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Speciation and Determination of Selenium Oxyanions at the Drinking Water Pollution Concentration Levels

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Abstract: The research on selenium presence in water resources has revealed the need to determine the respective aquatic species. As selenium oxyanions SeO_3^{2-} (Se^{IV}) and SeO_4^{2-} (Se^{VI}) predominate in natural waters, their determination is essential, mainly due to different ecotoxicity properties, as well as to different removal options from relevant-polluted waters. This study focuses on the $\text{SeO}_3^{2-}/\text{SeO}_4^{2-}$ speciation/separation and determination through the selective adsorption of SeO_3^{2-} only onto specific iron oxy-hydroxides (FeOOHs). For this purpose, the laboratory prepared FeOOHs examined along with the commercially available relevant material (Bayoxide), which was found to present optimum results for the speciation of selenium oxyanions, at the low concentration range 10–100 $\mu\text{g}/\text{L}$, using a dose of 0.5 g/L of adsorbent and gently stirring for 30 min at the usually encountered pH value of 7.3 ± 0.2 . Moreover, the relevant experiments showed that the other major ions Cl^- , HCO_3^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , possibly found in most natural waters at the concentration range 0–200 mg/L , as well as silicon, total organic carbon (TOC) of natural organic matter (NOM) and iron at the concentration range 0–50 mg/L , 0–5 mg/L and 0–1 mg/L , respectively, did not interfere with the selective adsorption of Se(IV). Furthermore, the most important advantage of this selective speciation method is its implementation/combination with all commonly applied analytical methods for the determination of total selenium.

Keywords: Se(IV)-Se(VI) speciation; separation and determination; adsorption; iron oxy-hydroxides; natural waters



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1. Introduction

The Swedish chemist Jöns Jacob Berzelius was the first scientist to discover selenium in 1817. Selenium can be found in natural water mainly with its inorganic forms, presenting various oxidative valent stages (i.e., -II, 0, IV, and VI), as well as (in trace levels) complexed with various organic forms, such as methylated compounds, seleno-amino acids and seleno-proteins [1]. However, the major forms encountered in most natural waters are the respective oxyanions of IV and VI valent states. Selenium is considered an essential nutrient for human growth at the concentration range within the drinking water regulation limits [2–4]; nevertheless, the long-term exposure to relatively higher concentrations (e.g., through potentially polluted drinking water sources) can cause severe toxic effects, due to its bioaccumulation [5].

In aquatic ecosystems (including groundwater), where the pH values usually range between 6 and 8, the most commonly encountered chemical species of selenium are the oxyanion forms, i.e., SeO_3^{2-} (Se^{IV}) and SeO_4^{2-} (Se^{VI}) [6]. Therefore, it is crucial to determine with high accuracy and precision the concentration of selenium species, in order to evaluate properly their corresponding ecotoxicity effects/differences in the aquatic environment [7]. Additionally, the selection of an appropriate drinking water treatment process, regarding the removal of selenium, should be also accordingly adapted to the specific

oxyanion that dominates each potentially polluted water body, since these oxyanions are showing different removal efficiencies, depending on the specifically applied treatment method [8,9].

A wide variety of analytical methods is used to determine the concentration of total selenium, such as titration [10], gravimetric methods [11], colorimetric methods [12], spectrophotometric methods [13], fluorometry [14], hydride generation–atomic absorption spectrometry [15], graphite furnace-atomic absorption spectrometry [16], inductively-coupled plasma atomic emission spectrometry (ICP-AES) [17], inductively-coupled plasma mass spectrometry (ICP-MS) [18], and isotope dilution-mass spectrometry [19]. The plethora of analytical options, available for the determination of total selenium, allows the analysts to apply the method most compatible with the available equipment in each laboratory.

Several analytical techniques have been applied for the speciation of Se, presenting different drawbacks that need to be carefully considered. For example, gas chromatography is usually incompatible with applications regarding natural water samples, because the usually applied fractionation may require the appropriate pre-treatment of different selenium oxyanions by applying organic/toxic solvents, possibly producing selenols, which may not be determined accurately, due to their high volatility. The use of High-Pressure Liquid Chromatography (HPLC) method as a separation technique for selenium species takes usually more than 10 min to separate the selenium oxyanions. Thus, when HPLC is combined, e.g., with ICP-MS (LOD 1.2 and 1.4 $\mu\text{g/L}$ for Se(IV) and Se(VI), respectively [20]) for the determination of selenium species, it requires approximately 1 min for each sample determination, and therefore, the total time for each sample pre-treatment and determination can overpass 10 min. In addition, this hybrid HPLC-ICP-MS method also presents higher operating cost per sample and capital cost one order of magnitude higher, when compared to GF-AAS [21]. Additionally, the selenium hydride generation performed within ~15 min, as applied in field studies by Omanovic et al. (2002), requires an additional 5–15 min to reduce SeO_4^{2-} to SeO_3^{2-} in a microwave digestion system, while the Supralab FD pre-treatment device for selenium determination uses a filter that requires subsequent drying for ~45 min, resulting in a significantly time-consuming procedure [22]. Capillary electrophoresis is an energy-consuming process that is usually hyphenated with ICP-MS. Deng et al. (2007) used a fused silica capillary (with sample throughput ~3 min) and reported selenium recoveries of 91–108%, using tap and river spiked water samples [23]. The selective sequential hydride generation and photochemical vapor pressure also require quite complicated and time-consuming pre-treatment steps with a prolonged pre-heating, or UV-irradiation for the Se(VI) reduction to Se(IV), producing volatile Se, due to UV irradiation, reducing the reliability of the analysis and resulting in substantial increase in cost, as they are usually combined with ICP-MS. Liquid–liquid micro-extraction is a more complex procedure, due to the production of selenols and requires the use of organic solvents that are toxic, while, at the same time, is a time-consuming determination method, as the procedure most usually requires a heating step at 100 °C. In addition, the solid phase micro-extraction, in which the adsorption step is followed by the extraction of adsorbed species, generates accuracy and precision issues. Liquid–liquid micro-extraction and solid phase micro-extraction are also usually combined with the application of ICP-MS [24,25].

