

Multielement Calibration Standard 1 (As, Be, B, Cd, Pb, Mn, Se, Zn) purchased from High-purity standards was used for calibration of ICP-MS.

Solution of polyhexamethylene guanidine chloride (Institute of Ecotechnological Problems, Moscow, Russia) with the concentration of 7.5 % (w/w) was prepared by dissolving of commercial reagent in deionized water. Solutions of Ferron (7-iodine-8-hydroxyquinoline-5-sulfonic acid) and HQS (8-hydroxyquinoline-5-sulfonic acid) purchased from Sigma-Aldrich with the concentration of 0.1 % (w/w) was prepared by dissolving of commercial reagents in deionized water. Reagent solutions with lower concentrations were prepared by dilution of stock solution with deionized water.

Silochrome C-120 (particle size of 0.1–0.2 mm, specific surface area of  $\sim 120 \text{ m}^2 \text{ g}^{-1}$ , average pore diameter of  $\sim 45 \text{ nm}$ ) (Luminofor, Russia) was used as a matrix for the adsorbents synthesis.

Hydrochloric and nitric acids of analytical grade were purified by distillation using distillacid<sup>TM</sup> BSB-939-IR (Berghof, Germany). Solutions of lower concentrations were prepared by dilution of concentrated acids with deionized water.

Deionized water (18.3 M $\Omega$ /cm) was prepared using E-pure D4642-33 (Barnstead International, USA).

## **2.2. Instrumentation**

The UV-Vis spectra of the solutions were registered using a Lambda 35 spectrophotometer (Perkin-Elmer, USA). The luminescence spectra of the solutions and on the surface of the adsorbent were registered using an Eclipse Cary spectrofluorometer (Varian, USA) with an accessory for measuring the luminescence of solid samples. Diffuse reflectance spectra (DRS) of adsorbents were recorded using Pulsar spectrophotocolorimeter (Khimavtomatika, Russia). The spectra are represented in the coordinates  $F(R)$  - wavelength, nm, where  $F(R)$  - Kubelka–Munk function.

Metal distribution was monitored by ICP-MS analyses of an aqueous phase using XSeriesII inductively coupled plasma mass spectrometer (Thermo Scientific, USA).

The pH of the solutions was measured using a SevenMulti ion meter (Mettler-Toledo, Switzerland).

A Masterflex L/S peristaltic pump (Cole-Parmer Instruments Company, USA) was used for pumping the solutions during the adsorbent synthesis.

### ***2.3. Layer-by-layer modification of SiO<sub>2</sub> with PHMG and 8-hydroxyquinoline sulfo derivatives***

In order to activate the surface a portion of silica gel of 5.0 g was soaked with the NaOH solution at pH 8.0–9.0 for 2 hours. This leads to the opening of siloxane bonds of silica (Si-O-Si) and the formation of silanol surface groups Si-OH. Then silica was washed with deionized water until pH 7.0. Then 100 mL of 7.5% PHMG solution was added to the adsorbent at the flow rate of 1.5 mL min<sup>-1</sup> under continuous stirring. Prepared adsorbent (SiO<sub>2</sub>-PHMG) was washed with deionized water until no positive reaction to PHMG in the rinsing water and dried at 60°C. Presence of PHMG in the rinsing water was determined visually by the test with bromophenol blue.

In order to investigate the adsorption capacity of SiO<sub>2</sub>-PHMG for Ferron or HQS 5.0 mL of  $2.5 \cdot 10^{-5}$ – $2.2 \cdot 10^{-3}$  mol L<sup>-1</sup> solution of Ferron or HQS was placed into a graduated test tube with a glass stopper; HCl or NaOH was added to adjust the required acidity; and water was added to a total volume of 10.0 mL. The adsorbent mass of 0.1 g was added, the tube was stopped and stirred for 10 min. The solution was decanted and the resulting adsorbent was washed with deionized water and air dried overnight. The prepared adsorbent does not lose its adsorption properties after a month of storage. The amount of the adsorbed reagent was determined by the difference in the reagent concentrations in solution before and after the adsorption by UV-Vis spectroscopy ( $\lambda_{\max}$ =430 nm for Ferron and  $\lambda_{\max}$ =305 nm for HQS).

### ***2.4. Solid-phase extraction and adsorption-fluorescent determination of Zn(II) using SiO<sub>2</sub>-PHMG-Ferron***

SPE of Zn(II) was carried out in the batch mode. For this, 1.0 mL of a solution containing 0.1–100 mg L<sup>-1</sup> of Zn(II) was placed into a test tube; HNO<sub>3</sub> or NaOH was added to adjust required acidity; and deionized water was added to a total volume of 10.0 mL. SiO<sub>2</sub>-PHMG-Ferron adsorbent mass of 0.100 g was added; the tube was stopped and stirred for 1–30 min.

The adsorbent was separated from the solution by decantation, placed in a cuvette with quartz glass with a diameter of 1.0 cm, dried with filter paper, and the spectra of excitation of luminescence and luminescence were measured.

Spectral characteristics were registered using spectrofluorometer under the following conditions: the spectral width of the slit for monochromators of the excitation and luminescence of 5 nm; wavelength range: excitation - 250–450 nm ( $\lambda_{\text{em}} = 500$  nm),

emission - 400–600 nm ( $\lambda_{\text{ex}} = 380$  nm); emission filters - 360–1100 nm, excitation filters - 250–395 nm.

