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REVIEW PAPER

Application of chitosan and its derivatives for solid-phase extraction of metal and metalloid ions: a mini-review

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Abstract Here we review chitosan-based materials for solid-phase extraction of metal and metalloid ions prior to their determination by atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, mass spectrometry, and some other spectrometric techniques. We show that nearly zero affinity of chitosan and its derivatives to alkali and alkali-earth metal ions is very beneficial for separation of analytes from the salt matrix, which is always present in natural waters, waste streams, and geological samples and interferes with analytical signals. Applicability of chitosan to selective recovery of different metal and metalloid ions can be significantly improved via functionalization with N-, S-, and O-containing groups imparting chitosan with additional electron donor atoms and capability to form stable five- and six-membered chelate rings with metal ions. Among most promising materials for analytical preconcentration, we discussed chitosan-based composites; carboxyalkyl chitosans; chitosan derivatives containing residues of aminoacids, iminodiacetic acid, ethylenediaminetetraacetic and diethylenetriaminepentaacetic acids; chitosans modified with aliphatic and aromatic amines, heterocyclic fragments (pyridyl, imidazole), and crown ethers. We have shown that most chitosan derivatives provide only group selectivity toward metal ions; however, optimization of recovery conditions allows metals and metalloids speciation and efficient separation of noble and transition metal ions.

Keywords Chitosan · Chitosan derivatives · Solid-phase extraction · Selectivity · Analysis

Introduction

Determination of low contents of metals in natural samples and technological solutions is a challenging task and a crucial issue for monitoring pollutants in the environment, investigation of microelements biological roles, and development of materials and technologies for recovery of valuable and/or toxic elements from wastes, ores and natural waters.

Analysis of metals, which are present at ppm and ppb levels, usually requires preconcentration on inorganic or polymeric sorbents to increase the sensitivity of determination and eliminate or substantially decrease the matrix effect interfering with analytical signal. In recent decades one has observed a significant growth of the interest to bio-based

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polymers and composites for the solid-phase extraction of metal ions (Oshita and Motomizu 2008; Mladenova et al. 2012; Wan Ibrahim et al. 2014). Chitosan, derived from chitin, the second-most abundant natural polymer after cellulose, is among the most promising biopolymers for this application due to its good complexing properties (Guibal 2004) and easy processability to granules, fibers, and films.

While the large industrial-scale usage of chitosan and its derivatives for removal/recovery of toxic or precious metals is limited by their relatively high cost in comparison with synthetic polymers and ion-exchange resins, zero affinity of chitosan to ions of alkali and alkali-earth metals and high selectivity of many N-, S-, and O-containing chitosan derivatives make chitosan-based materials attractive for analytical preconcentration.

This field can significantly benefit from numerous synthesis methods developed for chitosan functionalization to increase the native polymer affinity to ions of specific metals and to change selectivity rows and efficient sorption pH range. Introduction of functional fragments containing S- and N-atoms significantly enhances the affinity of chitosan to noble metals ions, whereas modification with residues of efficient complexing agents impart chitosan derivatives with the capability to bind numerous transition metal ions via formation of highly stable five- and six-membered chelate rings (Pestov and Bratskaya 2016). Different conditions of effective recovery of metal cations and anions provide a basis for their efficient separation and enable one to eliminate the negative effect of background ions on analytical determination of trace amounts of noble metals and some other metals existing in solution in the form of complex anions.

Most of the investigations on chitosan-metal ions interactions are focused on demonstration of sorption capacities of chitosan derivatives, whereas very few works deal with metal ions recovery from solutions containing trace amounts of metal ions, and even fewer report application of high affinity derivatives as solid-phase extractants in details sufficient for understanding the merits for analytical determination of the metals in environmental samples and solutions containing background ions interfering with analytical signal. The potential of chitosan application in analytical chemistry was recently discussed in a mini-review (Fu et al. 2013) briefly covering numerous fields, including preconcentration of metal ions by chitosan, chitosan-based coatings for capillary electrophoresis, stationary materials for chromatographic columns, and glassy carbon electrodes modified with chitosan for electroanalytical and bio-sensing. However, application of chitosan-based materials as solid-phase extractants for metal and metalloid ions has never been reviewed.

Here we present an overview of chitosan-based materials and derivatives with high potential for selective recovery of metal ions. The main attention is paid to the works, which were conducted in compliance with analytical chemistry criteria and provide sufficient details on analytical performances of the materials in solid-phase extraction of metal ions for their subsequent determination using atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and other spectrometric techniques.

Sorbents for metal and metalloid ions preconcentration

Native chitosan and chitosan-based composites

High affinity of unmodified chitosan to many transition metal ions and its insolubility in neutral and alkaline media allow direct application of non-cross-linked chitosan for metal ions preconcentration. In contrast to cross-linked derivatives, which have to be decomposed in aqua regia or treated with eluent to release analyte into solution, native chitosan can be simply dissolved in acetic acid after metal sorption yielding ready-for-analysis solution.

The method to determine trace amounts of copper in river, rain, sea, and industrial water streams using electrothermal atomization atomic absorption spectrometry (ETA-AAS) were reported in (Minamisawa et al. 1999). Upon Cu(II) sorption at pH = 5–9, chitosan was separated from the solution on a membrane filter, dissolved in 2 ml of 0.1 M acetic acid solution, and an aliquot of the obtained solution was introduced directly into a metallic tungsten furnace for absorption measurement. The copper detection limit was 0.02 μg/l. The relative standard deviations for the Cu(II) concentration of 1 μg/l was 3.8 %, for 0.5 μg/l–4.7 %. Similar approach was used by the same authors to determine Cu(II) after sorption on the hydrophobic membrane formed at the interface between the aqueous phase and nitrobenzene using graphite furnace AAS (Minamisawa et al. 2006): the Cu(II) detection limit in this case was 20 μg/l.

Native chitosan was also used to concentrate Cu(II), Zn(II), Co(II), Ni(II), Pb(II), and Cd(II) ions from natural and waste water streams at $pH = 5$ (Sun et al. 2004). The elements determination was performed by the method of flame AAS after elution with 1 M solution of H_2SO_4.

Although insolubility of chitosan in neutral and alkaline media favors its application for recovery of many transition metal cations, partial or complete dissolution of native polymer in acidic media significantly limits the possibility to use it for recovery of metal anions. Thus, cross-linked chitosan and chitosan-based composites containing inorganic compounds and carbon materials have found much more extensive application for preconcentration in comparison with native chitosan. The second component in the chitosan-based composites can either improve the sorption performance of chitosan or increase its mechanical strength and durability for column applications.