Therefore, the development of a speciation method, aiming to the selective and quantitative separation of selenium oxyanions that would be simple, cost effective, rapid, sensitive, and compatible with the majority of modern analytical determination instrumentation, is considered as crucial. For this purpose, batch adsorption experiments were conducted, using iron oxy-hydroxides (FeOOHs), to examine the selective uptake and quantitative separation of SeO_3^{2-} against SeO_4^{2-} from natural water samples. Although the FeOOHs have been previously examined for selenium removal [8], the obtained results showed the lack of 100% selective adsorption for selenium oxyanions. In addition, several other studies [26–32] have reported the removal of both SeO_3^{2-} and SeO_4^{2-} and the absence of effective separation between these species. Based upon the better affinity of FeOOHs against the SeO_3^{2-} rather than SeO_4^{2-} , and their relatively low cost, the qualified FeOOH

was verified, aiming to make this material the proper one for the selective uptake of Se(IV) by adsorption.

2. Materials and Methods

2.1. Reagents

Stock solutions of Se(IV) and Se(VI) were prepared from the analytical grade reagents Na_2SeO_3 (supplied by ACROS Organics, anhydrous 44–46% purity) and NaSeO_4 (supplied by Alfa Aesar, anhydrous >99.8% purity), respectively, dissolved in distilled water. Stock solutions of Cl^- , HCO_3^- , NO_3^- , SO_4^{2-} , Si, Ca^{2+} , Mg^{2+} , and Na^+ were prepared from the respective analytical grade reagents, i.e., NaCl (supplied by Merck, >99.0% purity), NaHCO_3 (supplied by Merck, >99.5% purity), NaNO_3 (supplied by Merck, >99.5% purity), Na_2SO_4 (supplied by Merck, >99.0% purity), $\text{NaSiO}_3 \cdot 5\text{H}_2\text{O}$ (supplied by Loufakis Chemicals S.A., >99.0% purity), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (supplied by Riedel-de Haen, >99.0 purity), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (supplied by Panreac, >98.0% purity), and NaCl, dissolved in distilled water. The 100 mg Fe^{2+} /L stock solution was prepared by diluting in 1 L of distilled water 0.51 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (supplied by Riedel de Haen, >99% purity), which was pre-treated to remove residual oxygen content with the supply of N_2 gas.

The natural test water was prepared according to the National Sanitation Foundation (NSF) standard, containing 252 mg NaHCO_3 , 12.14 mg NaNO_3 , 0.178 mg $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (supplied by Sigma-Aldrich, >98.0% purity), 2.21 mg NaF (supplied by Merck, >99.0% purity), 70.6 mg $\text{NaSiO}_3 \cdot 5\text{H}_2\text{O}$, 147 mg $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and 128.3 mg $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, diluted in 1 L of distilled water and the corresponding ion concentrations are shown in Table 1 [33]. The stock solution of humic acid was prepared by dissolving 1 g of reagent grade humic acid powder (supplied by Sigma-Aldrich, No. 53680) into 500 mL distilled water. The pH of this solution was adjusted to 12 with 1 N NaOH (prepared by sodium hydroxide pellets supplied by Chem-Lab, >99.0% purity), and then, the solution was filtered through a cellulose acetate membrane (MFS) of 0.45 μm pore size. The supernatant was collected and adjusted to neutral pH with HCl (supplied by Chem-Lab, 37% purity) and transferred in a plastic bottle for storage. Experimental solutions of the desired humic acid concentrations were obtained by successive dilutions. Working standards of Se(IV) and Se(VI) were prepared by the proper dilution of stock solutions into the NSF water matrix. All working solutions were prepared at least 12 h before the adsorption tests to allow sufficient time for the integration of selenium oxyanions into the water matrix and permitting to form similar species as those found in natural waters.

Table 1. Ion concentrations in the NSF water matrix, simulating natural water used for experiments.

Cations	mg/L	Anions	mg/L
Na^+	88.8	HCO_3^-	138
Ca^{2+}	40.0	SO_4^{2-}	50
Mg^{2+}	12.7	Cl^-	71
		N- NO_3^-	2
		F^-	1
		P- PO_4^{3-}	0.04
		Si/ SiO_2	10.5/22.4

2.2. Adsorbents

The examined iron oxy-hydroxides (FeOOHs) were prepared at kilogram scale using a laboratory two-stage continuous flow reactor (CSTR-1 and CSTR-2) with each stage having 1 h retention time, similar to the procedure described in the respective literature [34]. The preparation procedure included a sequence of Fe(II) oxidation ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$ supplied by Loufakis Chemicals S.A.), hydrolysis, and subsequent Fe(III) precipitation (as FeOOH) in aqueous environment at high redox value conditions (250–600 mV) and application of a wide range of pH values. Along with the laboratory-synthesized iron oxy-hydroxides, the commercially available Bayoxide, consisting mainly from goethite (α -FeOOH) and

produced by LANXESS Deutschland GmbH, was also comparatively examined for the selective separation of selenite. The main physicochemical parameters of these adsorbents are previously described [8] and summarized in Table 2, noting that the experimental procedures followed for the determination of these characteristics are described in Text S1 in the Supplementary Material.

Table 2. The main physicochemical characteristics of laboratory-synthesized and commercial adsorbents based on FeOOHs and used in this study for the separation of selenium species.