The distribution of Zn(II) was monitored by the analysis of aqueous phase using ICP-MS.

### **2.5. Sampling and sample preparation**

Water samples from the Yenisei and Kacha rivers and water from artesian wells were analyzed. Water from rivers (1.00 L) was collected from a depth of 0.5 m, water from artesian wells was collected on the territory of the Krasnoyarsk Krai (Russia) - village Novostroyka (Kozulsky district), village Malyy Kantat (Bolshemurtinsky district). Water was filtered through a cellulose membrane (Millipore, 0.45  $\mu\text{m}$ ), placed in polyethylene bottles, and acidified with nitric acid up to pH 1.0.

Water sample (200.0 mL) with a pH 1.00 was boiled for 30 min to decompose the organic compounds and cooled; 1.0 mL of 0.1 mol L<sup>-1</sup> hydroxylamine solution was added to reduce Fe(III) to Fe(II) and 0.2% thiourea solution was added to eliminate the interference of Cu(II).

10.0 mL of the prepared water sample was placed in graduated test tube with ground plug. The solution was intensively stirred with 0.1 g of SiO<sub>2</sub>-PHMG-Ferron adsorbent for 10 min. Then the adsorbent was isolated from solution by decantation and analyzed by fluorimetric method.

### **2.6. Calculations**

The Kubelka–Munk function ( $F(R)$ ) was calculated as:

$$F(R) = (1 - R)^2 / 2 \cdot R \quad (1)$$

$R$  - diffuse reflectance coefficient.

The extraction efficiency ( $R$ , %) of Ferron, HQS or Zn(II) extracted by adsorbents was determined as follows:

$$R = [(C_0 - C_{eq}) / C_0] \cdot 100\% \quad (2)$$

$C_0$  - initial concentration of Ferron, HQS or Zn(II) in the solution, mmol L<sup>-1</sup>,  
 $C_{eq}$  - equilibrium concentration of Ferron, HQS or Zn(II) in the solution, mmol L<sup>-1</sup>.

The desorption efficiency ( $R_{des}$ , %) of Ferron or HQS was determined as follows:

$$R_{des} = [C_{des} / (C_0 - C_{eq})] \cdot 100\% \quad (3)$$

$C_{des}$ - concentration of Ferron or HQS in the desorption solution, mmol L<sup>-1</sup>.

The quantity of Ferron, HQS or Zn(II) extracted ( $q$ , mmol g<sup>-1</sup>) by adsorbents was calculated from Eq.(4):

$$q = [(C_0 - C_{eq}) \cdot V] / m \quad (4)$$

$V$ – the solution volume, L,

$m$ –the mass of adsorbent, g.

Limit of detection (LOD) of Zn(II) in water using SiO<sub>2</sub>-PHMG-Ferron adsorbent was calculated by 3 $\sigma$ -criterion; limit of quantification (LOQ) was calculated by 10 $\sigma$ -criterion [19].

### 3. Results and discussion

#### *3.1. Optimal conditions for 8-hydroxyquinoline sulfo derivatives fixation on SiO<sub>2</sub>-PHMG surface*

Direct fixing of 8-hydroxyquinoline sulfo-derivatives on the silica surface is impossible, since the negatively charged sulfo group of the reagents is electrostatically repelled from the partially deprotonated silanol groups of silica. Pretreatment of silica with aqueous solution of PHMG which comprises a positively charged guanidinium group, gives the surface a positive charge. The 8-hydroxyquinoline sulfo-derivatives is fixed by electrostatic interaction between the positively charged guanidine groups of SiO<sub>2</sub>-PHMG and the negatively charged sulfo groups of the reagents.

Time of attainment of adsorption equilibrium for 8-hydroxyquinoline sulfo-derivatives extraction by SiO<sub>2</sub>-PHMG was less than 10 min.

The maximum extraction of Ferron (97-99 %) was observed in the pH range of 3.0-8.0, and HQS at pH 4.0–5.5 (Figure 1). An increase in the concentration of Ferron in the solution from  $2.8 \cdot 10^{-5}$  mol L<sup>-1</sup> to  $2.8 \cdot 10^{-4}$  mol L<sup>-1</sup> leads to a narrowing in the pH range of the reagent extraction to 3-5.5.

At  $\text{pH} < 3$  for Ferron and  $\text{pH} < 4$  for HQS, a decrease in the degree of reagent extraction was observed, since  $\text{pK}_a(\text{SO}_3^-) = 2.50$  (Ferron) [20] and  $\text{pK}_a(\text{SO}_3^-) = 3.40$  (HQS) [21], hence, the sulfo groups are protonated and reagents cannot be extracted by electrostatic attraction.

The maximum amount of reagent that can be fixed on the surface of  $\text{SiO}_2$ -PHMG determined from the horizontal section of the adsorption isotherms (Figure 2) was  $0.1 \text{ mmol g}^{-1}$  for Ferron and  $0.05 \text{ mmol g}^{-1}$  for HQS. The proposed method of fixing the reagent allows you to fix on the surface of the silica any controlled concentration of the reagent within its adsorption capacity.

