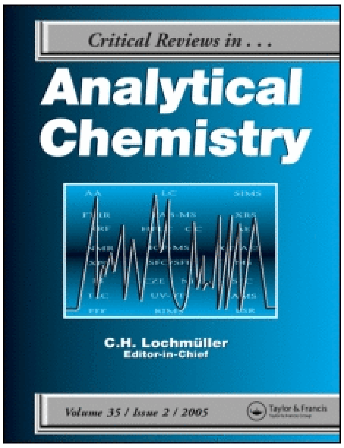

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Functionalized Cellulose Sorbents for Preconcentration of Trace Metals in Environmental Analysis

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ABSTRACT: Regardless the progress in detectability of various instrumentation for trace metal determination, the preconcentration steps are very often needed for the analysis of environmental samples. Among the different techniques that can be used for this purpose, solid-phase extraction using various sorbents has been developed very intensively in recent years. Besides preconcentration, it can also be used for matrix removal necessary in some procedures or for the speciation of trace elements.

This review is based on 42 literature references and shows favorable properties of cellulose sorbents for this purpose. Depending on the functional groups attached, the sorbent can be directly used for sorption of target analytes or can be loaded with ligands specifically binding certain species. Applications are reviewed for conventional batch procedures, flow-injection sample processing, and speciation of certain trace elements.

KEY WORDS: cellulose sorbents, preconcentration, trace metals, flow-injection analysis, chemical speciation.

I. INTRODUCTION

Despite continuous progress in the detectability of instrumental methods for analysis, a direct determination of trace metal ions in environmental samples is still very often difficult because of insufficient sensitivity and selectivity of the methods used. Therefore, pretreatment steps in analytical procedures, such as preconcentration and/or selective separation of the analyte before its determination, are frequently necessary in order to reduce the effect of interferences present in the matrix. Solvent and solid-phase extraction and also coprecipitation or electrodeposition are the most often used methods in environmental trace analysis.

The preconcentration methods utilizing solid sorbents are considered to be superior to the liquid-liquid extraction in terms of simplicity, rapidity, and the ability to obtain a high enrichment factor. Particularly, solid-phase extraction has been demonstrated in various procedures to be a very effective preconcentration technique in combination with atomic absorption spectrometry. The main advantage of this tefhnique is the possibility of using a relatively simple detection system with flame atomization instead of a flameless techniques, which require more expensive equipment and are usually much more sensitive to interferences from macrocomponents of various natural matrices.

A number of different solid sorbents have been investigated for the preconcentration of trace metals from an aqueous solution. They include activated carbon, porous organic polymers, ion-exchange resins, chelating resins with selective functional groups covalently attached to copolymer matrices and ligand-modified resins. The latter can be obtained easily by simple immobilization of complexing organic reagents by ion-exchange and/or adsorption onto conventional anion-exchangers or non-polar sorbents. The characteristics of these kind of sorbents have been presented in several reviews.[1-3] A sorbent that is the most essential component of the preconcentration system has to exhibit certain important properties such as sufficient capacity, high distribution coefficients for analyte but not for matrix components, fast kinetics of sorption and elution processes as well as tolerance against high flow rate. Among different kinds of sorption materials, growing attention has been paid to cellulose as a polymeric matrix for the synthesis of new sorbents. Cellulose-based sorbents largely fulfill the above-mentioned requirements and have several favorable properties. They are highly hydrophilic and easily accessible to chemical reactions. Due to their fibrous structures, exchange reactions are relatively fast.

The early literature on preparation and characterization of cellulose sorbents was already reviewed by Wegscheider and Knapp.[4] The number of studies on this subject is increasing in recent years, therefore, an updated review of the most relevant literature data in recent years is presented herewith. This report deals mainly with the application of cellulose sorbents for preconcentration and the separation of trace metal ions in environmental samples. Especially efficient preconcentrations can be carried out in the flow-injection mode.