Synthesis Parameters			Physicochemical Characteristics					
Abbreviation	Materials	pH	ORP ¹ (mV)	Fe wt. %	Surface Area (m ² /g)	IEP ²	ZPC ³	PSCD ⁴ mmol [OH ⁻]/g
FeOOH/2.5	FeSO ₄ /H ₂ O ₂	2.5	600	44.8	48	6.9	2.7	3.25
FeOOH/4	FeSO ₄ /H ₂ O ₂	4.0	380	50.4	120	7.1	3.2	2.23
FeOOH/5.7	FeSO ₄ /H ₂ O ₂	5.7	380	50.1	168	7.3	4.2	1.42
FeOOH/8	FeSO ₄ /H ₂ O ₂	8.0	250	50.2	226	6.6	7.9	1.04
Bayoxide				52.0	135	7.4	7.8	0.80

¹ Oxidation–reduction potential. ² Isoelectric point. ³ Point of zero charge [35]. ⁴ Positive surface charge density.

2.3. Experimental Procedure

Quantities (0.25–2 g FeOOH/L) of finely powdered (<63 µm) adsorbent samples were dispersed into 200 mL of selenium solution (in NSF water matrix), using 300 mL conical flasks and were stirred gently for 1 h contact time at 20 °C. The solution pH was adjusted with either 1 M HCl or 1 M NaOH to set/determine the optimum pH range. The subsequent solid/liquid separation was performed by filtration, using a common membrane filter of 0.45 µm, and the resulting solution was further analyzed to determine the selenium content.

Initially, all adsorbents were examined in three replicates at 1 h contact time and at the optimum pH value of 7.3 ± 0.2, while samples were received every 5, 15, 30, and 60 min to determine the kinetics/equilibrium of selenium species adsorption. The adsorption of Se(IV) and Se(VI) was examined in the concentration range of 10–100 µg/L. The adsorbent that presented the optimal selectivity was further tested using additional adsorption experiments to clarify the interference of commonly co-existing ions in natural waters at various concentrations. Specifically, 0.5 g FeOOH/L of finely powdered (<63 µm) adsorbent was dispersed into 200 mL of selenium solution in NSF water matrix with the addition of 25, 50, 100, and 200 mg/L of Cl⁻, HCO₃⁻, NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺, and Na⁺ ions or of 10, 25, 40, and 50 mg/L of Si or of 1, 2.5, 4, and 5 mg/L of humic acid that represents the presence of natural organic matter (NOM) or of 0.1, 0.25, 0.5, and 1 mg/L of Fe²⁺ in 300 mL conical flasks that were stirred gently for 30 min at 20 °C and at pH value of 7.3 ± 0.2.

The initial and residual elemental concentrations of metals and silicon were determined either by Graphite Furnace or by Flame Atomic Absorption Spectrophotometry, using a PerkinElmer Analyst 800 instrument. The detection limits of calcium, magnesium, silicon, sodium, iron, and selenium were 50 µg Ca/L, 10 µg Mg/L, 2 mg Si/L, 20 µg Na/L, 50 µg Fe/L, and 1 µg Se/L, respectively. In order to cross check the Se(IV) concentrations, the determination was also conducted by following the Ahmed et al. (2015) spectrophotometric analytical method (detection limit 1 µg/L) [36], using the spectrometer UV-VIS HITACHI U-5100. Nitrate, chloride, and sulfate were measured with the Alltech 600 ion chromatography system, using an Allsep anion, 150 mm × 4.6 mm, 7 µm, PEEK 51209 column and applying a 1.7 mM NaHCO₃/1.8 mM Na₂CO₃ (supplied by Merck, >99.5% purity) solution as eluent. The detection limits were 1 mg NO₃⁻/L, 1 mg SO₄²⁻/L, and 1 mg Cl⁻/L, respectively. Bicarbonate was determined by titration with 0.1 M HCl. The NOM content was measured with the Shimadzu TOC-V_{CSN} Total Organic Carbon (TOC) Analyzer.

3. Results and Discussion

3.1. Effect of pH on Adsorption

The previously published relevant experimental results [8] showed the good adsorption efficiency of Se(IV) by several iron oxy-hydroxides, achieving residual concentrations at sub-ppb level within the common pH range (6–8), existing in most natural waters [8]. In contrast, the respective uptake capacity for the case of Se(VI) was verified as extremely low and almost zero for some of the examined adsorbents. To clarify further the pH effect, regarding the selective adsorption of Se(IV) only, 2 g FeOOH/2.5/L was added to a solution containing initial concentrations either of 100 µg Se(IV)/L or of 100 µg Se(VI)/L in NSF water matrix and were stirred gently for 1 h. According to the obtained experimental results (Figure 1), equilibrium (i.e., residual) concentrations below the detection limit of 1 µg Se(IV)/L were determined for pH values lower than 7.5, while at higher pH values, the Se(IV) was not fully adsorbed/separated/removed from the aqueous solution. Figure 1 also shows that for the initial concentration of 100 µg Se(VI)/L, minor adsorption/separation takes place at pH values lower than 7, while at higher pH values, almost zero adsorption was observed, since equilibrium concentrations equal to the initial Se(VI) concentration of 100 µg/L were determined. In conclusion, the optimum pH range for the selective Se(IV) adsorption/separation is between 7 and 7.5. Thus, the experiments to verify the optimum adsorbent type, adsorbent quantity, and contact time were subsequently performed at the pH value of 7.3 ± 0.2 .