The stability of the fixation of sulfo derivatives of 8-hydroxyquinoline on the surface of  $\text{SiO}_2$ -PHMG was studied by treatment with  $0.01 - 1 \text{ mol L}^{-1}$  NaCl solutions (Table 1).

HQS was easily desorbed from the surface of  $\text{SiO}_2$ -PHMG by solutions with a low salt background, so when using a  $0.01 \text{ mol L}^{-1}$  NaCl solution ( $0.58 \text{ g L}^{-1}$ ), the degree of desorption of HQS was almost 50%, which complicates the use of  $\text{SiO}_2$ -PHMG-HQS for preconcentration and determination of  $\text{Zn(II)}$  in natural waters.

Therefore, in further work, we used the  $\text{SiO}_2$ -PHMG-Ferron adsorbent to develop procedure of adsorption preconcentration and fluorimetric determination of  $\text{Zn(II)}$ .

Proposed method of adsorbent preparation allows to save the chromophore properties of the reagent on the surface of the adsorbent. This is confirmed by a comparison of the absorption spectra of Ferron in solution and the diffuse reflection spectra on the adsorbent surface (Figure 3).

The maximum of the absorption spectrum of the Ferron solution ( $\lambda = 430 \text{ nm}$ ) coincides with the maximum in the diffuse reflectance spectrum of the reagent on the surface of  $\text{SiO}_2$ -PHMG.

### ***3.2. Conditions for the quantitative extraction and luminescence of $\text{Zn(II)}$ on the surface of $\text{SiO}_2$ -PHMG-Ferron***

During  $\text{Zn(II)}$  adsorption, a complex compound is formed on the adsorbent surface, which, under UV irradiation of adsorbent fluoresces yellow-green light at room temperature. The excitation and fluorescence spectra of the  $\text{Zn(II)}$  complex on the  $\text{SiO}_2$ -PHMG-Ferron surface are broad structureless bands with maxima at  $370 \text{ nm}$  and  $500 \text{ nm}$ , respectively (Figure 4a). The  $\text{Zn(II)}$  complex with Ferron in solution at  $\text{pH } 2.0 - 7.0$



has similar spectral characteristics (Figure 4b), which indicates the preservation of the luminescent properties of Ferron on the surface of SiO<sub>2</sub>-PHMG.

In this work, for the preconcentration and adsorption-fluorimetric determination of Zn(II), a SiO<sub>2</sub>-PHMG-Ferron adsorbent with a fixed reagent amount of 1.4 μmol g<sup>-1</sup> and 2.8 μmol g<sup>-1</sup> was used, since at high content of reagent the adsorbent was colored in intense yellow, which led to the reabsorption of the exciting light and a decrease in the fluorescence intensity of the Zn(II) complex with Ferron.

Quantitative extraction (95–99%) of Zn(II) with SiO<sub>2</sub>-PHMG-Ferron adsorbent was achieved in the pH range of 5.0–7.0 and did not depend on the concentration of the reagent on the adsorbent surface.

The maximum fluorescence intensity of the Zn(II) surface complex was observed at pH 5.0–7.0 and coincides with the range of its quantitative extraction using the SiO<sub>2</sub>-PHMG-Ferron adsorbent (Figure 5).

The time of attainment of adsorption equilibrium for the extraction of Zn(II) depends on the amount of Ferron on the surface of SiO<sub>2</sub>-PHMG (Figure 6).

The time of attainment of adsorption equilibrium for SPE of Zn(II) with a SiO<sub>2</sub>-PHMG-Ferron adsorbent (1.4 μmol g<sup>-1</sup>) was 10 minutes, and for SiO<sub>2</sub>-PHMG-Ferron (2.8 μmol g<sup>-1</sup>) – 5 minutes. An increase in the amount of the reagent on the surface of SiO<sub>2</sub>-PHMG leads to a decrease in the time of attainment of adsorption equilibrium for Zn(II) SPE.

The adsorbent is characterized by good kinetic characteristics. So, with an increase in the volume of the solution from which Zn (II) was extracted, from 10 to 20 mL, the time of attainment of adsorption equilibrium did not exceed 10 min (adsorbent with a surface Ferron concentration of 1.4 μmol g<sup>-1</sup>). When using 10 mL of solution and 0.1 g of adsorbent, the preconcentration factor was 100. With an increase in the volume of the solution to 20 mL, the preconcentration factor increases to 200.

### ***3.3. Selectivity of Zn(II) determination in natural water using SiO<sub>2</sub>-PHMG-Ferron***

To estimate the selectivity of the determination, binary systems containing zinc and increasing concentration of the accompanying element were prepared. The adsorption-fluorimetric determination of 20 μg L<sup>-1</sup> of Zn(II) (0.1 g SiO<sub>2</sub>-PHMG-Ferron, pH 6.0) was not affected by 1000-fold excess of Na(I), K(I), Ca(II), 500-fold excess of Mg(II), Sr(II), and equal amount of Al(III), Cu(II), Cd(II), Mn(II), Fe(III). Co(II) interferes to

the determination of zinc. The luminescence intensity decreases by half even at the ratio Zn (II): Co (II) = 1:1. The interfering effect of Cu(II) was eliminated by adding of 0.2% thiourea solution. To eliminate the interfering effect of Fe(III), it was reduced to Fe (II) with a 5% hydroxylamine solution.