II. GENERAL PROPERTIES OF CELLULOSE SORBENTS

Unsubstituted cellulose has a very low ion-exchange capacity, in the range of 0.01 to 0.05 mmol/g. The greatest fraction of the exchange sites is attributed to the presence of carboxyl groups. In neutral solution (pH 5 to 8) the distribution coefficient values for such metal ions as Be(II), Cd(II), Cr(III), Fe(III), and Pb(II) are in the range of 10^1 to 10^4 (see Ref. 5). The sorption of metal ions on cellulose proceeds considerably faster than on many inorganic collectors (e.g., Al_2O_3 or SiO_2); therefore, cellulose as a component of the solid phase in natural aquatic systems can play an important role in of metal traces in these natural media.

In the literature the term “ion-exchange cellulose” is used commonly for substituted cellulose. Its modification is accomplished by oxidation, esterification, and etherification reactions in conditions that retain the fiber structure of cellulose. The obtained products do not dissolve or swell significantly in dilute aqueous acids or bases. The modified cellulose sorbents can retain metal ions from solutions much more effectively than natural cellulose. A number of different experimental procedures have been reported for the preparation of cellulose-based ion-exchange materials.[4] The carboxymethylated, diethylaminoethylated, and triethylaminated cellulose, as well as phosphorylated cellulose, have been mostly applied for preconcentration of metal ions.

III. BATCH PRECONCENTRATION PROCEDURES

Cellulose sorbents with anion-exchange groups have been found to be useful for the preconcentration of anionic metal complexes.[7-10] Despite the lower capacity of Cellex T (triethylamino cellulose) to chloride complexes of palladium and iridium, it allowed obtaining higher preconcentration factors compared with similar anion-exchangers with styrene matrix.[7] The greater affinity of these resins to Pd(II) results in a larger volume of eluent, which is required to obtain the complete recovery of the analyte. Also, Cellex T offers an attractive efficiency for enrichment of Au(III) as anionic chlorocomplexes.[8] Pyrzyñska[10] has demonstrated that sorption of Se(IV) on Cellex T and Cellex QAE (diethylhydroxypropyloamine cellulose) was almost complete over a wide pH range. Thus, selenium can be preconcentrated effectively at the acidity of environmental waters, that is, without any pH adjustment.

The breakthrough curves obtained for the hydrogen and sodium forms of Cellex CM (with carboxymethyl functional groups) indicate a strong affinity of Ni(II) for this cellulose-based sorbent.[6] The selectivity of Cellex CM toward other investigated metal ions was established as follows Cd(II) < Zn(II) < Cu(II) < Fe(III) < Mn(II) < Pb(II) < Ni(II).

Phosphate cellulose sorbents, such as Cellex P with —O-PO(OH)$_2$ functional groups, act as weakly acid exchangers.[11] It was shown by Fiesel and Bilba[12] that the formation of some very stable complexes on this sorbent can occur. The increased electronic density of oxygen double bound to phosphorus helps in the formation of some coordinative linkages, incorporating metal ion into a chelate complex. Phosphate cellulose sorbents besides exhibiting satisfactory sorption kinetics also allows avoiding drastic changes in the swelling as it was observed for similar resins with styrene matrix.[13] The complexation affinity of metal ions to phosphate groups can be modified in the presence of other complexing agent in solution.[11,13,14] In the pH range 4 to 8 the selectivity order of Cellex P sorption in the presence of glycine decreased in the order: Ti(IV) > Fe(III) > Cr(III) ~ Mn(II) > Pb(II) > Cu(II), while in the absence of this ligand sorption of these metal ions was similar.[11] Also, the transformation of palladium[15] and gold[16] into amine complexes improved their preconcentration and separation from other platinum metals by the use of Cellex P. Examples of the application of the most commonly used phosphate cellulose sorbents for the preconcentration of metal ions are showed in Table 1.