Gao et al. (2000) investigated adsorption of sixty elements from solutions with metal contents of 10 ng/ml on high-porosity cross-linked chitosan, which manifested high affinity to oxoanions and anionic chlorocomplexes of Ti, V, Mo, W, Ga, Bi, Au, Pt, and Pd. High efficiency for molybdenum and tungsten was observed at pH 1–6, for tin—at $pH > 2$, for bismuth—at pH 1–9, for titanium, vanadium, and gallium—at $pH > 4$. After preconcentration, the majority of metal ions can be eluted with 1 M HNO_3 solution with the efficiency higher than 90 %. Due to strong binding of noble metal ions to chitosan, addition of the complexing agent (0.05 M thiourea) to 1 M HCl was required to elute noble metal ions (Pt, Pd, Au) from the sorbent phase with high efficiency (close to 100 %). The metals were determined in eluates by the ICP-MS and applicability of the method to determine trace quantities of oxoanions in river waters was proven (Gao et al. 2000).

It should be noted that involvement of redox processes to adsorption of Au(III) and Pt(IV) ions on chitosan results in significantly lower efficiencies of these noble metals elution from the sorbent phase in comparison with Pd(II) ions (Azarova et al. 2015). This effect was used to separate gold and palladium on chitosan cross-linked with glutaraldehyde (Park et al. 2013); however, a detailed quantitative information on the separation efficiency was not presented.

Due to very low affinity of native chitosan to metalloid ions, direct application of chitosan to their recovery is not efficient. To concentrate arsenic from flowing, underground, and sea water Shinde et al. (2013) suggested modification of chitosan membrane with Fe(III) (Fig. 1). Despite relatively low degree of As(III) ions extraction (about 35 %), total arsenic content can be determined after mild oxidation of As(III) to As(V), whose extraction efficiency at pH 3–9 was 91 ± 2 % in the concentration range 5–250 μg As/l. Such high efficiency of the chitosan-Fe(III) complex for As(V) ions recovery was related to the fact that this complex functioned simultaneously as a Lewis acid and as a cationic center, which can sorb the arsenate ion via charge neutralization mechanism (Fig. 1). Selectivity of this material was preserved even in high-salinity solutions, in particular, sea water, which enables one not only to improve the detection limit due to preconcentration, but also to eliminate the interfering effect of the salt background (Shinde et al. 2013).

Another composite sorbent—the cross-linked chitosan modified with FeC nanoparticles—was applied for quantitative separation of Cr(III) and Cr(VI) ionic forms, and selective preconcentration of Cr(III), Cu(II), and Cd(II) ions from natural waters containing up to 5 g/l Na^+, 1 g/l Ca^{2+}, 3 g/l Mg^{2+}, 1 g/l F^-, and 0.5 g/l $H_2PO_4^-$ and SO_4^{2-} ions (Wu et al. 2007). The chitosan-FeC composite was selective to Cr(III), Cu(II), and Cd(II) ions at pH 7.5 showing sorption capacities 10.5, 17.8, and 20.3 mg/g, respectively. Total chromium content could be determined after reduction of Cr(VI) to Cr(III) with ascorbic acid (Wu et al. 2007).

Chitosan with grafted multiwalled carbon nanotubes (Fig. 2) was used as a sorbent for solid-phase extraction of heavy metal ions. V(V), Cr(VI), Cu(II), As(V), and Pb(II) can be analyzed using ICP-MS method after elution with 0.5 M HNO_3 solution for the ions detection limits were 1.3–3.8 ng/l at enrichment factors 52–128. The method was successfully applied for determination of trace quantities of metals in herring, spinach, river and tap water streams at the extraction efficiency of 91–100 % (Dai et al. 2012).

The chitosan/silica gel composite combining mechanical strength and high surface area of the silica

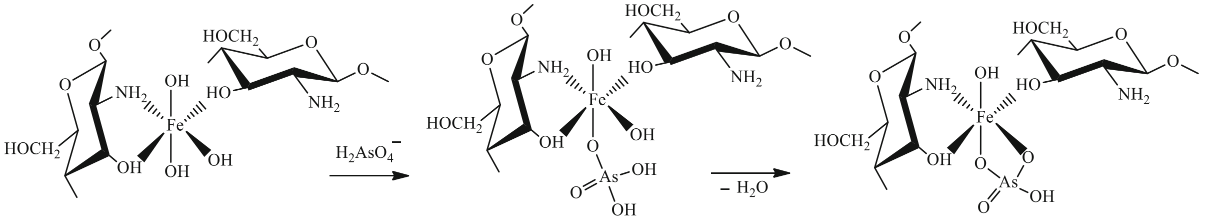


Fig. 1 Suggested structural unit of the sorbent based on the chitosan complex with Fe(III) and the scheme of its interaction with As(V) (Shinde et al. 2013)

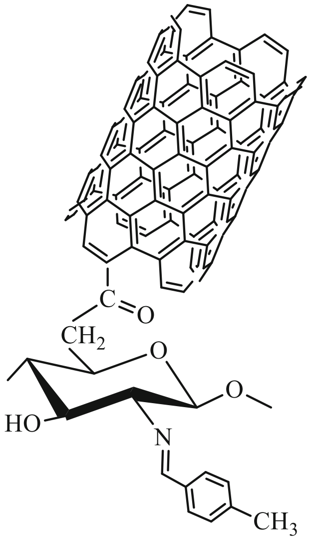


Fig. 2 Structural unit of chitosan grafted with multiwalled carbon nanotubes [adapted from (Dai et al. 2012)]

gel with high affinity of chitosan to metal ions was used for selective preconcentration of Cd(II) and Cu(II) from natural water streams—lake, well, or river (He et al. 2013). The metal ions contents were determined by the AAS after elution with 0.1 M HNO_3 solution. The detection limits were 20 and 38 ng/l for Cd(II) and Cu(II), respectively, at the enrichment factor of 166.7. Metal ions preconcentration on this composite sorbent allows elimination of the negative effect of the salt background, improvement the detection limit and the analysis accuracy. It was demonstrated that the sorbent preserved its efficiency after five cycles of sorption-regeneration (He et al. 2013).

To facilitate separation of sorbent from solution, chitosan-modified magnetic nanoparticles were synthesized and applied for Cr(III) and Cr(VI) speciation in lake and tap waters using inductively coupled plasma optical emission spectrometry (ICP-OES) (Cui et al. 2014). The material exhibited excellent adsorption performance for Cr(III) at pH 9 and total Cr (Cr(III) and Cr(VI)) at pH 6. At enrichment factor of 100, the detection limits were 0.02 and 0.03 ng/ml with the relative standard deviations of 4.8 and 5.6 % for Cr(III) and total Cr, respectively.