In the presence of 0.2% thiourea solution, the determination of zinc affected by 10-fold amounts of copper, and in the presence of 5% hydroxylamine - 50-fold amounts of iron.

The adsorption-fluorimetric determination of Zn(II) using SiO<sub>2</sub>-PHMG-Ferron was not affected by salt background up to 2 g L<sup>-1</sup> for Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>.

### ***3.4. Adsorption-fluorimetric determination of Zn(II) using SiO<sub>2</sub>-PHMG-Ferron***

The formation of a fluorescent complex of Zn(II) on the surface of SiO<sub>2</sub>-PHMG-Ferron and an increase in the fluorescence intensity at 500 nm ( $\lambda_{\text{ex}} = 380$  nm) with increasing metal concentration was used as the basis for the adsorption-fluorimetric method of Zn(II) determination. Dependence of fluorescence intensity vs. concentration is shown in Figure 7.

The amount of Ferron fixed on the surface of the adsorbent did not affect the slope of the calibration plot. An increase in the surface concentration of the reagent from 1.4  $\mu\text{mol g}^{-1}$  to 2.8  $\mu\text{mol g}^{-1}$  leads to a twofold increase in the range of Zn(II) detectable contents (Figure 7, Table 2).

The detection limit of Zn(II) calculated by the 3 $\sigma$ -criterion directly on the surface of the adsorbent was 0.04  $\mu\text{g}$  per 0.1 g of adsorbent with a surface concentration of reagent 1.4  $\mu\text{mol g}^{-1}$  and 0.1  $\mu\text{g}$  per 0.1 g of adsorbent with a surface concentration of reagent 2.8  $\mu\text{mol g}^{-1}$ . This amount of Zn(II) is the minimum concentration that can be detected by this method on this sample of adsorbent (0.1 g) against to the background signal. When Zn(II) was extracted from 10 mL of the solution, the relative limit of its detection in the solution was 4  $\mu\text{g L}^{-1}$  when using an adsorbent with a surface concentration of reagent of 1.4  $\mu\text{mol g}^{-1}$  and 10  $\mu\text{g L}^{-1}$  when using an adsorbent with a surface concentration of reagent 2.8  $\mu\text{mol g}^{-1}$  (Table 2). An increase in the detection limit of Zn (II) with an increase in the surface concentration of the reagent is a consequence of an increase in the color intensity of the adsorbent.

The ratio of reacting components on the surface of the adsorbent, determined by comparing the surface concentration of Ferron with the maximum amount of adsorbed Zn(II) (from the inflection point on the calibration plot) is Zn: Ferron = 1: 2.3, which

allows to conclude about formation of surface complex with the stoichiometry of Zn:Ferron = 1: 2. The complex of Zn(II) with Ferron of similar composition is formed in aqueous solutions [12].

Table 3 compares the detection limits of Zn(II) using the developed procedure with the previously known ones.

As can be seen from the table, the proposed method for adsorption-fluorescent determination of Zn(II) is characterized by low detection limits, which are comparable with other adsorption-spectrometric methods.

### ***3.5. Determination of Zn (II) in natural water by adsorption-fluorimetric method using SiO<sub>2</sub>-PGMG-Ferron***

The developed adsorption-fluorimetric procedure was used for determination of Zn(II) in natural water. Water samples were taken from the Yenisei and Kacha rivers and artesian wells (Table 4). The correctness of the obtained results was confirmed by the analysis of spiked solutions and ICP-MS analysis.

## **4. Conclusion**

A simple and express method for preparation of the adsorbent based on silica, modified with polyhexamethylene guanidine and Ferron, is described in the present work.

Adsorption-fluorimetric determination of Zn(II) using SiO<sub>2</sub>-PHMG-Ferron adsorbent allows preconcentration and separation of Zn(II) from the matrix components and its determination directly in the phase of the adsorbent avoiding elution. According to the detection limit ( $4 \mu\text{g L}^{-1}$ ), the developed method is better than the direct fluorimetric determination of zinc, and is comparable to its adsorption-spectrometric determination using FAAS. The proposed method can be used to determine zinc in natural waters and technological solutions of different composition.

## **Disclosure statement**

No potential conflict of interest was reported by authors.

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## Figure captions

**Figure 1.** Extraction of Ferron (1, 3) and HQS (2) by SiO<sub>2</sub>-PHMG adsorbent vs. pH (0.1 g SiO<sub>2</sub>-PHMG; C<sub>Ferron</sub> : 2.8·10<sup>-5</sup> (1), 2.8·10<sup>-4</sup> (3) mol L<sup>-1</sup>; C<sub>HQS</sub> = 2.8·10<sup>-5</sup> mol L<sup>-1</sup>; V =10 mL, contact time 10 min)

**Figure 2.** Adsorption isotherms of Ferron (1) and HQS (2) by SiO<sub>2</sub>-PHMG (0.1 g of SiO<sub>2</sub>-PHMG, pH 5.0, V = 10 mL, t = 10 min)

**Figure 3.** Absorption spectrum (1) of an aqueous solution of Ferron and diffuse reflectance spectrum (2) of SiO<sub>2</sub>-PHMG-Ferron