TABLE 1
Application of Phosphate Cellulose Sorbents for Preconcentration of Metal Ions

Metal	Medium	Eluent	Application	Ref.
Cr(III)		1 *M* HCl	Natural waters	9
Al, Ti(IV), Pb, Cu, Cr(III), Mn(II), Cd, Fe(III), Co, Ni, Zn, Pd(II)	Glycine	Batch experiments	Standard solutions	11
Bi(III)	Tetrene	2 *M* HNO3	Metallic lead	14
Pd(II)	Ethylenediamine	1 *M* HCl	Alloys	15
Au(III)	Ethylenediamine Diaminopropan	0.2 *M* glycine 1 *M* HCl	Palladium and platinum salts	16
Cd, Cu, Co, Pb, Zn, Cr(III),V(V)		Batch experiments	Standard solutions	17
Cu, Ni, Mn(II), Cd, Zn, Pb		1 *M* HNO_3	Potable waters	18
Pb		1 *M* HNO_3	Natural waters	19
Inorganic and organic lead		1 *M* HNO_3	Natural waters	20
Cd, Cr(III), Cu, Ni		1 *M* HCl	Natural waters	21

Cellulose sorbents with chemically bound chelating groups offer new possibilities for trace metals preconcentration, but more gentle procedures have to be employed for their preparation in order to avoid a loss of the fibrous cellulose structure. Frequently an activation step is carried out before the attachment of the ligand.[4] The sorption properties of cellulose sorbents with amino-carboxylic groups results from a high complexation ability of these chelating groups that form 1:1 complexes with numerous metal ions. The cellulose sorbents containing iminodiacetic,[22,23] ethylenediaminetriacetic[24] diethylenetriaminetetraacetic[25] or triethylene-tetra-aminepentaacetic acids[26] have been developed for multielement preconcentration. Metal-complexing dissolved compounds present in natural media (e.g., humic substances) can, however, considerably decrease the recovery of some metals such as Cu, Fe(III), and Ni.[26] In the case of high salt concentrations (2.5 *M* NaCl), lower preconcentration efficiency was observed only for iron (III). The sorbent with EDTA as functional group has been reported to give excellent preconcentration characteristics for 14 rare earth elements as well as for a range of transition metals from synthetic sea-water solution.[24] The other matrix components such as monovalent and some divalent ions (Na, Mg, Ca) was either not retained on the column or was weakly chelated and subsequently removed by washing with a buffer solution.

Recently, some efforts have been made to improve selectivity, exchange capacity, and physicochemical stability of these sorbents. A wide variety of complex-forming groups can be introduced by chemical modification of the cellulose sorbents.[27–32] The selectivity order of noble metals reported for solutions with high salt contnet using cellulose Hyphan (with 1-(2-hydroxyphenyl-azo-)-2-naphthol groups) was as follows: Pt(IV) > Pd(II) > Ag(I) > Au(III) 27. Fischer and Lieser[28] have examined several tailormade exchangers with respect to their capacities and distribution coefficients for sixfold coplanar coordination of UO_2^{2+}. The anchor groups fixed by chemical bounds on cellulose included 8-oxa-2,4,12,14-tetraoxo-pentadecane, malonic acid linked together by n-alkanes of various chain length, amidooxime/hydroxamic acid groups, and amidrazone/hydrazide groups also linked together by n-alkanes. The chelating amidoxime/hydroxamic groups offered the most favorable conditions for complexation of UO_2^{2+}, and the equilibrium loading was significantly higher than that reported in the literature for most compounds reported for selective preconcentration of uranium.

A method utilizing a column with SO_3-oxine CM-cellulose has been developed to increase the sensitivity for multielement measurements by ICP-MS method.[31] This matrix/analyte separation has been used to preconcentrate Mn, Co, Ni, Cu, Cd, and Pb from natural water samples. The quantitative recovery was obtained with a mixture of 0.1 *M* hydrochloric and 0.1 *M* nitric acids. The column can stand at least 50 to 70 preconcentration/elution cycles without loss in dynamic capacity.[31] The cellulose sorbent with chemically bound quinolin-8-ol was successfully applied for the preconcentration of traces of copper.[32]

Sutton et al.[33] compared a number of polystyrene resins with cellulose sorbent with immobilized Procion Violet for the sorption of metal ions. The latter, despite of its low capacity, had a strong affinity for Cu(II).