N-containing chitosan derivatives

Functionalization of chitosan with *N*-containing groups is carried out via introduction of residues of aminoacids, aliphatic and aromatic amines, heterocyclic fragments (pyridyl, imidazole). This group of derivatives is the most extensive and most efficient in recovery of various metal ions existing in solutions in cationic and anionic forms. Depending on the substituent structure, introduction of N-containing functionalities can increase the number of electron-donor nitrogen atoms and, therefore, the number of the anion-exchange sites in chitosan, and/or impart it with the capability to form stable five- and six-membered chelate rings with metal ions (Baba et al. 1994, 1998). Heterocyclic substituents such as pyridyl and imidazolyl significantly increase the chitosan sorption capacity toward both—anionic complexes of noble metals in acidic media and cations of transition metals at pH > 4 (Baba et al. 1996; Bratskaya et al. 2012; Pestov et al. 2012).

Amine derivatives

Studies of 27 ions sorption on polyaminated chitosan chelating resin revealed the selectivity row Hg(II) > UO_2(II) > Cd(II) > Zn(II) > Cu(II) > Ni(II) which is in rather good agreement with the stability of ammonia complexes of these metals in solution (Kawamura et al. 1993). This fact allows prediction of comparative recovery efficiency of amine derivatives from solutions of complex compositions. However, despite similarity of electron-donor properties of functional groups of the native chitosan and its amino derivatives, steric effects and differences in substituents structures can affect the selectivity of metal ions removal.

Katarina et al. have shown that cross-linked chitosan itself could adsorb silver ions quantitatively only at pH 5–6, while the ethylenediamine-type chitosan resin allowed silver recovery in much broader pH range from 1 to 8 (Katarina et al. 2006). The same resin was applicable for recovery of Sn(II) at pH = 4–9, Bi(III) at pH = 3–9, and Th(IV) at pH = 6–9 through a chelating mechanism and/or an anion- exchange mechanism. At pH = 1 the resin adsorbs silver selectively, although chelation is rather weak. Since the efficiency of Ag(I) recovery does not decrease with the increase of the NaCl background concentration up to 0.75 M, ethylenediamine-type chitosan resin is applicable for seawater samples. The silver detection limit using ICP-MS after elution with 1 M HNO_3 solution was equal to 0.7 ng/l at the enrichment factor 50 (Katarina et al. 2006). The resin was also stable after using in more than 30 cycles of extraction/regeneration.

Another amine derivative – N-(3-nitro-4-aminobenzoyl)chitosan cross-linked with ethylene glycol diglycidyl ether (Fig. 3) – was used for solid-phase extraction of anionic complex of Mo(VI) from river and sea water streams (Sabarudin et al. 2007a). The sorption capacity of the derivative at pH = 3-4 was 380 mg/g. The molybdenum determination was performed using ICP-AES and ICP-MS methods after elution with 1 M HNO_3; the detection limit using ICP-MS was 0.19 μg/l.

The possibility to use amine derivatives for noble metal ions preconcentration and determination using flame AAS was demonstrated in (Wang et al. 2010a, 2011). The chitosan derivative containing 3′-nitro-4-aminoazobenzene (Fig. 4) manifested high selectivity toward Pd(II) and Pt(IV) ions. The optimal conditions for extraction were found at pH = 4-6 for Pd(II) and pH = 3 for Pt(IV) ions (Wang et al. 2011). Chitosan functionalized with 4′-nitro-4-aminoazobenzene (Fig. 4) was used for analytical preconcentration of Au(III) and Pd(II) (Wang et al. 2010a). The maximal extraction efficiency was reached at pH = 3 for Au(III) ions and at pH = 2 for Pd(II) ions: the sorption capacities were 69.93 and 58.58 mg/g, respectively, and the efficiency of elution by the 1 M thiourea/0.5 M HCl solution was 82–87 %.

Due to very low affinity of the N-containing derivatives to transition metal ions in acidic media, extraction of Pd(II), Pt(IV), Au(III) ions allows not only elimination of salt background (K^+, Na^+, Ca^{2+}, Mg^{2+}) influence but provides selectivity for noble metals recovery in the presence of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} ions that makes them useful in analysis of different water streams and ores (Wang et al. 2010a).

In contrast to native chitosan, which has low affinity to metalloid ions, aminated and aminoarylated chitosan derivatives showed high sorption capacities to As(V), Se(IV), Se(VI) (Sabarudin et al. 2005a; Dai et al. 2011), Ge(IV) (Sabarudin et al. 2011) and B(III) (Sabarudin et al. 2005b)—Table 1. The maximum extraction efficiency was found at pH = 3 for As(V), Se(IV) and Se(VI), at pH = 2 for Se(VI) on N-(3,4-diaminobenzoyl)chitosan (Fig. 3) (Sabarudin et al. 2005a), and at pH = 6 for Ge(IV) on N,N-bis(2-hydroxypropyl)-3-amino-2-hydroxypropylchitosan (Sabarudin et al. 2011) and for B(III) on chitosan with N-methyl-D-glucamine moiety (Fig. 4) (Sabarudin et al. 2005b). The sorption capacity and selectivity of diethylenetriamine-containing chitosan (Fig. 4) toward Se (VI) were very close to those of N-(3,4-diaminobenzoyl)chitosan (Sabarudin et al. 2005a)—Table 1. The highest sorption capacity was found for N-methyl-D-glucamine derivative toward B(III) ions—2.1 mmol/g (Sabarudin et al. 2005b). Due to the efficient separation of metalloid ions from high-salinity matrix containing chlorides, phosphates, and nitrates on aminated and aminoarylated derivatives, the above mentioned derivatives can be used for preconcentration of As(V), Se(IV), and Se(VI) from bottled drinking water, tap and river water streams and other complex media (Table 1). The metalloids detection limits significantly depend on the method of analysis used and were equal to 0.09 μg/l and 0.39 μg/l for arsenic and selenium, respectively, using ICP-MS (Sabarudin et al. 2005a); 12 ng/l for selenium using the ICP-OES (Dai et al. 2011); and 0.07 μg/l and 0.14 μg/l for boron using ICP-MS and ICP-AES, respectively (Sabarudin et al. 2005b). It is worth mentioning that efficient separation of germanium from selenium, which limits direct germanium determination in river and sea water streams, was achieved using N,N-bis(2-hydroxypropyl)-3-amino-2-hydroxypropylchitosan) (Sabarudin et al. 2011).