**Figure 4.** Normalized spectra of excitation (1) and luminescence (2) of the Zn(II) complex with Ferron on the surface of SiO<sub>2</sub>-PHMG (a) and in solution (b) (0.1 g of SiO<sub>2</sub>-PHMG-Ferron, C<sub>Zn</sub>: 0.2 mg L<sup>-1</sup> (a), 1 mg L<sup>-1</sup> (b), V = 10 mL, pH 6.0, t = 10 min)

**Figure 5.** Dependence of Zn(II) extraction (1) and the surface complex luminescence intensity (2) on SiO<sub>2</sub>-PHMG-Ferron vs. pH (0.1 g of SiO<sub>2</sub>-PHMG-Ferron, C<sub>Zn</sub> = 0.2 mg L<sup>-1</sup>, V = 10 mL, t = 10 min)

**Figure 6.** Dependence of Zn(II) extraction (1) and the surface complex luminescence intensity (2) on SiO<sub>2</sub>-PHMG-Ferron vs. phase contact time (0.1 g of SiO<sub>2</sub>-PHMG-Ferron, C<sub>Zn</sub> = 0.2 mg L<sup>-1</sup>, V = 10 mL, pH 6.0, C<sub>Ferron</sub>: 1.4 μmol g<sup>-1</sup> (1), 2.8 μmol g<sup>-1</sup> (2))

**Figure 7.** Dependence of the surface complex luminescence intensity vs. concentration of Zn(II) in solution (n = 3, 0.1 g of SiO<sub>2</sub>-PHMG-Ferron, V = 10 mL, pH 6.0, C<sub>Ferron</sub>: 1.4 μmol g<sup>-1</sup> (1), 2.8 μmol g<sup>-1</sup> (2))

Figure 1.

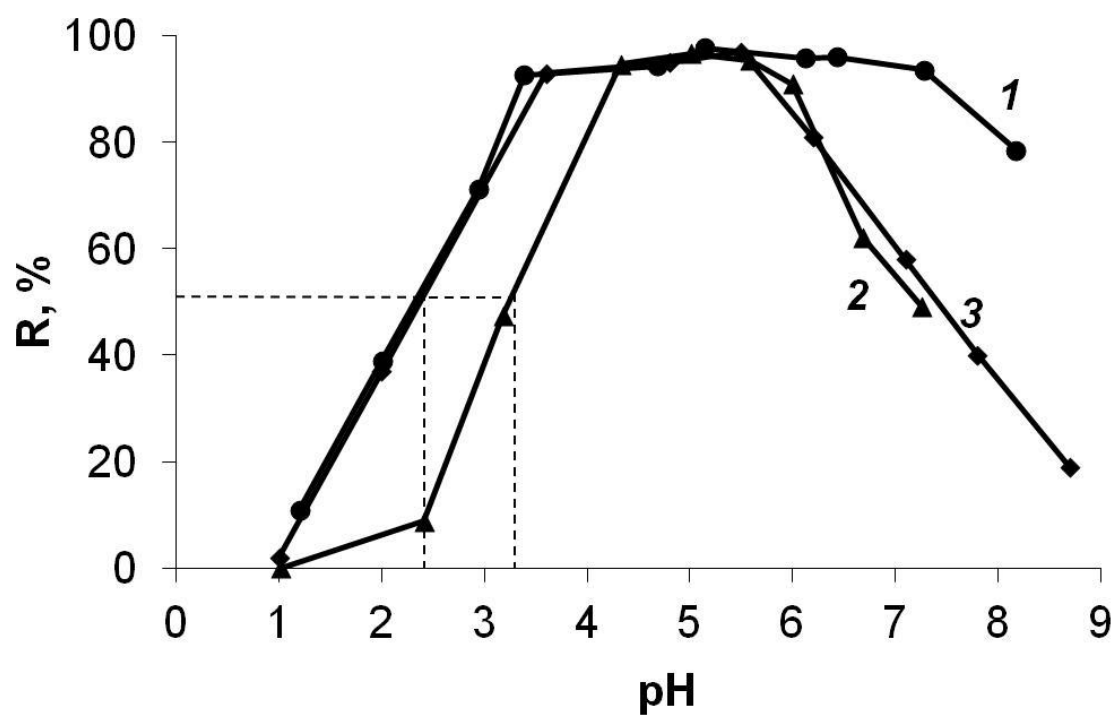


Figure 2.