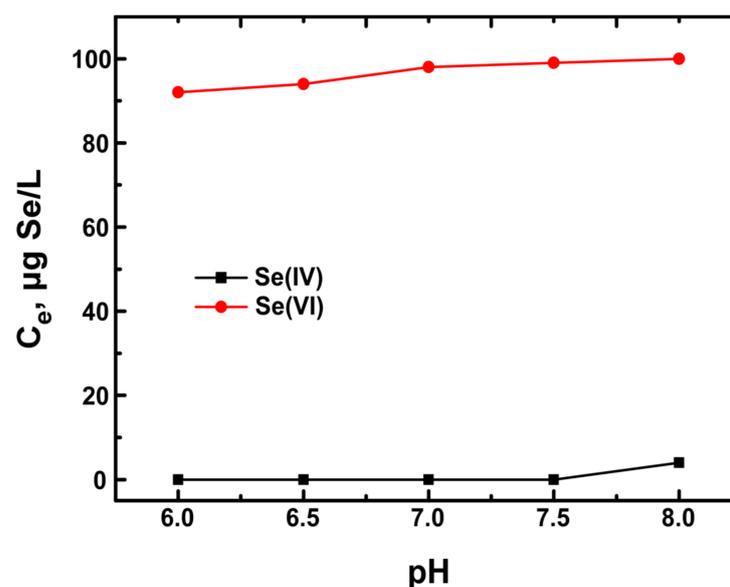


Figure 1. Effect of pH on adsorption of Se(IV) and Se(VI) species (examined separately), using FeOOH as adsorbent (synthesized at pH 2.5). Experimental conditions: initial concentration is 100 µg Se(IV)/L, 100 µg Se(VI)/L, adsorbent dose 2 g FeOOH_{2.5}/L.

3.2. Examined Adsorbents

As aforementioned, the iron oxy-hydroxides were selected as sorbent materials mainly due to their good affinity against Se(IV) and poor affinity for the Se(VI) species. The FeOOHs examined for the selective adsorption of Se(IV) were those synthesized in the laboratory at different pH values (i.e., pH 2.5, 4.0, 5.7, and 8.0), as well as (for comparison reasons) the commercially available Bayoxide material. The selection of these adsorbents was based on the variation of Positive Surface Charge Density (PSCD), which ranges between 0.8 and 3.2 mmol [OH⁻]/g (Table 2), attempting to examine the relation of PSCD with the complete Se(IV) uptake (i.e., under the limits of detection) and in comparison with the respective almost null Se(VI) uptake, i.e., the selective separation between the major inorganic selenium species/oxyanions.

Figure 2 shows the adsorption of a mixture of selenium species from a solution containing initially equal concentrations of 10 µg Se(IV)/L and of 10 µg Se(VI)/L at pH 7.3 ± 0.2 . The equilibrium concentrations, i.e., the residual selenium concentrations after the adsorption procedure lower than 10 µg/L, indicate the total adsorption of Se(IV) along with a part of Se(VI), while the equilibrium concentrations greater than 10 µg/L indicate the near-zero adsorption of Se(VI) along with a part of residual concentration (i.e., indicating insufficient adsorption) of Se(IV). In contrast, the equilibrium concentrations equal to 10 µg/L show the selective uptake/separation of only Se(IV). The adsorbents FeOOH/2.5 and FeOOH/4 showed the total uptake of Se(IV), however, with significant adsorption/separation of Se(VI) for all the examined concentrations (Figures 2–5), due to the highest PSCD values of 3.25 and 2.23 mmol [OH⁻]/g, respectively (Table 2). In contrast, the FeOOH/8 with the lowest PSCD value (1.04 mmol [OH⁻]/g) showed insufficient Se(IV) uptake. These results verify that the Positive Surface Charge Density (PSCD) is the major factor, controlling the effective selenium adsorption.

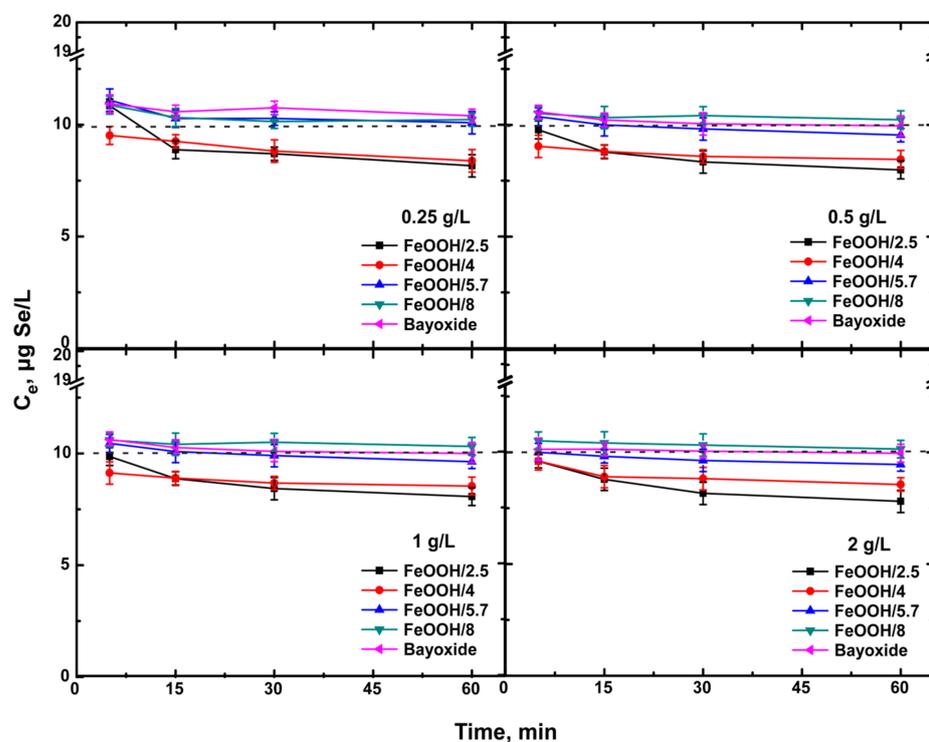


Figure 2. Adsorption of selenium species onto several FeOOHs (used as adsorbent media) in relation to the adsorbent dose and contact time. Experimental conditions: the initial concentration of Se in the samples is a mixture containing 10 µg Se(IV)/L and 10 µg Se(VI)/L (i.e., total Se 20 µg/L), pH 7.3 ± 0.2 , and temperature 20 °C.

