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Review

A Brief Overview of Nanomaterials in Inorganic Selenium Speciation

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Abstract: Although total selenium content is still useful in many areas, knowledge of its speciation is gaining importance as its various chemical forms have different environmental effects, toxicities and biological utilization. Among several methods used for the isolation and enrichment of selenium species, solid-phase extraction and its alternative approaches are often applied due to their simplicity and high efficiency. This brief overview summarizes the progress made in using different nanostructure sorbents to separate and preconcentrate inorganic selenium species in environmental waters. Nanomaterials are finding increasing applications as they have a large specific surface area and high chemical stability. Functionalizing their surface by covalent or noncovalent interactions with other components, grafting or doping with heteroatoms can improve the separation and removal efficiency. Strategies based on combining selective chemical reactions and separation procedures are discussed.

Keywords: nanomaterials; selenium; speciation; preconcentration; separation

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1. Introduction

Selenium is an important trace element for human and animal health. It plays a key role in several major metabolic pathways, such as antioxidant defense systems, thyroid hormone metabolism, DNA synthesis and infection [1–3]. Its deficiency is associated with risk factors for various forms of cancer and several serious diseases [4,5]. On the other side, there is some evidence that selenium at higher concentrations is toxic [6]. The upper limit for adult selenium daily intakes is 400 µg [7]. The World Health Organization recommends a daily intake of 30 µg and 40 µg for women and men, respectively [8]. The association between Se intake or status and mortality has a hermetic effect and has been characterized by a U-shaped relationship [2,9]. The concentration range between these two opposite effects of selenium is narrow; thus, additional information on its chemical forms present in environmental and biological samples is necessary [2,10].

Selenium is introduced into the environment due to the weathering of minerals, mainly containing sulphur, and through human activity, such as industrial and agricultural uses [11,12]. In environmental samples, selenium exists in the form of inorganic species, such as elemental selenium, selenides, selenites (Se(IV)) and selenates (Se(VI)), and as organic selenoamino acids and their derivatives. Microbial action of fungi can transform inorganic selenium into volatile methylated selenides. Organic selenium species are mainly found in biological systems. Diet is a major source of selenium for humans, and its food content reflects this element's level in soil [13]. Different selenium species have different environmental effects, toxicities, biological utilizations and nutritional values. Organic compounds are less toxic and more bioavailable than inorganic forms and (Se(IV)) are

generally less toxic than (Se(VI)) in an aquatic environment [14]. However, the different toxicities of selenium species are not considered in the water guidelines.

Although the total selenium content is still useful in many areas, the knowledge of its speciation is gaining importance from an environmental, and toxicological perspective. The most common tools for trace element speciation are combining separation techniques with highly sensitive detectors. Despite the huge improvement in hyphenated techniques, in some cases, the appropriate sample treatment can provide quantitative data about specific Se forms [15,16]. Selenium determination in complicated materials is often difficult due to matrix interferences and/or insufficient detection sensitivity. To overcome these problems, a separation-and-preconcentration step could be applied before measurement. Among several methods that have been used for the isolation and enrichment of selenium species, solid-phase extraction (SPE) is very often applied due to its simplicity, high efficiency and lack of harmful organic solvents. Solid-phase microextraction (SPME) and dispersive micro-solid-phase extraction (DMSPE), the alternative approaches to conventional column-packing SPE, have been also evaluated [17–19]. Moreover, the combination of a given sorbent with magnetic nanoparticles makes their separation much easier after the enrichment process by using an external magnet [20].

Several solid materials have been reported recently for the preconcentration and speciation analysis of selenium [21–24]. The development of novel approaches for easy operation, reagent-free preconcentration and in situ speciation analysis of that element have still drawn widespread attention. In the group of novel sorbents, nanomaterials are finding increasing applications in analytical procedures as they can significantly improve the existing pretreatment and preconcentration techniques [25,26]. In addition, it opens up the possibility for selenium speciation analysis by new approaches in surface-enhanced Raman spectroscopy, colorimetric and fluorescence sensing [27,28].