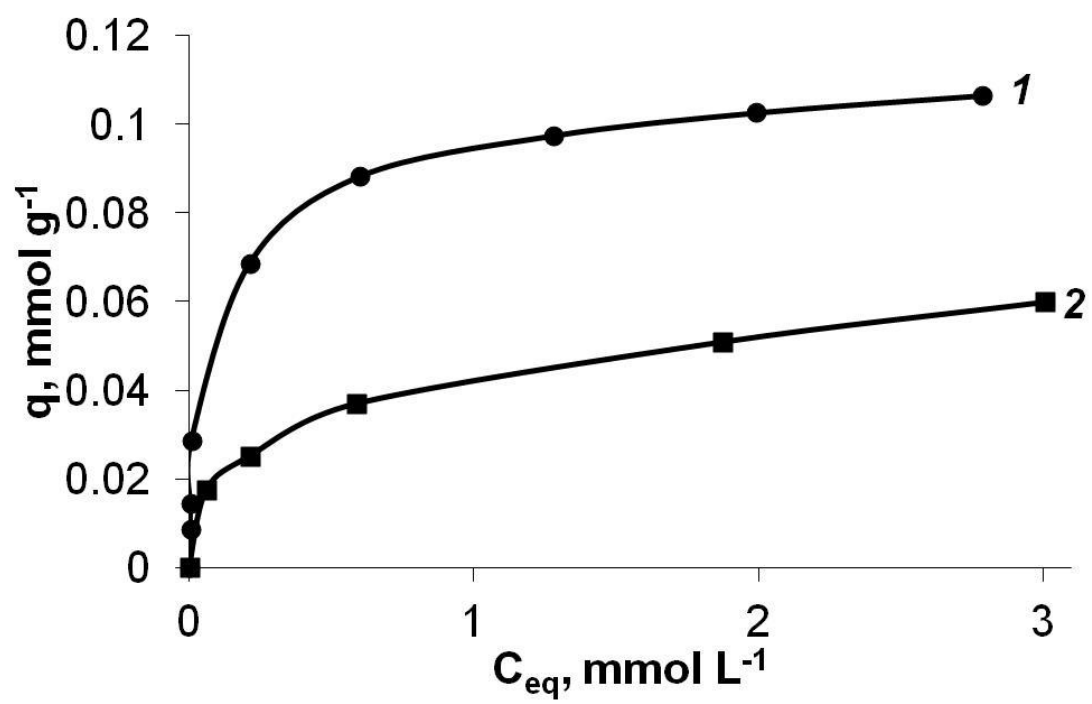




Figure 3.

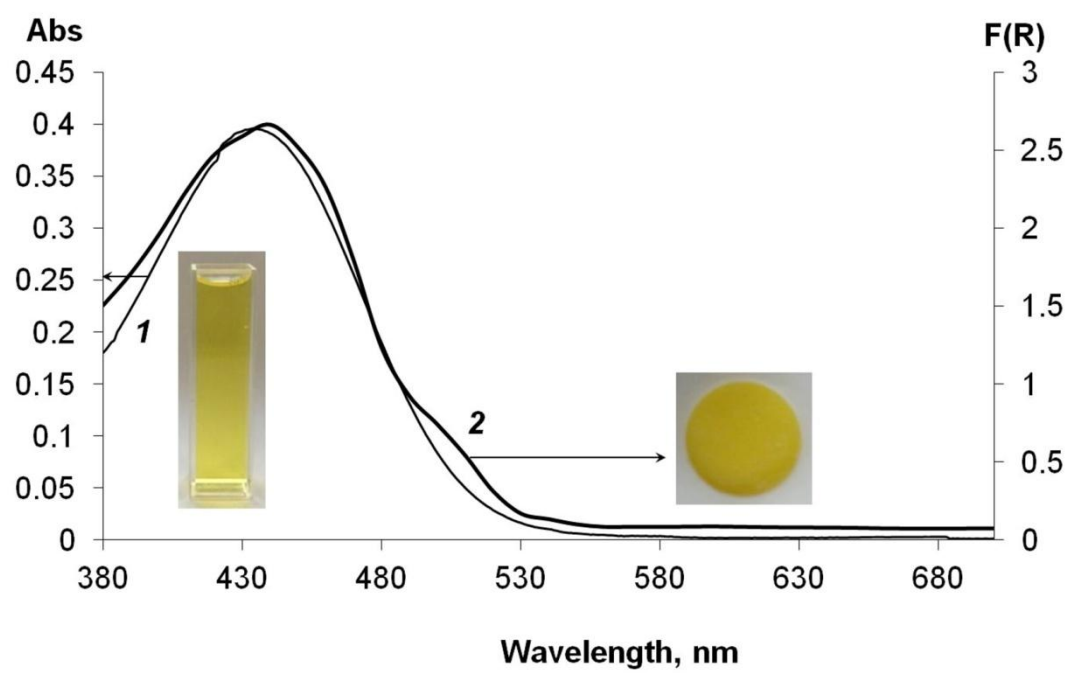


Figure 4.

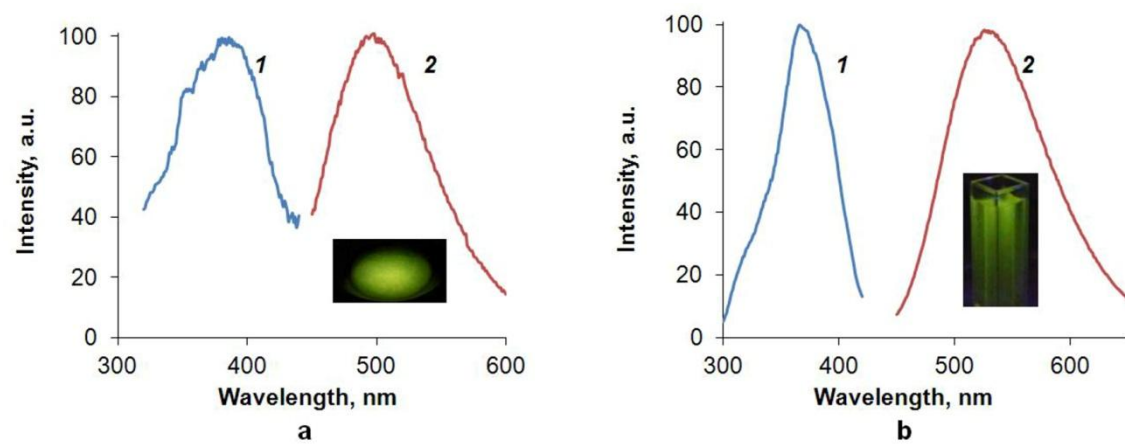


Figure 5.