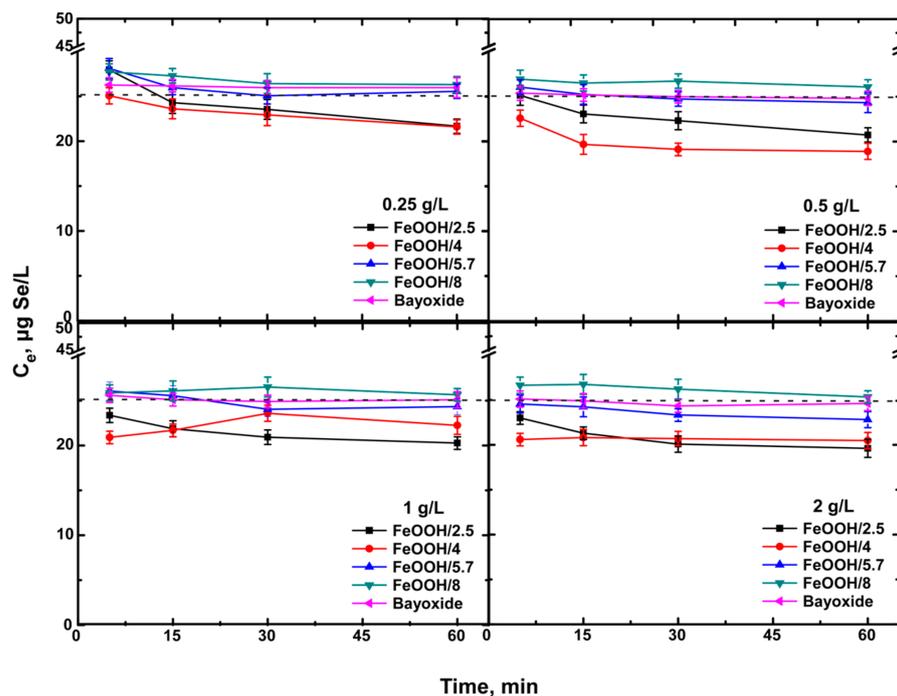


Figure 3. Adsorption of selenium species onto several FeOOHs materials in relation to the adsorbent dose and to contact time. Experimental conditions: the initial Se concentration in the samples is a mixture containing 25 µg Se(IV)/L and 25 µg Se(VI)/L (i.e., total Se 50 µg/L), at pH 7.3 ± 0.2, and temperature 20 °C.

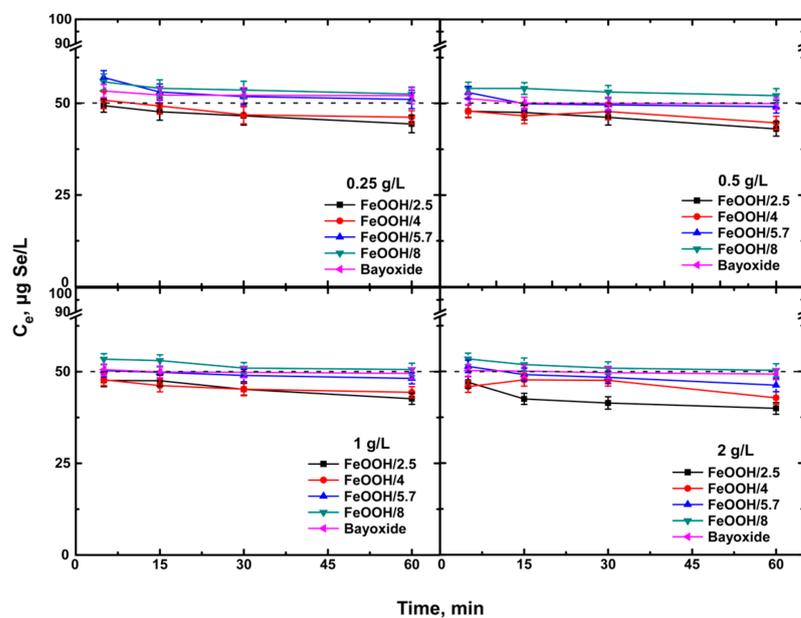


Figure 4. Adsorption of selenium species onto several FeOOHs materials in relation to adsorbent dose and to contact time. Experimental conditions: the initial concentration of samples is a mixture containing 50 µg Se(IV)/L and 50 µg Se(VI)/L (i.e., total Se 100 µg/L), at pH 7.3 ± 0.2 and temperature 20 °C.

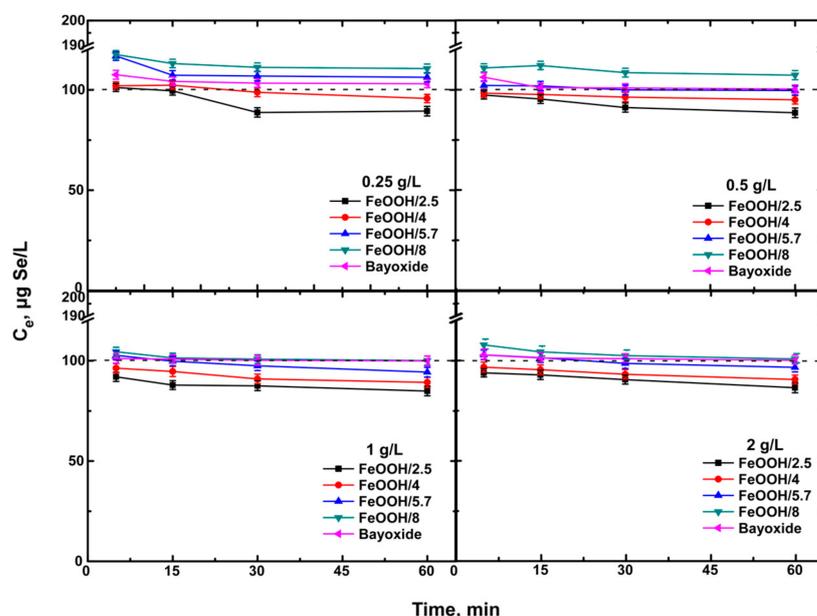


Figure 5. Adsorption of selenium species onto several FeOOHs materials in relation to adsorbent dose and to contact time. Experimental conditions: the initial concentration in the samples is a mixture containing 100 µg Se(IV)/L and 100 µg Se(VI)/L (i.e., total Se 200 µg/L), at pH 7.3 ± 0.2 and temperature 20 °C.