This brief overview summarizes the recent progress in using different nanostructure sorbents in solid-phase extraction to separate and preconcentrate inorganic selenium species in environmental waters. Strategies based on combining selective chemical reactions and separation procedures were discussed.

2. Nanomaterial Sorbents

Nanoscale materials, which have a minimum of one dimension with a size in the range of 1–100 nm, have been widely used as powerful adsorbents for trace metal preconcentration and removal [29,30]. They exhibit large surface area, exceptional porosities, numerous adsorption sites and easy functionalization or coatings. The surface reactivity of these nanoparticles (NPs) can be further increased by combining their properties with metal and metal oxide nanoparticles or chelating polymers creating nanocomposites. NPs can strongly retain several pollutants through various interactions, such as π-π and electrostatic interactions, hydrophobic effect and covalent bonding. The sorption processes are highly dependent on their surface area, pore diameter, interior and exterior morphology and the presence of functional groups. Besides that, the extraction conditions such as sample pH, sorbent dosage, contact time and temperature may affect the performance of the process to various extents. Carbon nanotubes (CNTs), graphene and its derivatives, metal oxides, silica and polymer-based nanomaterials, nano-scale zero-valent iron (nZVI), layered double oxides (LDHs) and metal–organic frameworks (MOFs) have been most often used for environmental applications.

Carbon nanotubes and graphene derivatives are two major carbon-based nanostructures used for the preconcentration of metal ions and speciation analysis from environmental samples [31–33]. Generally, single-walled carbon nanotubes (SWCNTs) have better sorption capacities but lower mechanical strength than multi-walled carbon nanotubes

(MWCNTs). The advantage of graphene over CNTs is that it can be synthesized from graphite, a very common and cheap material. Graphene sorbents can be also easily chemically modified through graphene oxide (GO), which is more hydrophilic than graphene and possesses large amounts of epoxy, hydroxyl and carboxyl groups [33].

Metal oxide nanoparticles, such as TiO_2, Al_2O_3, ZrO_2 and Fe_2O_3/Fe_3O_4, have large surface areas and high thermal, mechanical and chemical stability with high adsorption capacity [34]. Although silica nanoparticles generally suffer from low selectivity, their surface can be easily modified through the silanol groups; thus, they can serve as the support for other nanocomposites. Nanoscale zero-valent iron (nZVI) with a metallic iron core and iron oxide shell has attracted attention for toxic ion removal due to its large specific surface area, good reactivity and low cost. To avoid its aggregation, oxidation and instability, some functional groups and stabilizers are added to the nZVI surface [35]. The removal of Se(VI) by nZVI confined in a polymeric anion exchanger consisted of a synergetic process involving ion exchange, adsorption and reduction [36].

Layered double hydroxides, known as hydrotalcite-like compounds, consist of metal oxide layers with a positive charge. Hydrated anions between these layers attract interest as adsorbents for anionic selenium species [37,38]. Combining nZVI, carbon nanostructures or organic compounds enhances their adsorption efficiency and selectivity. Different possible mechanisms are proposed using LDH structures such as surface adsorption through electrostatic interactions and outer-sphere complexation (suitable for Se(VI)), chemisorption via inner sphere complexation (effective for Se(IV)) and anion exchange applicable to both Se forms [38]. Figure 1 shows the schematic representation of the most often employed mechanisms for the sorption of selenium oxyanions using LDH structures.