IV. ON-LINE PRECONCENTRATION

A highly effective enrichment of trace analyte with a simplified analytical procedure can be achieved in a flow-injection (FI) sample processing systems, where pre-concentration is performed on-line prior to the detection. The growing interest in the use of FI technique in atomic spectrometry has been demonstrated in several reviews.[34-36] An increase in the enrichment ratio is favored by the miniaturization of the whole set-up for transport of solutions, including a substantial decrease of bed volume, which allows the using much smaller eluent volumes.

Flow-injection systems with on-line solid-phase extraction step can be designed in two ways regarding the method of sample delivery. In the systems with volume-based loading a fixed volume of the sample solution is introduced using the injection valve. In the systems with time-based loading the sample solution is aspirated at a constant flow rate in an appropriate time interval through a column. In the conditions of fast FI measurement of special importance is the kinetics of sorption and elution processes. Because the efficiency of preconcentration essentially depends on time taken for the sample solution to pass through the microcolumn, the use of larger loading time improves the enrichment, but simultaneously leads to a decrease in the sampling rate. Hence, it seems to be very appropriate to use a concentration efficiency (CE) value for the comparison of the efficiency of various flow-injection systems with a preconcentration step (Table 2). Concentration efficiency is the product of an enrichment factor and sampling rate (sample per min).

Among the sorbents applied for preconcentration of metal ions in FI systems, cellulose sorbents are very suitable for such application owing to very fast sorption and desorption properties. Comparison of signal profiles for elution of lead(II) with 1.0 ml of 1 *M* nitric acid recorded on an expanded time scale from the same bed volume of different sorbents is presented in Figure 1. The highest recovery of lead in transient conditions were obtained using cellulose sorbents, indicating a fast elution process of retained lead.[20] The elution peaks from styrene-based resins — Chelex 100 and Dowex 50W × 4 — were smaller and broad, indicating that the recovery process using this eluent was much slower.

Several on-line preconcentration and matrix/analyte separation systems utilising cellulose sorbents have been developed for flame atomic absorption spectrometry (FAAS),[8,9,20,32] inductively coupled plasma atomic emission (ICP-AES),[23,30] and ICP-mass spectrometry detection.[31] With several obvious advantages over off-line procedure, the on-line mode improved the detection limit of these methods by one to two orders of magnitude.

V. CHEMICAL SPECIATION

Speciation of elements in natural matrices, especially of trace metals, is one of the predominant development trends in modern

TABLE 2
Concentration Efficiency (CE) Obtained in Flow-Injection Systems Using Microcolumns with Celulose Sorbents

Determined species	Sample volume [ml]	Sampling rate h^{-1}	CE	Ref.
Au(III)	5–10	4–20	2–8	8
Cr(III), Cr(VI)	50	4–6	5–7	9
Pb	50	4–6	10-15	20
Cd, Co, Cu, Pb	7.5	10–12	13–14	23
Au(III)	10	20	13	30
Mn(II), Co, Ni, Cu, Cd, Pb	15	25	6	31
Cu	3	17	8.5	32