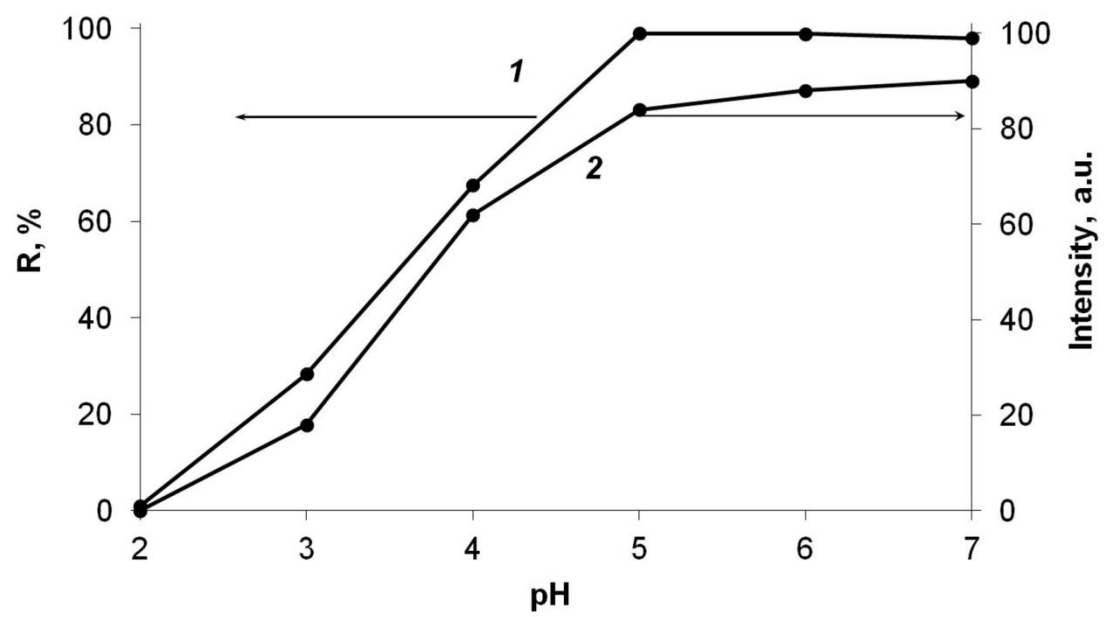


Figure 6.

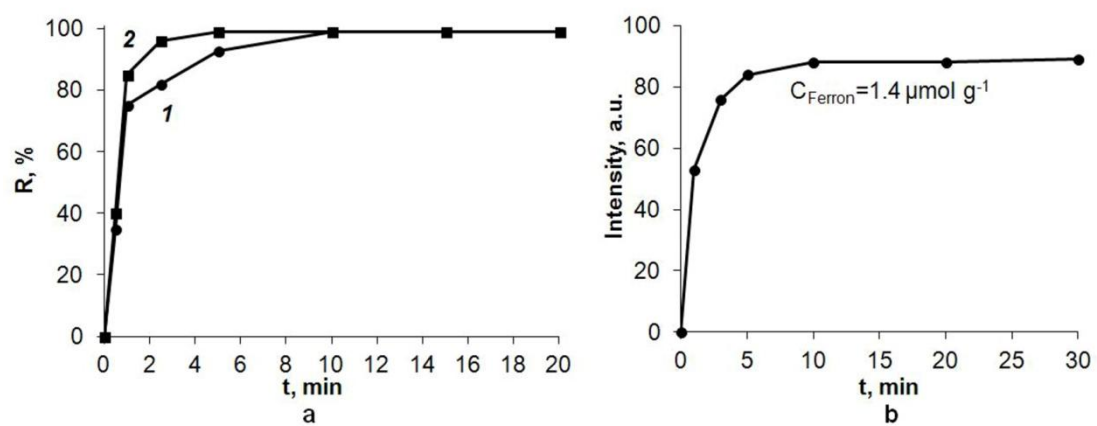


Figure 7.