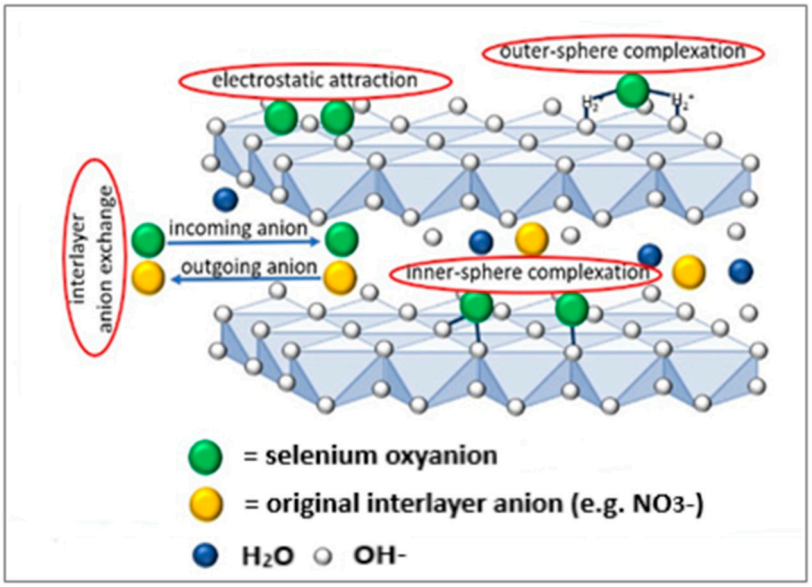


Figure 1. Selenium oxyanions could be retained in the LDH structures by various mechanisms such as surface adsorption through electrostatic interactions, outer-sphere complexation, chemisorption via inner sphere complexation and anion exchange. Reprinted under the terms of a CC BY license from reference [38]. Copyright 2024 MDPI.

Metal-organic frameworks, a relatively young group of sorptive materials, are constructed by coordinating metal ions (or their clusters) and organic ligands [39]. In addition to the large surface area and high porosity, they have high mechanical strength and thermal stability, but limited chemical stability. One of the remarkable attributes of MOFs is their structural flexibility, which facilitates the adjustment of their sorptive characteristic. Compared with the single metal MOFs, the combination of Fe/Zr bimetallic nodes produces

synergistic effects and shows good removal performance for the selenium species removal in waters [40].

3. Speciation of Inorganic Selenium Using Nanomaterials

Selenite and selenate are the most frequent inorganic selenium species in environmental waters. Selenides are readily oxidized to red elemental selenium, which is insoluble in water and resistant to oxidation/reduction processes. Generally, two main strategies for the determination of selenite and selenate contents have been used. In the first method, only one of the selenium forms, Se(IV) or Se(VI), is selectively retained, then eluted, and its content is determined. In a second aliquot of a sample, Se(IV) is oxidized, or Se(VI) is reduced by the appropriate treatment. The total inorganic selenium is then determined after retention on solid sorbent and elution. Quantification of the second Se form is calculated by the difference. In most proposed procedures, selenites are selectively sorbed and then eluted [41–52]. This is probably because Se(IV) easily forms connections with sorbent active surfaces, while the higher stability of the oxyanion of Se(VI) prevents it from interacting [38]. However, this indirect speciation approach has disadvantages, such as a tedious operation that increases time, but the preconcentration of selenites can be realized.

One of the few works on the selective sorption of Se(VI) is the paper by Chen et al. [53]. They used dispersive micro-solid-phase extraction with magnetic $ZnFe_2O_4$ nanotubes to isolate selenates from selenites at acidic media. The nanosorbent, after isolation from the solution by an external magnet, was treated with a small volume of NaOH solution to elute preconcentrated Se(VI). Its concentration was then determined by the ETAAS method with a detection limit of 1.3 pg/mL, and an enrichment factor of 200. Se(IV) in the upper aqueous phase of DMSPE was enriched by dispersive liquid–liquid extraction using chloroform and ethanol as extraction and disperser solvents, respectively, in the presence of ammonium pyrrolidinedithiocarbamate (APDC) as a chelating agent. The detection limit for Se(V) determination was 1.0 pg/mL.