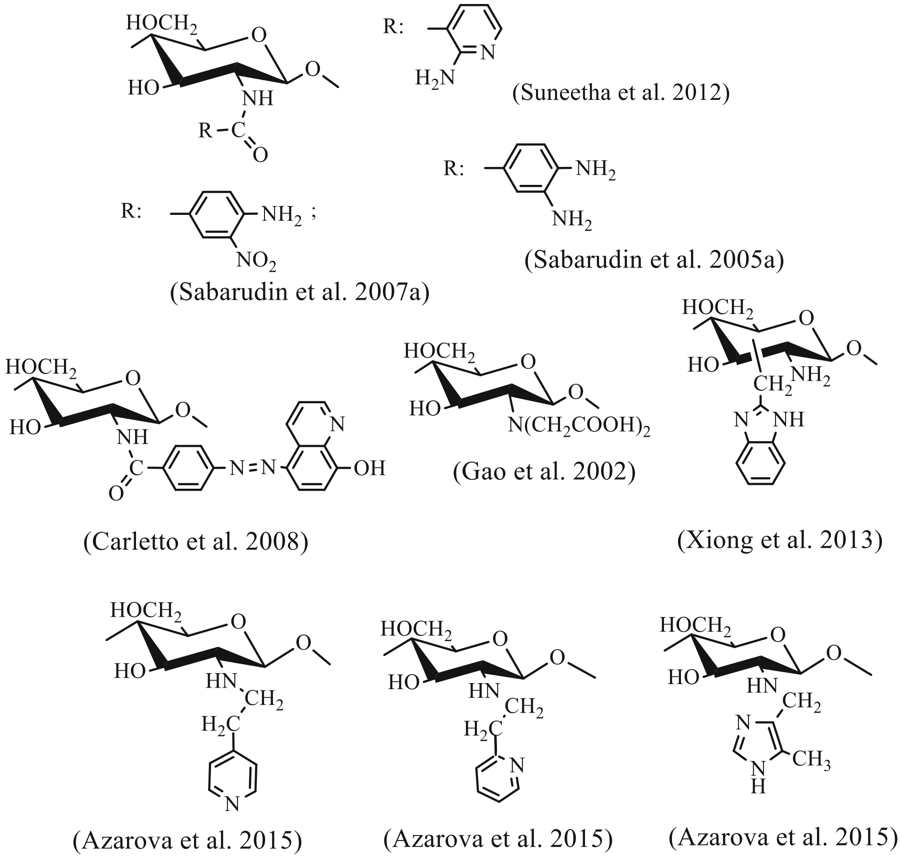


Fig. 3 Structural units of N-containing chitosan derivatives without linkers

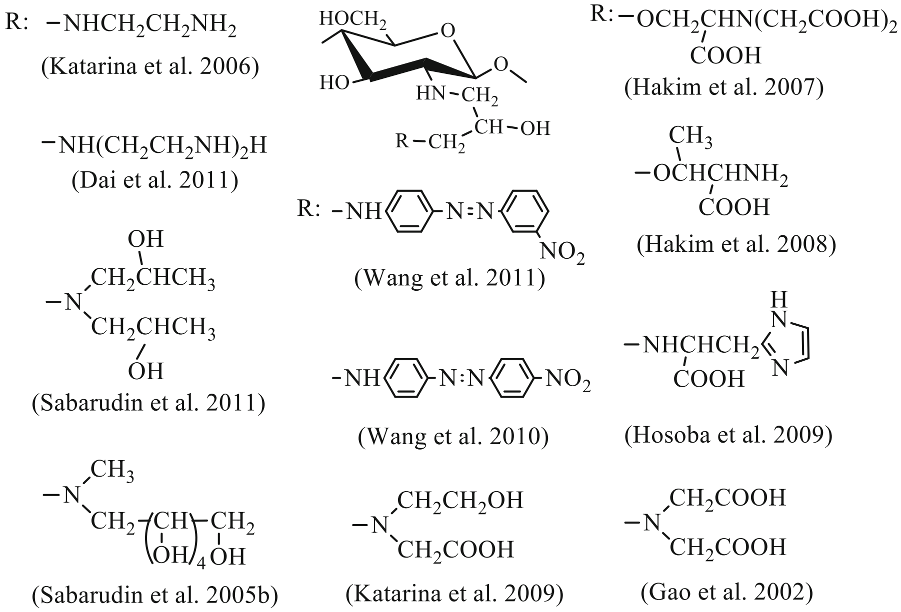


Fig. 4 Structural units of N-containing chitosan derivatives with 1-aminopropanol-2 linker

Table 1 Some examples of application of chitosan-based materials for solid-phase extraction of the metal and metalloid ions prior spectrometric determination

Sorbent	Sample	Analyte	Sorption capacity, mmol/g	EF	DL	Detection method	Reference
Chitosan	Natural waters, industrial streams	Cu(II)	n/d	52–128	2 μg/l	ETA-AAS	Minamisawa et al. (1999)
Chitosan	Natural waters	Cu(II)	n/d	250	20 ng/l	GF-AAS	Minamisawa et al. (2006)
Chitosan/silica gel composite	Natural waters	Cd (II)	n/d	166.7	20 ng/l	AAS	He et al. (2013)
		Cu (II)			38 ng/l		
Chitosan with grafted multilayer nanotubes	Herring, spinach, river and tap water	V(V), Cr(VI), Cu(II), B(V), Pb(II)	n/d	52–128	1.3–3.8 ng/l	ICP-MS	Dai et al. (2012)
Magnetic chitosan nanoparticles	Lake and tap water	Cr(III)	0.65	100	0.02 ng/l	ICP-OES	Cui et al. (2014)
		Cr(VI)	0.10		0.03 ng/l		
Chitosan N-acetylated by 2-aminopyridine-3-carboxylic acid	Natural waters	Cd(II)	0.88	90	21 ng/l	AAS	Suneetha et al. (2012)
		Zn(II)	1.51		65 ng/l		
N-(3-nitro-4-aminobenzoyl)chitosan	River and sea water	Mo (VI)	3.96	10	0.19 μg/l	ICP-MS	Sabarudin et al. (2007a)
Conjugate of ethylenediamine and chitosan	Fresh and sea water	Ag(I)	0.37	50	0.7 ng/ml	ICP-MS	Katarina et al. (2006)
N-(3,4-diaminobenzoyl)chitosan	Bottled drinking water, tap and river water	As (V)	1.09	10	0.09 μg/l	ICP-MS	Sabarudin et al. (2005a)
		Se (IV)	0.81		0.39 μg/l		
		Se (VI)	1.11		0.39 μg/l		
N-(5-methyl-4-imidazolyl)methylchitosan	Ore	Au(III)	n/d	50	2.4 μg/l	AAS	Azarova et al. (2015)
		Pd(II)			1.96 μg/l		
		Pt(IV)			15 μg/l		
Chitosan with residues of threonine	Natural waters	Mo(VI)	3.47	13	0.09 μg/l	ICP-AES	Hakim et al. (2008)
		V(V)	0.95	26	0.09 μg/l		
		Cu(II)	0.62	35	0.05 μg/l		
Conjugate of diethylenetriamine and chitosan	Natural waters	Se(VI)	0.92	20	12 ng/l	ICP-OES	Dai et al. (2011)
Chitosan with residues of histidine	River and drinking waters	Ag(I)	0.16 mmol/cm^3	73	0.03 μg/l	ICP-AES	Hosoba et al. (2009)
Chitosan functionalized with 8-oxyquinoline	Mineral water	Zn(II)	n/d	17.6	0.8 μg/l	AAS	Carletto et al. (2008)
Composite silica gel/carboxymethylchitosan grafted with cyclodextrin	Natural and waste waters	Cd(II)	0.101	280	7.1 ng/ml	AAS	Lü et al. (2013)
Chitosan with fragments of 2,5-dimercapto-1,3,4-thiodiazole	Geological samples	Pd(II)	0.14	10	15 μg/l	AAS	Li et al. (2010)