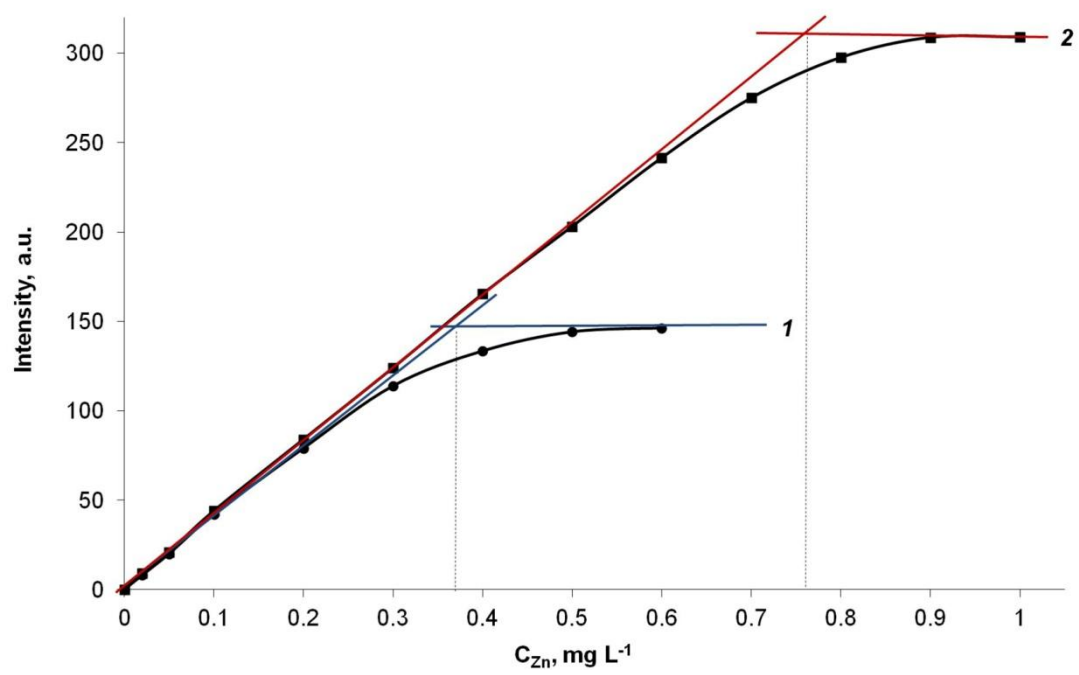


Table 1. Desorption degree of sulfo derivatives of 8-hydroxyquinoline from the surface of SiO<sub>2</sub>-PHMG (C<sub>Reagent</sub> 2.8 μmol g<sup>-1</sup>; V<sub>NaCl</sub>=10 mL; 0.1 g of adsorbent; t<sub>des</sub>=10 min)

Reagent	0.01 mol L <sup>-1</sup> NaCl	0.1 mol L <sup>-1</sup> NaCl	1 mol L <sup>-1</sup> NaCl
Ferron	1.0	29.8	50.2
HQS	45.5	89.1	99.9

Table 2. Characteristics of the adsorption-luminescent determination of Zn(II) using SiO<sub>2</sub>-PHMG-Ferron adsorbent (0.1 g of SiO<sub>2</sub>-PHMG-Ferron, V = 10 mL, pH 6.0, n = 3, P = 0.95)

C <sub>Ferron</sub> , g <sup>-1</sup>	μmol	LOQ, μg L <sup>-1</sup>	LOD, μg L <sup>-1</sup>	Equation	R <sup>2</sup>	S <sub>r</sub>
1.4		10–300	4	$\Delta I_{lum}=387.1 \cdot C_{Zn}$	0.9998	0.06
2.8		20–600	10	$\Delta I_{lum}=407.7 \cdot C_{Zn}$	0.9991	0.07

Comparative data from some recent studies for Zn(II) determination in water

Determination method	Reagent/ SPE material		LOD (µg/L)	Ref.
Fluorescence spectroscopy	HMQP <sup>a</sup>		14.4	[13]
Fluorescence spectroscopy	quinoline-based probe	fluorescent	4.1	[22]
High-resolution continuum source flame atomic absorption spectrometry	-		12.0	[23]
X-ray fluorescence spectroscopy	APDC <sup>b</sup>		2.0	[24]
Flame atomic absorption spectrometry (FAAS)	MPAEMA-co-DVB-co-VIM <sup>c</sup>		1.4	[25]
FAAS	Zn-IIP <sup>d</sup>		7.3	[26]
Fluorescence spectroscopy	SiO <sub>2</sub> -PHMG-Ferron		4.0 <sup>e</sup>	This work

<sup>a</sup> 4-methyl-2-((2-(quinolin-2-yl)hydrazono)methyl)phenol

<sup>b</sup> ammonium pyrrolydine dithiocarbamate

<sup>c</sup> poly[2-(4-methoxyphenylamino)-2-oxoethyl methacrylate-co-divinylbenzene-co-N-vinylimidazole]

<sup>d</sup> Zn<sup>2+</sup> ion-imprinted polymer

<sup>e</sup> V=10 mL, 0.1 g of SiO<sub>2</sub>-PHMG-Ferron



Table 4. Results of the adsorption-luminescent determination of Zn(II) in natural water (0.1 g of SiO<sub>2</sub>-PHMG-Ferron, V = 10 mL, pH 6.0, n = 5, P = 0.95)

Water sample	Added, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	Found (ICP-MS), $\mu\text{g L}^{-1}$
Yenisei River	-	14 $\pm$ 3	13 $\pm$ 1
	10	23 $\pm$ 3	23 $\pm$ 2
Kacha River	-	18 $\pm$ 3	18 $\pm$ 2
	10	29 $\pm$ 4	28 $\pm$ 2
Artesian well	-	12 $\pm$ 3	13 $\pm$ 2
(Kozulsky district)	10	21 $\pm$ 2	22 $\pm$ 2
Artesian well	-	-	4 $\pm$ 1
(Bolshemurtinsky district)	10	14 $\pm$ 1	13 $\pm$ 1
	20	23 $\pm$ 2	23 $\pm$ 2