The second approach for inorganic selenium speciation using nanomaterials includes the sorption of both Se(IV) and Se(VI) followed by their separate elution under different conditions. Zhu et al. reported very high sorption efficiency of both inorganic Se species onto cationic layered rare-earth hydroxide, $Y_2(OH)_5Cl{\cdot}1.5H_2O$ with a maximum sorption capacity of 150 mg/g for Se(IV) and 102 mg/g for Se(VI) at pH 7–8.5 [54]. It was postulated that selenates are exchanged with Cl^- ions in the interlayer space of this sorbent. In contrast, selenates, besides the anion exchange mechanism, are directly bound to the Y^{3+} center through strong bidentate binuclear inner-sphere complexation. Se(IV) was eluted using a 1M NaCl solution, and 5M NaCl was effective as an eluting reagent for Se(VI). Several nanostructure sorbents exhibited high affinity to both inorganic selenium species, particularly layered double hydroxides; however, their sequential elution was not investigated [38,55–60]. They were mainly applied to remove selenium from water samples.

Simultaneous high sorption of Se(IV) and Se(VI) on nanomaterials under optimal conditions can be utilized for their elution together followed by species separation and determination by liquid chromatography or capillary electrophoresis [61,62]. Both inorganic selenium species were preconcentrated and isolated from matrix components using magnetic silica nanoparticles functionalized with 5-sulfosalicylic acid at pH 4 for 5 min with ultrasounds [61]. In total, 0.5 M of Na_2CO_3 solution was used for their elution. Then selenium species were separated and determined by capillary electrophoresis (CE) with electrothermal atomic absorption spectrometry (ETAAS) detection. The modified interface between CE and ETAAS allowed for the introduction of effluent directly through the end of the graphite tube, increasing the detection sensitivity. The limits of detection for Se(VI) and Se(IV) were 0.17 and 0.18 ng/mL, respectively. Without the preconcentration step, these val-

ues were more than 10 times bigger (2.5 and 3.2 ng/mL). The enhancement factors were 29 and 21 for Se(IV) and Se(VI). Meng et al. used a magnetic nanocomposite containing boronic acid groups and aminated MWCNTs combined with chromatographic quantification for the speciation of Se(IV) and Se(VI) in water and milk samples [62]. The preparation of that nanocomposite is schematically presented in Figure 2. Additionally, *o*-phenylenediamine (OPA) was added to the samples for the complexation of selenites. According to the authors, the nanocomposite could produce multiple interactions with Se(IV)-OPA complex, such as B-N coordination, π-π and hydrogen-bonding and dipole–dipole forces. The selective sorption of Se(IV)-OPA was very fast (4 min from 50 mL sample), and a maximum sorption capacity of 178 mg/g was obtained. The mixture of methanol and formic acid (1.5%, *v*/*v*) was applied for its elution. The Se(VI) concentration was calculated by the differences after its reduction with concentrated HCl and quantification of total inorganic selenium. Connection with HPLC equipment with diode array detection allows the achievement of a detection limit of 0.0082 μg/L and 0.013 μg/L for Se(IV) and Se(VI), respectively. It was found that the identification and quantification of the Se(IV)-OPA complex was not influenced by sample matrix components.