Considering the influence of different adsorbent doses (Figure 2):

- At the lower dose of 0.25 g/L, the adsorbents with the relatively lower PSCD values (i.e., FeOOH/5.7, FeOOH/8, and Bayoxide) resulted in the partial adsorption of Se(IV), whereas the adsorbents with the higher PSCD values (i.e., FeOOH/2.5 and FeOOH/4) showed the adsorption/separation of both Se species.
- At the higher doses of 0.5, 1, and 2 g/L, the FeOOH/8 showed the insufficient uptake of Se(IV), whereas the Bayoxide presented complete Se(IV) uptake. In contrast, the adsorbents FeOOH/2.5, FeOOH/4, and FeOOH/5.7 showed the adsorption of both species.
- The relative standard deviation of selenium species adsorption was under 5% (i.e., RSD <5%) for all these experiments.

Aiming to investigate the selective adsorption of Se(IV) at different naturally occurring concentrations of selenium, relevant experiments were conducted also in NSF water matrix, but by increasing equally the initial concentrations of selenium at 25 µg Se(IV)/L and 25 µg Se(VI)/L (Figure 3), 50 µg Se(IV)/L and 50 µg Se(VI)/L (Figure 4), and 100 µg Se(IV)/L and 100 µg Se(VI)/L (Figure 5). The obtained results were similar to those presented in Figure 2 for the equal initial concentrations of 10 µg Se(IV)/L and 10 µg Se(VI)/L, i.e.,

- FeOOHs with the higher PSCD values can adsorb both selenium species at any examined concentration/adsorbent dose.
- FeOOH/8 partially adsorbs Se(IV) at any adsorbent dose.
- When using the quantities 0.5 and 1 g/L, the adsorbents FeOOH/5.7 and Bayoxide can completely adsorb/separate Se(IV), while at the higher dose of 2 g/L, they can also adsorb a part of Se(VI).
- At the quantities 0.5 and 1 mg/L, Bayoxide demonstrated the complete adsorption of only Se^{IV} (and not of Se^{VI}) within 30 min of contact time.

Conclusively, based on the results shown in Figures 2–5, Bayoxide proved to be the optimal adsorbent for the selective adsorption of Se(IV), when applying the following experimental conditions: adsorbent dose 0.5 g/L, initial selenium concentration range 10–100 µg/L (for a mixture of both species), contact time 30 min, pH 7.3 ± 0.2, and temperature 20 °C with RSD <5%.

The different initial concentrations of Se(IV) and of Se(VI) in NSF water samples were subsequently examined to verify the selective adsorption of Se(IV) by the qualified adsorbent Bayoxide. Figure 6 presents the data regarding the selective adsorption of Se(IV) in water samples, containing 100 µg/L total selenium, for the Bayoxide doses of 0.5, 0.7, and 1 g/L at pH 7.3 ± 0.2 and 30 min contact time. The experimental results indicate that the selective separation (and speciation) of selenium species can be effectively achieved in the aforementioned optimized conditions using the 0.5 g/L Bayoxide dose. The equilibrium concentrations, i.e., the residual concentrations of dissolved selenium, correspond to the initial concentrations of Se(VI) in the examined water samples, indicating indirectly that only the Se(IV) was able to be completely adsorbed (and separated) by the applied adsorbent from the aqueous mixtures of selenium species.

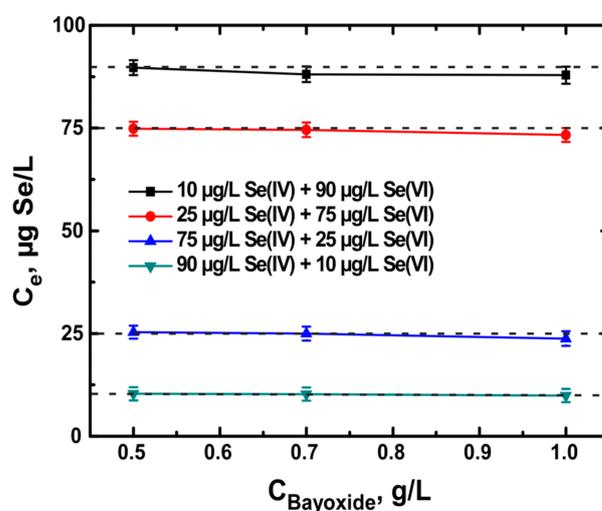


Figure 6. Equilibrium concentration of total Se, after the adsorption of selenium species mixtures in relation to Bayoxide dose. Experimental conditions: the total initial concentration of Se is 100 µg/L, but using different ratios between the concentrations of examined Se(IV) and Se(VI) species at pH 7.3 ± 0.2 , temperature 20 °C and contact time 30 min.

3.3. Effect of Different Commonly Co-Existing Ions on the Selective Adsorption of Se(IV), Using the Bayoxide Material

It is well known that the physicochemical characteristics of natural waters can vary widely. Thus, different concentrations ranges of the main co-existing ions were also examined, aiming to determine their potential influence on the Se(VI) lack of adsorption/separation, when using the qualified adsorbent Bayoxide and in the presence of initial Se(VI) concentration range of 10–100 µg/L.