Table 1 continued

Sorbent	Sample	Analyte	Sorption capacity, mmol/g	EF	DL	Detection method	Reference
Chitosan with fragments of phenylarsonic acid	Natural waters, including sea water	U(VI)	0.046 mmol/cm^3	25	0.1 ng/ml	ICP-AES	Oshita et al. (2008)
Chitosan with moiety of N-methyl-D-glucamine	Tap and river water	B(III)	2.1	10	0.07 µg/l	ICP-MS ICP-AES	Sabarudin et al. (2005b)

DL detection limit, *EF* enrichment factor, *AAS* atomic absorption spectrometry, *ETA-AAS* electrothermal atomization atomic absorption spectrometry, *GF-AAS* graphite furnace atomic absorption spectrometry, *ICP-AES* inductively coupled plasma atomic emission spectrometry, *ICP-OES* inductively coupled plasma optical emission spectrometry, *ICP-MS* inductively coupled plasma mass spectrometry

Heterocyclic derivatives

Synthesis of chitosan derivatives containing heterocyclic fragments with good chelating properties has been known since 1990s. Functionalization of chitosan with the pyridine ring is usually carried out via reductive alkylation of Schiff bases of chitosan with 2- or 4-pyridinecarboxaldehyde yielding N-(2-pyridyl)-methyl chitosan or N-(4-pyridyl)methyl chitosan (Baba et al. 1996, 1998; Rodrigues et al. 2000; Hu et al. 2001; Tong et al. 2005; Dhakal et al. 2008; Leonhardt et al. 2010) or their homologs (Bratskaya et al. 2012) via aza-Michael reaction of direct addition of amino group to 2- or 4-vinylpyridines.

Another heterocyclic fragment used in chitosan modification is imidazole. This functionalization proceeds via the reaction of substitution of chloromethyl derivative (Hu et al. 2006) or 4(5)-imidazolemethanol (Pestov et al. 2012) with chitosan or via reductive alkylation using imidazole-4- or imidazole-2-carbaldehyde (Muzzarelli et al. 1994).

As in the case of amine chitosan derivatives, introduction of pyridyl and imidazolyl fragments substantially increases the chitosan sorption capacity not only toward transition metal cations, but also toward anionic complexes of noble metals (Baba et al. 1996; Bratskaya et al. 2012; Pestov et al. 2012). The sorption capacity of this type of derivatives usually changes in the row Au(III) > Pd(II) > Pt(IV) that is typical for N-containing polymeric sorbents.

Here, it is important to mention that the sorption capacity and selectivity depend significantly not only on the degree of substitution of the derivative, but also on the structure of the material formed in the crosslinking process, which is used to prevent material dissolution in acidic media. The decrease of the sorption capacity and the increase of selectivity along with the increase of the crosslinking degree and the polymer matrix rigidity was demonstrated for imidazolylchitosan derivatives (Pestov et al. 2012). The derivative with highest cross-linking degree and lowest sorption capacity has shown the best performance as solid-state extractant (Azarova et al. 2015).

N-heterocyclic chitosan derivatives—N-2-(2-pyridyl)ethylchitosan (2-PEC), N-2-(4-pyridyl)ethylchitosan (4-PEC), and N-(5-methyl-4-imidazolyl)methylchitosan (IMC) (Fig. 3) have been used for group preconcentration of Au(III), Pt(IV), and Pd(II) for subsequent determination by AAS in solutions with high background concentrations of iron and sodium ions (Azarova et al. 2015). It has been shown that Au(III) reduction to Au(0) upon sorption on epichlorohydrin-cross-linked chitosan and 2-PEC influences the sorption capacity of the materials and the efficiency of metal ions elution, thus affecting the accuracy of gold determination by flame AAS. While chitosan was applicable for Pd(II) and Pt(IV) recovery, the group preconcentration of Au(III), Pd(II), and Pt(IV) with subsequent quantitative elution using 0.1 M HCl/1 M thiourea solution was possible only on IMC and 4-PEC. The detection limits of the flame AAS at enrichment factor 50 were 2.4, 15, and 1.96 µg/l for gold, platinum, and palladium, respectively (Azarova et al. 2015).

Another imidazole-containing chitosan derivative—chitosan microspheres modified with 2-(chloromethyl) benzimidazole (Fig. 3)—was suggested for selective extraction of Hg^{2+} from contaminated natural water streams under dynamic conditions (Xiong et al. 2013). The sorption capacity toward Hg^{2+} ions was high (257.8 mg/g); however, neither detection limit nor selectivity of material was reported.

The cross-linked chitosan N-acetylated with 2-aminopyridine-3-carboxylic acid (Fig. 3) with the sorption capacities 98.7 mg/g for Cd(II) ions and 98.6 mg/g for Zn(II) ions was suggested for solid-phase extraction of these elements from natural waters under dynamic conditions (Suneetha et al. 2012). The detection limits of AAS after elution with 1 M HNO_3 were 21 ng/l for Cd(II) ions and 65 ng/l for Zn(II) ions. The method is applicable for determination of Cd(II) and Zn(II) in the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Co^{2+} ions.

Chitosan functionalized with widely used in analytical practice complexing agent—8-oxyquinoline (Fig. 3)—was used for preconcentration of Zn(II) ions from solutions containing Ca^{2+}, Mg^{2+}, Na^+, K^+, Cu^{2+}, and Fe^{3+} ions (Carletto et al. 2008). The detection and quantitative determination limits using AAS at enrichment coefficient 17.6 were equal to 0.8 and 2.5 µg/l, respectively. It was shown that Ca^{2+}, Mg^{2+}, Na^+, K^+, Cu^{2+}, and Fe^{3+} ions did not interfere with determination of Zn(II).

Derivatives with residues of amino acids and iminodiacetic acid

Chitosan derivatives modified with residues of amino acids and iminodiacetic acid represent the largest and most extensively investigated type of chitosan-based solid extractants for metal ions.

Chitosan modified by N-(2-hydroxyethyl)glycine fragments (Fig. 4) was used as a chelating sorbent allowing efficient separation of transition and rare earth metals (57 elements) from alkaline-earth metal ions in analysis of river water streams using the ICP-AES (Katarina et al. 2009). Chitosan functionalized with histidine fragments (Fig. 4) was applied for determination of trace silver quantities in river water streams and water stored in containers with silver coating using the ICP-AES (Hosoba et al. 2009). The polymer sorption capacity for Ag(I) ions was 0.16 mmol/cm^3 in the pH range 5–9; the detection limit for silver was 0.03 µg/l.