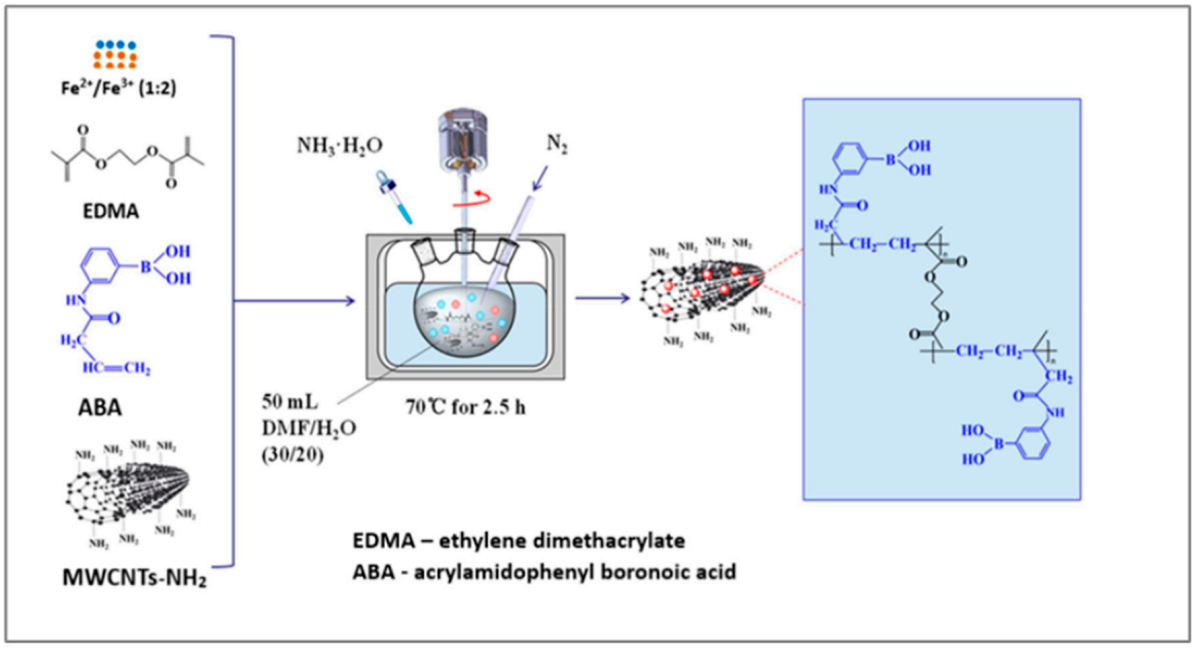


Figure 2. Scheme for one-pot hydrothermal synthesis of magnetic nanocomposite containing boronic groups and aminated MWCNTs. Reprinted with permission from reference [62]. Copyright 2016 Elsevier.

Selective Sorption of Se(IV)

Different types of nanosorbents were proposed to selectively remove Se(IV) in the presence of Se(VI) [42–51], especially since the magnetic nanocomposites can be easily dispersed in aqueous samples and then collected together with sorbed analyte by a piece of permanent magnet. The main factors affecting their performance, such as sample pH, sorbent amount, eluent concentration and volume, sample volume and the influence of coexisting ions, have been investigated and optimized. Table 1 presents examples of the application of nanomaterials for selective Se(IV) sorption. The enhancement factor (EF), calculated as the ratio of the slopes of the calibration graphs after and before preconcentration, is widely used as a parameter to determine the efficiency of a given preconcentration method [44,45,47,48,50]. In some papers, the values of enrichment factors were reported as the ratio of sample to eluent volume [37,49]. Maximum sorption capacity (Q_{max}) is used

to represent the overall sorption capability of the nanosorbent. Nanomaterials with the lowest equilibrium time are the best choice as a practical and applicable sorbent [49,50].

Table 1. Examples of the application of nanomaterials for Se(IV) sorption.

Sorbent	Sorption Conditions				Elution	Detection (LOD, μg/L)	EF/EF *	Q_{max} (mg/g)	Ref.
	Dose (mg)	Volume (mL)	pH	Time (min)					
Fe_3O_4@MWCNTs-Bis	30	100	6	30	1 M HNO_3	ETAAS (0.003)	na	na	[42]
G@CeO_2	1	25	3	5		EDXRF (0.11)	na	14.1	[43]
G@TSC	1	100	1.5	10		TXRF (1.73)	215 *	na	[44]
GO@Fe_3O_4	60	40	2	30	0.1 M EDTA	HG-AAS (30 **)	70 *	na	[45]
GO@TiO_2	30	25	6	12.5	6 M HNO_3	ETAAS (0.04)	33.3	3.77	[46]
Al_2O_3-Aliquat-336	50	150	7	5	1 M HNO_3	ICP OES (1.4)	850 *	35.3	[47]
SiO_2 + 1% APDC	5	50	2	6	Ethyl acetate at 60 °C	ETAAS (0.0014)	90 *	0.470	[48]
Fe_3O_4@SiO_2@PANI	10	50	3	2	0.1 M NaOH	ICP MS (0.005)	100	10.8	[49]
Zr-NPs	10	30	2	1.25	Concentrated HCl	SQT-FAAS (5.3)	415 *	na	[50]
Fe_3O_4-ADTC@MOF	16	50	1.85	14	0.64 M HCl	ETAAS (0.01)	208	197	[51]