All these experiments were conducted in triplicate, applying the following optimum conditions: Bayoxide adsorbent dose 0.5 g/L, pH 7.3 ± 0.2 , and contact time 30 min. The examined samples were prepared in NSF water matrix (Table 1) with the additional concentrations of 25, 50, 100, and 200 mg/L for Cl^- , HCO_3^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , as well as of 10, 25, 40, and 50 mg/L for the case of Si and 1, 2.5, 4, and 5 mg/L of humic acids (NOM), measured as mg TOC/L, simulating the different concentration ranges of the aforementioned components, commonly existing in most natural waters. Iron was also examined with the additional concentrations of 0.1, 0.25, 0.5, and 1 mg Fe^{2+} /L, since only Fe^{2+} is the soluble form in anaerobic natural groundwater at the common concentration range of 0–1 mg/L. All the performed adsorption experiments resulted in equilibrium/residual Se(VI) concentrations very close to the initial ones within the RSD of 3% (Figures 7–9), therefore, verifying the almost zero selectivity of the qualified adsorbent against the Se(VI).

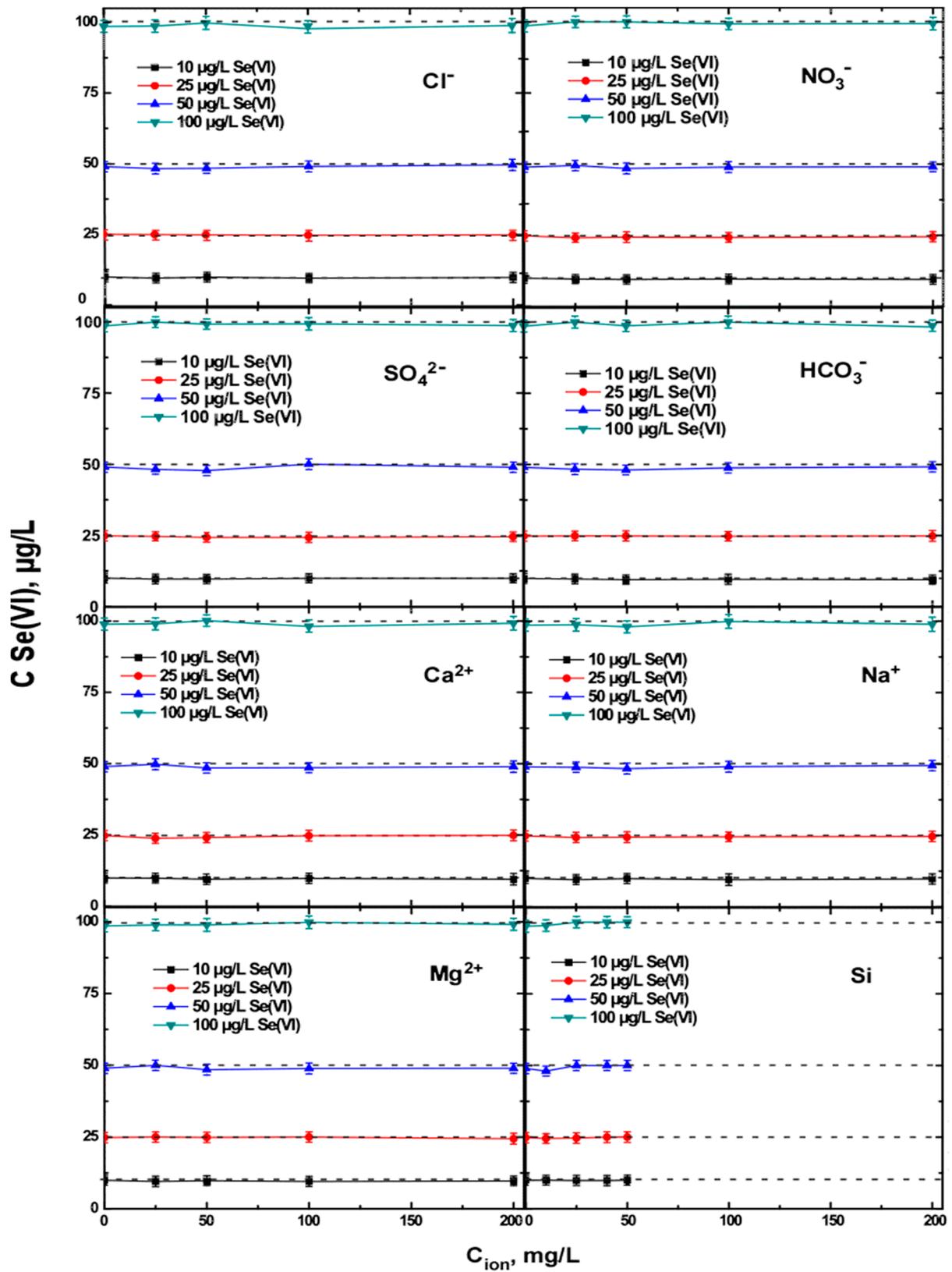


Figure 7. Influence of common water ions on the Se(VI) adsorption by Bayoxide. Experimental conditions: Bayoxide concentration 0.5 g/L, initial Se(VI) concentration range 10–100 µg/L, pH 7.3 ± 0.2 , temperature 20 °C, and contact time 30 min.

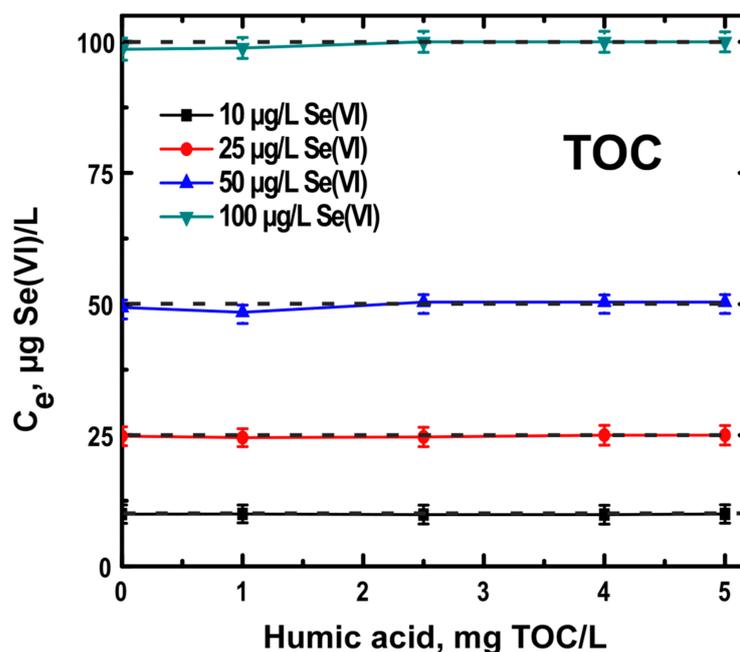


Figure 8. Influence of commonly found in natural waters NOM concentrations (as determined by TOC) on Se(VI) adsorption by Bayoxide. Experimental conditions: Bayoxide concentration 0.5 g/L, initial Se (VI) concentration range 10–100 µg/L, pH 7.3 ± 0.2, temperature 20 °C, and contact time 30 min.