The cross-linked chitosan containing a fragment of N,N-dicarboxymethylated serine (Fig. 4) was used as a chelating sorbent for solid-phase extraction of microelements (cadmium, lead, copper, nickel, vanadium, gallium, scandium, indium, thallium etc.) from natural water streams and their determination by the ICP-AES (Hakim et al. 2007). The adsorbed elements were eluted with 1 M HNO_3 solution with the efficiency of 90–100 %. The detection limits for Cd, Pb, V, Sc, Cu, and Ni were 0.002, 0.036, 0.033, 0.005, 0.024, and 0.095 µg/l, respectively.

Chitosan modified by threonine residues (Fig. 4) was used to concentrate Mo(VI), V(V), and Cu(II) ions from natural water streams (Hakim et al. 2008). Group quantitative extraction of ions of all three metals occurs at pH = 5, whereas the selective sorption of Mo(VI) is possible at pH = 3. The sorption capacity of this chitosan derivative was 3.47 mmol/g for Mo(VI), 0.62 mmol/g for Cu(II), and 0.95 mmol/g for V(V) ions. Determination of the metals contents was performed by the ICP-AES after elution with 2 M HNO_3 solution. The negative effect of the salt background on the determination accuracy was eliminated after preconcentration, the detection limits were in the range of dozens ppb.

Chitosan derivatives modified with the iminodiacetate fragment, which can act as a tridentate ligand, also show very high efficiency in solid-phase extraction of metal ions. Simultaneous determination of microelements by the ICP-MS in combination with discrete microsampling technique after concentration on this derivative was reported in (Lee et al. 2000). It was shown that such metals as Al, Fe, Ni, Co, Cu, Zn, Ag, Cd, Pb, and U were sorbed quantitatively at pH = 6 and eluted with 1 M HNO_3 solution, whereas the background elements (Na, K, Mg, and Ca) were separated completely through washing the column with ammonium acetate solution.

Sorption properties of chitosan derivatives functionalized with residues of N,N-iminodiacetic and N-(2-hydroxypropyl)iminodiacetic acids (Fig. 4) toward to 54 elements at their contents of 10 ng/ml and the possibility of sorbents application for preconcentration and determination of metal ions in water using ICP-MS were investigated (Gao et al. 2002). For more than 20 elements (Ti, V, Fe, Ni, Cu, Zn, Ga, In, Pb, Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and U), the efficiency of extraction was close to 100 % in the pH range 2–7. The efficiency of extraction of Al, Co, Cd, La, Ce, and Pr ions was 98 % at pH 3–7. Be, Mn, and Ag ions were extracted efficiently at pH 4–7. Li, B, Na, K, Rb, Cs, Ru, As, Sb, and Tl ions were sorbed insignificantly allowing efficient separation of target analytes from salt matrix. The sorption capacity of both iminodiacetic acids derivatives of chitosan changed in the row Fe–Cu > Ni > Zn > Co > Mn, which corresponds to changes in stability constants of complexes with free iminodiacetic acid (log K_1: Cu—10.56; Fe—10.72; Ni—8.3; Zn—7.15; Co—6.96; Mn—4.72) (Smith and Martell 1989). The sorption properties of the chitosan derivative containing fragments of N-(2-hydroxypropyl)iminodiacetic acid differed significantly only with respect to Group II metal ions.

It is important to mention that the derivative with longer linker (fragment of N-(2-hydroxypropyl)iminodiacetic acid) manifests higher selectivity toward heavy metal ions in the presence of alkali-earth metals at pH < 7 that almost completely eliminates the effect of sea water macrocomponents (Na, K, Mg, Ca) interfering with determination of transition and rare earth elements using ICP-MS (Gao et al. 2002). These results are in good agreement with the data (Kumagai et al. 1998) demonstrating that the selectivity to rare earth metal ions of ion-exchange resins based on poly(glycidyl methacrylate) and poly(styrene divinylbenzene) modified by iminodiacetic acid fragments increases along with the increase of the length of the linker binding the functional group to the polymer matrix. According to the authors' opinion, this effect is related to higher mobility and steric accessibility of such functional fragments.

Chitosan cross-linked with ethylene glycol diglycidyl ether and modified with fragments of iminodiacetic acid, glycine, valine, leucine, and serine was applied for solid-phase extraction of heavy meatal ions, whose concentrations in natural water streams were at the level of 10 ng/l (Oshita 2004). It was demonstrated that the selectivity of derivatives to specific ions to a great extent depended on the functional fragment. Chitosans modified with glycine, leucine, and serine fragments showed good sorption properties for Bi(III), Mo(VI), and U(VI), respectively. Cross-linked chitosan modified with iminodiacetic acid provided the highest efficiency of group preconcentration of heavy metal ions and their separation from salt matrix. The method was used for solid-phase extraction of the metal ions from natural water streams prior to their determination with ICP-MS, ICP-AES, and ETA-AAS (Oshita 2004).

O-containing chitosan derivatives

Enhancement of metal binding properties of O-containing chitosan derivatives is provided mainly via introduction of hydroxyl and carboxyl groups. The most thoroughly studied derivatives of this type are carboxyalkyl chitosans (Skorik et al. 2005; Sun and Wang 2006a, 2006b, 2006c; Sokovnin et al. 2009; Wang et al. 2009; Yan et al. 2011) and derivatives containing fragments of ethylenediaminetetraacetic acid (EDTA) (Inoue et al. 1999; Ge and Huang 2010; Repo et al. 2010) and diethylenetriaminepentaacetic acid (DTPA) (Inoue et al. 1999; Repo et al. 2010). Carboxyalkylation of chitosan leading to formation of structures similar to iminodiacetic acid and its homologs with good chelating properties is an alternative functionalization method to enhance the selectivity of chitosan derivatives (Skorik et al. 2005). Twofold and larger increase of the sorption capacity of O-containing chitosan derivatives, as compared to that of unmodified polymer, was observed for a wide range of metal ions—Cu(II) (Sabarudin et al. 2005b; Sun and Wang 2006a, 2006c; Sokovnin et al. 2009; El-Sherbiny 2009; Ge and Huang 2010; Julkapli and Ahmad 2010; Yan et al. 2011), Ni(II) (Sun and Wang 2006a, 2006c; Ge and Huang 2010; Repo et al. 2010), Co(II) (Sun and Wang 2006c; Ge and Huang 2010; Repo et al. 2010), Zn(II) (Sun and Wang 2006c; Ding et al. 2007).