Bis-bismuthiol II, 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thionepotassium salt; ADTC-amino dithiocarbamate; APDC—ammonium pyrrolidinedithiocarbamate; G—graphene; GO—graphene oxide; TSC—thiosemicarbazide; PANI—polyaniline; NPs—nanoparticles; MOF—metal–organic framework; EDXRF—energy dispersive X-ray fluorescence; TXRF—total-reflection X-ray fluorescence; SQT-FAAS—slotted quartz tube-flame atomic absorption spectrophotometry; EF—enrichment factor, calculated as the ratio of sample to eluent volume; EF *—enhancement factor, defined as the ratio of the slopes of the calibration graphs after and before preconcentration; na–not available; ** LOD expressed in ng/g.

Magnetic multi-walled carbon nanotubes modified with 5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium salt (bismuthiol II) were used for the separation and preconcentration of Se(IV) before its determination by ETAAS or the analysis of river and seawater [41]. An enhancement factor of 196 and detection limit of 0.003 μg/L were reported. The method was successfully applied for the quantification of inorganic selenium species in water and total selenium in food samples.

Another procedure includes DMSPE with ceria nanoparticles deposited on graphene nanosheets (G@CeO_2) [43] or thiosemicarbazide-incorporated graphene (G@TSC) [44]. In both of these proposed procedures, X-ray fluorescence spectrometry (XRS) was used that allows the analysis of solid samples and determination of Se(IV) without elution. The reported values of LODs were sufficient to determine ultra-trace amounts of this selenium form in the different types of water according to the permissible levels of current legislation; however, the energy-dispersive XRS became more sensitive (LOD 0.11 μg/L) than total-reflection XRS (1.73 μg/L) (Table 1).

Do Nascimento et al. incorporated iron oxides onto graphite oxide for the preconcentration of Se in digested fish samples with detection by hydride generation atomic absorption spectrometry and a flow injection methodology [45]. The optimum sorption conditions in the presence of major inorganic matrix ions were reached with 60 mg of nanoparticles at pH 2. After a relatively long extraction time of 30 min, compared to other nanomaterials presented in Table 1, an enhancement factor of 70 was obtained. The surface of GO was also modified by TiO_2 nanoparticles [46]. The comparison of Se(IV) and Se(VI) sorption behavior on the GO@TiO_2 nanocomposite and TiO_2 alone showed that selenites were quantitatively retained on both sorbents at a pH of 0.5–10, while selenates were quantitatively retained only at pH 0.5–2 on GO@TiO_2 and at pH 0.2–3 on TiO_2 (Figure 3). The extended span of pH for the different behavior of both selenium forms was observed on GO@TiO_2 in comparison to TiO_2. Thus, separating these forms is possible at pH 6 for speciation analysis using GO@TiO_2. However, the content of selenate in the effluent was not quantified. Instead, the authors decided to elute Se(IV) retained on a microcolumn with

HNO_3 solution and determine its content by ETAAS. Then, after reducing all selenium in the sample to Se(IV) with concentrated HCl and KBr, the extraction procedure was repeated for total Se. The difference was used to calculate Se(VI) content.