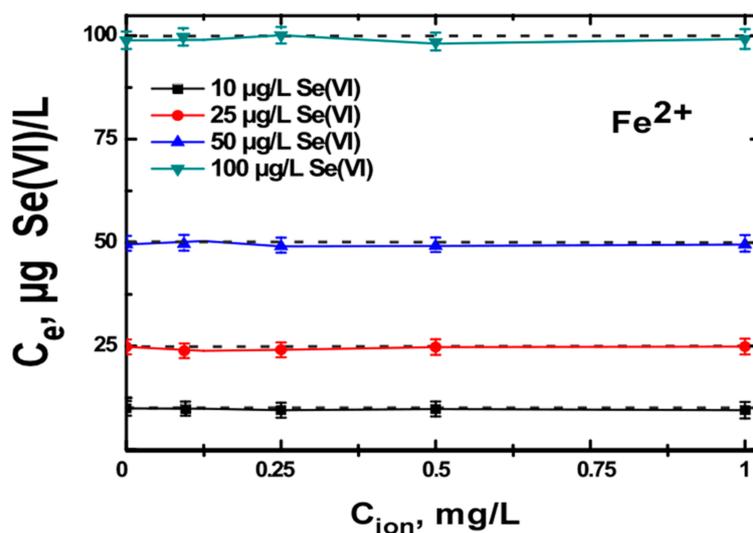


Figure 9. Influence of iron found in natural waters on Se(VI) adsorption by Bayoxide. Experimental conditions: Bayoxide concentration 0.5 g/L, initial Se(VI) concentration range of 10–100 µg/L, pH 7.3 ± 0.2, temperature 20 °C, and contact time 30 min.

In contrast, all the adsorption experiments with Se(IV) resulted in equilibrium/residual concentrations below the method’s detection limit (1 µg/L)—see also Figures S1–S3 in the Supplementary Material, thus verifying the complete uptake/separation of Se(IV). Therefore, the effective adsorption, separation, and determination of main inorganic selenium species were not influenced from the presence of major commonly co-existing ions and for the concentration ranges usually found in natural waters.

4. Conclusions

A novel analytical method for the efficient speciation/determination of major (inorganic) selenium species/oxyanions, i.e., Se(IV)-SeO₃²⁻ and Se(VI)-SeO₄²⁻, in natural

waters was developed by employing the selective adsorption of Se(IV) onto several FeOOHs materials. The examined FeOOHs showed good adsorption affinity but only for the case of Se(IV), resulting in equilibrium/residual concentrations below the analytical detection limit of 1 µg/L, irrespective of the initial concentration range (between 10 and 100 µg/L). Regarding the Se(VI) adsorption, the FeOOHs with the highest PSCD values showed low adsorption capacity for SeO_4^{2-} , while the FeOOH/8 and the Bayoxide with the lowest PSCD values and at the dose range 0.5–2 g FeOOH/L, resulted in almost zero adsorption capacity.

The optimum adsorbent for the selective Se(IV) adsorption was found to be the Bayoxide material by applying the following experimental parameters: adsorbent dose 0.5 g/L, pH 7.3 ± 0.2 , temperature 20 °C, and contact time 30 min. The presence of other ions, such as Cl^- , HCO_3^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Na^+ , commonly co-existing in natural water in the concentration range 0–200 mg/L, as Si in the concentration range 0–50 mg/L and as humic acid (NOM) in the concentration range 0–5 mg/L (as TOC), as well as of Fe^{2+} in the concentration range 0–1 mg/L, did not show any interference on the quantitative selective adsorption of Se(IV) (i.e., below the detection limit) and the simultaneous near-zero adsorption capacity for Se(VI) in the concentration range of selenium species between 10 and 100 µg/L, when the Bayoxide material was applied. Therefore, the commercially available Bayoxide provides the advantage of selective separation of selective separation of selenium oxyanions, permitting the subsequent determination of Se species using any available analytical laboratory method for total selenium determination. Furthermore, this novel speciation method is considered as low-cost, requiring simple reagents and handling procedures, and can be also potentially applied in field studies, using the appropriate simple portable determination equipment.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2297-8739/8/3/27/s1>, Text S1, Figure S1: Influence of common water ions on Se(IV) residual concentration (due to adsorption) by the use of Bayoxide material. Experimental conditions: Bayoxide concentration 0.5 g/L, initial Se(IV) concentration range 10–100 µg/L, pH 7.3 ± 0.2 , temperature 20 °C, and contact time 30 min., Figure S2: Influence of natural organic matter, as simulated by different humic acid concentrations, on the Se(IV) adsorption by the use of Bayoxide material. Experimental conditions: Bayoxide concentration 0.5 g/L, initial Se(IV) concentration range 10–100 µg/L, pH 7.3 ± 0.2 , temperature 20 °C, and contact time 30 min. Figure S3: Influence of iron found in natural waters on Se(IV) adsorption by Bayoxide. Experimental conditions: Bayoxide concentration 0.5 g/L, initial Se(IV) concentration range 10–100 µg/L, pH 7.3 ± 0.2 , temperature 20 °C, and contact time 30 min.

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