Studies of the sorption properties of chitosans modified with the most efficient complexing agents—EDTA and DTPA (Inoue et al. 1999; Ge and Huang 2010; Repo et al. 2010)—demonstrated that the rows of selectivity of metal ions removal corresponded to the rows of stability of their chelates with respective low-molecular ligands [Ga(III)–In(III)–Fe(III) > Cu(II)–Mo(VI) > Ni(II) > V(IV)–Zn(II)–Co(II)–Al(III) –Mn(II)], thus showing that the chelating ability of the ligand was not significantly changed upon its grafting to the chitosan backbone.

Despite extensive studies of sorption properties of O-containing chitosan derivatives toward different metal ions, comprehensive studies of their applicability for analysis of low concentrations of the metals are not numerous. A composite based on silica gel and carboxymethylchitosan with grafted fragments of cyclodextrin was suggested for concentration of cadmium ions (Lü et al. 2013). The composite sorption capacity was equal to 11.3 mg/g, and the metal quantitative elution was attained using 0.3 M HCl solution. The detection limit for Cd(II) ions with the AAS was 6.1 ng/ml. The method is applicable for determination of trace quantities of Cd(II) ions with an error not higher than 5 % in natural and waste waters.

Another composite material based on magnetic chitosan nanoparticles grafted with β-cyclodextrin (sorption capacity for Co(II)—5 mg/g) has been suggested for the fast determination of trace amounts of Co(II) ions in tap, rain, and sea water using the AAS (Moghimi 2014). The detection limit for cobalt was 1.0 ng/ml at the enrichment factor 100.

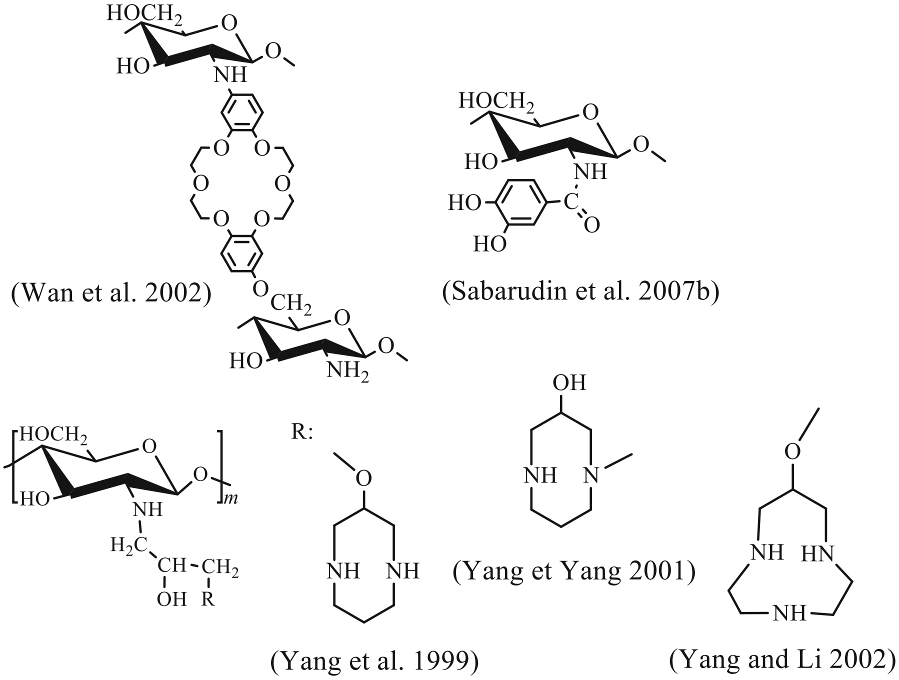
Chitosan with fragments of 3,4-dihydroxybenzoic acid (Fig. 5) was suggested to concentrate uranium from tap, river, and sea water prior to its determination using the ICP-MS (Sabarudin et al. 2007b). The derivative sorption properties were investigated in the pH range 1–9 with respect to 60 elements from solutions with metal concentrations of ~10 ng/ml. It was shown that vanadium, uranium, bismuth, and gallium ions were sorbed in both acidic and alkaline media, molybdenum was recovered from neutral solutions; copper, beryllium, nickel, aluminum, indium, lead, and silver were extracted at pH > 7. The selective solid-phase extraction of uranium ions was possible at pH = 3, and the sorption capacity of this chitosan derivative was 1.39 mmol U/g.

Thermally sensitive grafted copolymers of chitosan and N-isopropylacrylamide containing maleic and hydroxamic acids were used for preconcentration of heavy metal ions (Cu(II), Cd(II), and Pb(II)) from river, tap, and drinking water (Owawa et al. 2007). At the level of the metal ions concentrations of a few nmol/l, the degree of extraction by chitosan derivatives was about 90 %.

S-containing chitosan derivatives

Functionalization of chitosan with S-containing fragments is widely used to improve sorption properties of chitosan toward ions of noble (Guibal et al. 2000, 2002; Arrascue et al. 2003; Chassary et al. 2005; Zhou et al. 2009; Bratskaya et al. 2011) and some transition metals (Baba et al. 2002; Gavilan et al. 2009; Chang et al. 2009; Kannamba et al. 2010). Up to present, the sorption properties of chitosans modified by thiourea (Guibal et al. 2002; Donia et al. 2007; Butewicz et al. 2010; Pestov et al. 2010; Wang et al. 2010b; Bratskaya et al. 2011), dithiooxamide (Guibal et al. 2002; Arrascue et al. 2003; Pestov et al. 2010), dithiocarbamate (Humeres et al. 2002; Khan et al. 2011) and mercapto groups (Cárdenas et al. 2001; Chassary et al. 2005; Zhou et al. 2009; Emara et al. 2011; Fan et al. 2011) have been investigated in detail. Comparative

Fig. 5 Structural units of O-containing chitosan derivatives and crown ethers

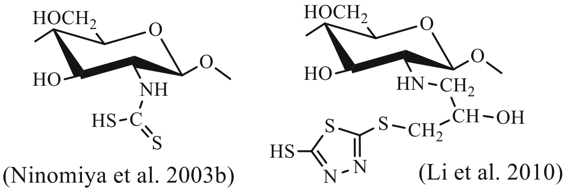


analysis of sorption properties of S-containing chitosans, which were modified with (Guibal et al. 2000, 2002; Arrascue et al. 2003; Chassary et al. 2005) or without (Butewicz et al. 2010; Pestov et al. 2010; Bratskaya et al. 2011) linker, demonstrates that the pendant modification by thiocarbonyl compounds enables one to fabricate materials with high sorption capacity at low degrees of substitution thanks to the higher flexibility of the grafted functional fragment.

Although S-containing polymeric and inorganic materials are the most efficient sorbents for solid-phase extraction of “soft” metal ions (Zougagh et al. 2005; Mladenova et al. 2012), the analytical application of S-containing chitosan derivatives with superior sorption capacities and selectivity is surprisingly underinvestigated.