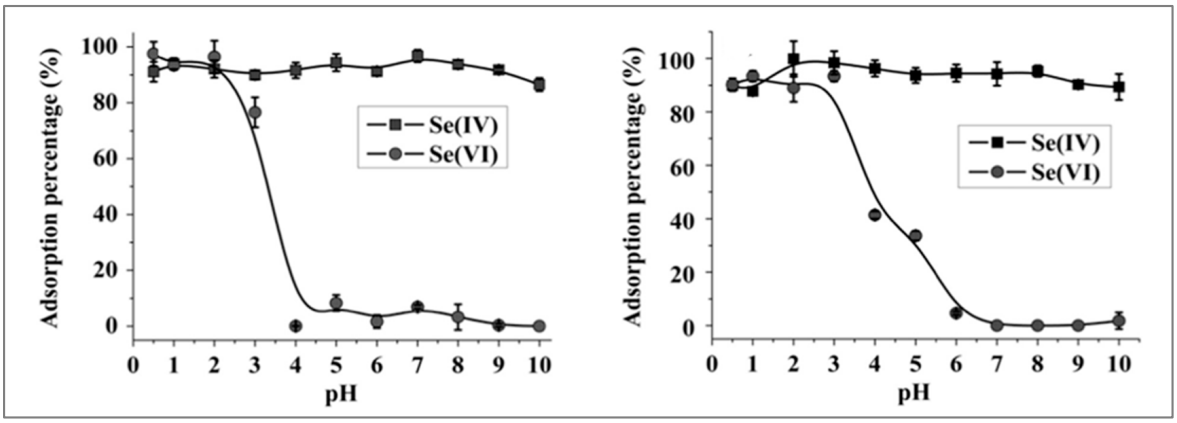


Figure 3. Effect of pH on Se(IV) and Se(VI) sorption of GO@TiO_2 nanocomposite and TiO_2 alone. Reprinted with permission from reference [46]. Copyright 2016 Elsevier.

Nano-alumina modified with Aliquat 336 at pH 7 exhibits a very high affinity to Se(IV) with a Q_{max} of 35.3 mg/g [47]. Aliquot 336 was chosen because it acts as an anion exchanger at a wide pH range and, according to the authors, enhances the selectivity of nano-alumina. It can be used for preconcentration and separation of selenites from large volumes of water samples due to a high enhancement factor of 850. The proposed nanosorbent was stable and could be re-used 78 times without an obvious decrease in the recoveries of Se(IV). Pure nanosilica without functionalization, which avoids typical time-consuming steps, was applied by Llaver and Wuilloud [48]. Se(IV) was retained in the form of its complex with ammonium pyrrolidine dithiocarbamate (APDC) at pH 2 due to the hydrophobic interactions. The monolayer Langmuir model described the studied system; however, a significant deviation from homogeneity was observed. Under these conditions, Se(VI) remained unextracted. The treatment of the selenium-loaded nanosilica with ethyl acetate at 60 °C was used in the elution step. However, reusing nanosilica encountered difficulties as Se(IV) retention was reduced by 60% after a washing step with ethyl acetate under ultrasonic stirring. Another sorbent was proposed by He et al. [49]. Magnetic SiO_2 nanoparticles were coated with polyaniline, and the resulting nanocomposite had a positively charged surface under a pH of <9. Se(IV) was quantitatively sorbed in the pH range of 2–4 by electrostatic interactions with an adsorption capacity of 10.8 mg/g. The proposed procedure exhibits a relatively high tolerance ability to commonly co-existing cations such as K^+, Na^+, Ca^{2+} and Mg^{2+}. The IR spectra indicated that the shell of that nanocomposite was damaged to a certain extent after 10 repeated adsorption/desorption steps.

A metal–organic framework sorbent composed of MOF (MIL-101(Cr)) and magnetite nanoparticles modified with dithiocarbamate was evaluated for sorption of Se(IV) [51]. It was found that selenites are quantitatively sorbed on a surface in the pH range of 1–4, while selenates are retained at a pH of 6. Thus, a pH of 1.85 was selected for the selective extraction of Se(IV) species and a high sorption capacity (125 mg/g) was obtained. Among the studied acidic eluents, dilute HCl solution recovered selenite ions more effectively. Se(IV) content was determined by the ETAAS method with a detection limit of 0.01 µg/L. The quite complicated process of sorbent synthesis can be considered as a limitation of this procedure.

The metal–organic framework with amino groups (UiO-66-NH_2) was employed for Se enrichment [63]. A schematic diagram of this experimental process is shown in Figure 4. MOF material together with adsorbed selenium was collected by filtration and then converted to slurry for in situ hydride generation (HG) for detection by ICP-MS. Direct slurry sampling avoided additional elution procedures and eliminated matrix and isobaric interferences. The adsorption process was very fast at room temperature and reached equilibration after only 5 min. The maximum adsorption capacity for Se(IV) calculated by the Langmuir model was 91.7 mg/g, The detection limits without and with the preconcentration step were 0.02 μg/L and 0.001 μg/L, respectively. No significant interferences from Co(II), Ni(II), Cu(II) and Fe(III) were observed even when their concentrations were 200-fold that of selenium.

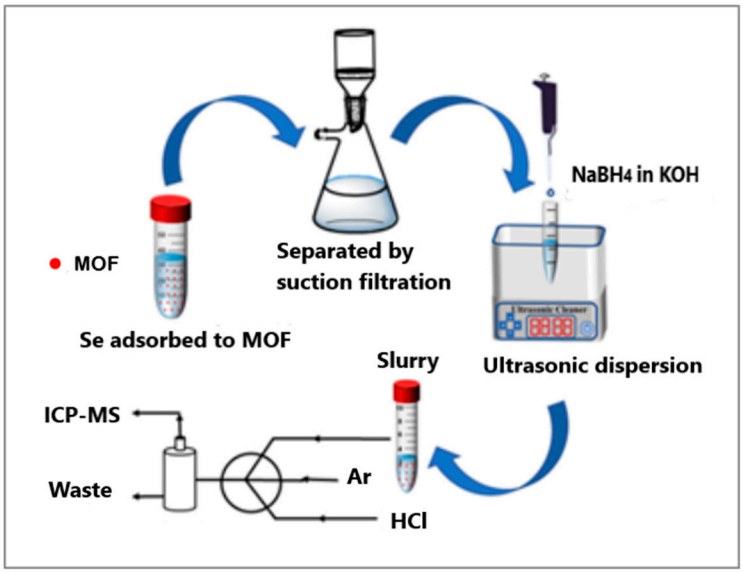


Figure 4. Schematic diagram of an experimental process for determination of selenium [63]. The MOF adsorbent was used for Se preconcentration before direct slurry sampling HG-ICP-MS determination. Reprinted with permission from reference [63]. Copyright 2023 Elsevier.

The analytical performance of most of the proposed methods for inorganic selenium speciation was confirmed by analyzing different kinds of water samples spiked with these Se forms. The recoveries above 95% were often achieved, which indicates the reliability of a given procedure. The accuracy was also evaluated using different certificated reference materials (CRM), but the analyzed CRMs had only certified content for total selenium content [64].

4. Conclusions

There is a trend to develop simple methods supported by an enrichment and separation methodology that can be used to monitor selenium inorganic forms in environmental samples. Differences in toxicity, bioavailability, bioaccumulation and mobility of these species are the main driving forces for the expansion of such procedures. Nanomaterials, due to their unique physical and chemical properties, have attracted continuous interest in selenium preconcentration, removal and speciation analysis [18,65–67]. Modification of their surfaces with different functional groups, polymers or metal oxides allows the use of various types of interactions to increase sorption efficiency.

The most frequently used procedure for speciation analysis of selenium with nanostructure sorbents is selective sorption of Se(IV) and its determination after the elution step. Then after the reduction of Se(IV), this procedure is repeated to determine the total

selenium. Finally, the concentration of Se(VI) is calculated by the difference. This methodology, however, requires additional steps and is time-consuming. In our opinion, the better speciation strategy is the sorption of both Se forms and then their selective elution under different conditions or eluents. Such an approach was proposed by Zhu et al., using cationic layered rare-earth hydroxide [54]. The lower popularity of this method is probably caused by Se(VI) strong retention and difficulties in its quantitative elution.

A membrane-based system could be considered in the search for new procedures for preconcentration and separation of Se inorganic species [68,69]. As an example, Zhang et al. fabricated a multi-functional nanofiltration membrane by immobilizing powdered Co-MOF-74-SH with dual active sorption sites to enhance its capabilities for selenium removal [70]. This membrane showed Se removal of over 99%, surpassing the original membrane of about 74%, which was attributed to the synergetic mechanism of adsorption and separation. The maximum adsorption capacity of Co-MOF-74-SH was 213 mg/g.

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