Chitosan containing dithiocarbamate fragment (Fig. 6), one of the most efficient ligand for transition and precious metal ions, was applied for micro-column solid-phase extraction of Cu, Mo, Ag, Te, W, Hg, and Bi ions from acidic and neutral media with recovery close to 100 % (Ninomiya et al. 2003). However, the ions elution was complicated. To facilitate elution, the method of sorbent pretreatment with copper sulfate solution was suggested. This allowed quantitative elution of target ions with 1 M HNO_3 solution and their subsequent determination by ICP-MS with an error of less than 5 %. The method was applicable for determination of metal ions in river water.

Determination of trace quantities of Pd(II) in geological samples by AAS with preliminary solid-phase extraction on chitosan containing fragments of 2,5-dimercapto-1,3,4-thiodiazole (Fig. 6) was reported in (Li et al. 2010). The polymer sorption capacity at pH = 2 was 16.2 mg/g, and the quantitative elution of palladium was attained using 1 M thiourea solution. The derivative application provides high selectivity of Pd(II) extraction at high background concentrations of transition metal ions: Cu(II), Fe(III), Cd(II), Ni(II), Mg(II), and Zn(II). The detection limit for Pd(II) was 0.015 mg/l.



(Ninomiya et al. 2003b) (Li et al. 2010)

Fig. 6 Structural units of S-containing chitosan derivatives

Crown ethers

Crown ethers represent another extensive class of chitosan derivatives with high potential for application as solid-phase extractants of trace amounts of metal ions, although the sorption capacity of this type of materials is rather low in comparison with other derivatives. The possible explanations of low sorption capacity is high cross-linking degree (Yang et al. 1999) and significant increase of hydrophobicity providing lower degree of swelling.

It was shown that changes in the chemical structure of azacrown ethers had virtually no effect on the sorption capacity. However, despite low sorption capacities, 1,5-diazacyclooctane chitosan (Fig. 5) provides high selectivity of Cu(II) (Yang et al. 1999) and Hg(II) ions (Yang et al. 2000) recovery. Ag(I) ions were recovered selectively on 3-hydroxyl-1,5-diaza-cyclooctane chitosan, 3-hydroxyl-1,5,8-triaza-cyclodecan chitosan (Fig. 5), N-allyl dibenzo 18-crown-6 crown ether crosslinked chitosan, and N,N’-diallyl dibenzo 18-crown-6 crown ether crosslinked chitosan (Yang and Yang 2001; Yang and Li 2002; Yang and Cheng 2003; Ding et al. 2006; Zhang et al. 2006).

The possibility of selective solid-phase extraction of Pb(II) ions at pH 6 from tap and lake water in the presence of Cu(II) and Ni(II) ions was investigated using chitosans functionalized by dibenzo-18-crown-6 ether (Fig. 5) (Wan et al. 2002). The sorption capacity of the derivatives decreases in the row Pb(II) > Ag(I) > Ni(II) > Cu(II). The selectivity coefficients for N-substituted derivatives ($K_{Pb(II)/Ni(II)}$ 35.5, $K_{Pb(II)/Cu(II)}$ 55.3) were somewhat higher than those for O-derivatives ($K_{Pb(II)/Ni(II)}$ 24.4, $K_{Pb(II)/Cu(II)}$ 41.4). and.

Other derivatives

Chitosan containing fragments of phenylarsonic acid (Fig. 7) was suggested for concentrating trace quantities of uranium with subsequent determination using the ICP-AES method. The sorbent provides virtually 100 % of uranium ions extraction in the pH range 4–8. The sorbent sorption capacity towards U(VI) was 0.046 mmol/cm^3: uranium elution was carried out by 1 M solution of HNO_3. The limit of uranium detection using this method in combination with 25-fold

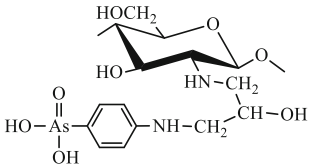


Fig. 7 Structure of the sorbent structural unit according to (Oshita et al. 2008)

preconcentration is 0.1 ng/ml. The method is applicable for determination of uranium trace quantities in various natural waters, including sea water, provides efficient separation of the target component and highly concentrated salt matrix containing Na, K, Mg, and Ca ions (Oshita et al. 2008).

Conclusions

Thanks to the nearly zero affinity of chitosan to alkali and alkali-earth metal ions, even in the unmodified form, it can be very useful for separation of target metal ions from the salt matrix, which is always present in natural waters, waste streams, and geological samples and interferes with spectrometric determination of metals and metalloids.

However, chemical modification of chitosan with N-, O-, S-containing functional fragments offer virtually unlimited possibilities to extend the variety of metal and metalloid ions, which can be efficiently recovered using chitosan-based solid-phase extractants and then determined with spectrometric techniques providing detection limits below ng/l (Table 1).

Depending on the substituent structure, its introduction to chitosan backbone can increase the number of electron-donor atoms and, therefore, the number of the anion-exchange sites and/or impart it with the capability to form stable five- and six-membered chelate rings with metal ions that significantly increases the selectivity of metals recovery.

Different conditions of effective recovery of metal cations and anions provide basis for their efficient separation and elimination of the negative effect of background ions on analytical determination of trace amounts of noble metals, which cannot be determined directly in most environmental samples and technological solutions even using highly sensitive spectrometric techniques.

The literature survey shows that the most extensively studied group of chitosan-based solid-phase extractants is represented by N-containing chitosan derivatives functionalized with residues of amino acids, aliphatic and aromatic amines, heterocyclic fragments (pyridyl, imidazole). These derivatives can be applied for preconcentration of many transition and noble metal ions, actinides; and such metalloids as boron, germanium, arsenic, and even non-metals such as selenium. Derivatives containing fragments of N,N-iminodiacetic acid, which manifested one of the best efficiency in group recovery of many transition metals, were the only example of chitosan-based extractants applicable for preconcentration of lanthanides.

It is important to take into account that there is no direct correlation between high sorption capacity and good efficiency of the derivatives in solid-phase extraction. Although one can predict selectivity of derivatives toward different ions on the basis of complex stability constants of the corresponding low molecular weight ligands, the synthetic procedures—introduction of functional fragment via linker or without linker, cross-linking degree and type of cross-linking agent—play a significant role in mobility and steric accessibility of grafted functional group and, as a result, in the sorbent capacity and selectivity.

Chitosan is still insufficiently explored as material for analytical preconcentration of metal ions, but a unique combination of its properties (high affinity to many precious and transition metal ions, high reactivity in processes of chemical modification using different chelating ligands, and good processability allowing fabrication of various forms of chitosan - films, porous granules, fibers and composites) indicates to its very high potential in solid-phase extraction.

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