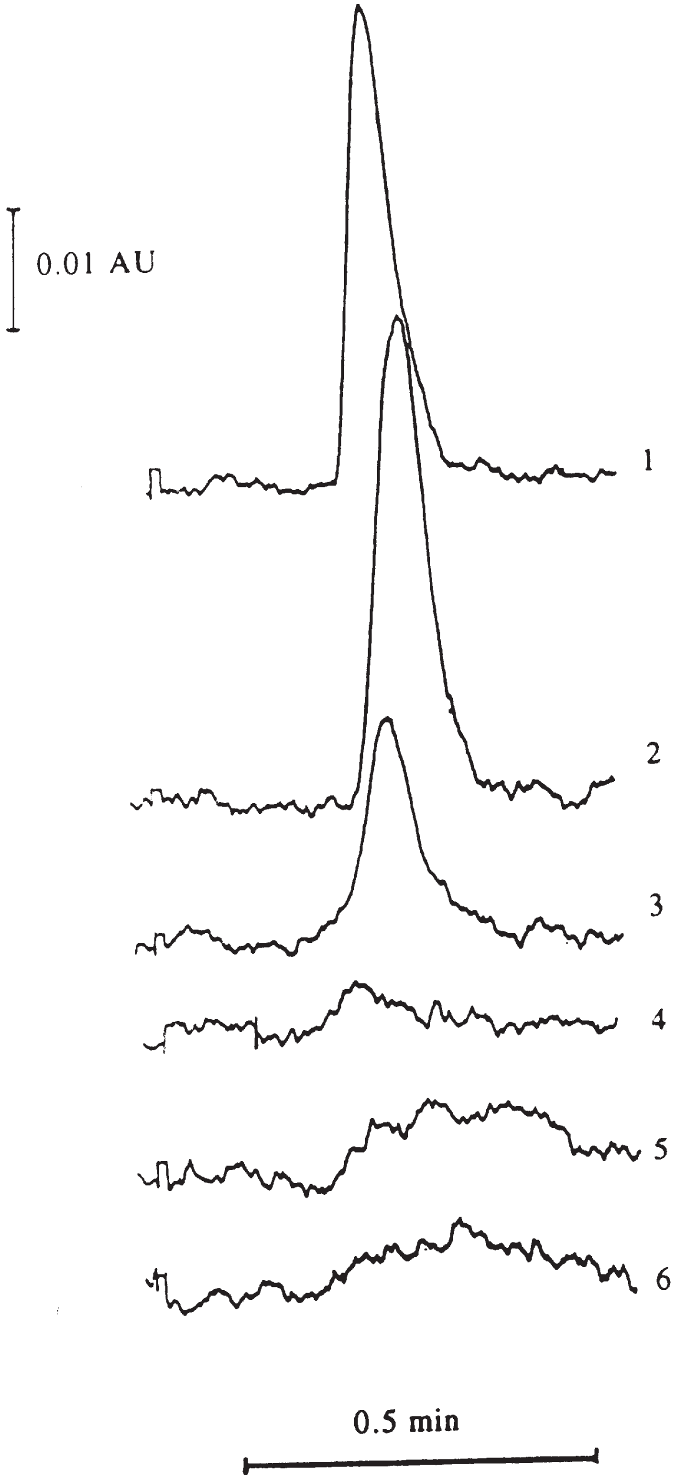

FIGURE 1. Elution peaks recorded for 5 µg of Pb(II) from microcolumns (0.4 ml bed volume) filled with: Cellex P (1), Cellex CM (2), Spheron Oxin 1000 (3), Pyrocatechol Violet loaded XAD-2 (4), Chelex 100 (5), Dowex 50W × 4 (6). Elution with 1.0 ml of 1 *M* HNO_3.[20]

inorganic analysis. In the most common meaning "chemical speciation" is the analytical procedure developed for the identification and quantitative determination of various species of a given element in a particular material. The total content of trace element to very limited extent decides its role in complex materials such as different ecosystems or living organisms. True toxicity, reactivity, or bioavailability of the element depends mainly on the chemical forms present, oxidation state, chemical bounds in which they are involved, as well as association with other components of a given matrix.

The application of solid sorbents is quite common in the determination of different oxidation states of metals.[37-39] The procedures developed for this purpose employ the retention of one or several species on suitable solid sorbents. Numerous analytical speciation procedures have been developed with cellulose-based sorbents and AAS detection.[9,10,20] Both inorganic selenium species, Se(IV) and Se(VI), could be quantitatively preconcentrated on Cellex T.[10] The effective elution of Se(IV) was achieved using 0.01 *M* nitric acid, while Se(VI) remains completely in the column. For the elution of selenite retained on the polystyrene matrix anion-exchange resins a more concentrated (0.5 *M*) solution of nitric acid had to be used. Moreover, under these conditions small amounts of selenate was coeluted together with Se(IV). These results indicate that from the point of view of column separation, the lower affinity of cellulose sorbents, than styrene resins, should be regarded as an advantage. The kinetic properties of the former allow the obtaining a quantitative elution.

For the speciation of chromium in natural waters two columns with different functionalized cellulose sorbents were used for selective preconcentration of Cr(III) and Cr(VI) from a continuously aspirated sample.[9] Sequential elution with appropriate eluents provides two peaks for each injected sample (Figure 2).

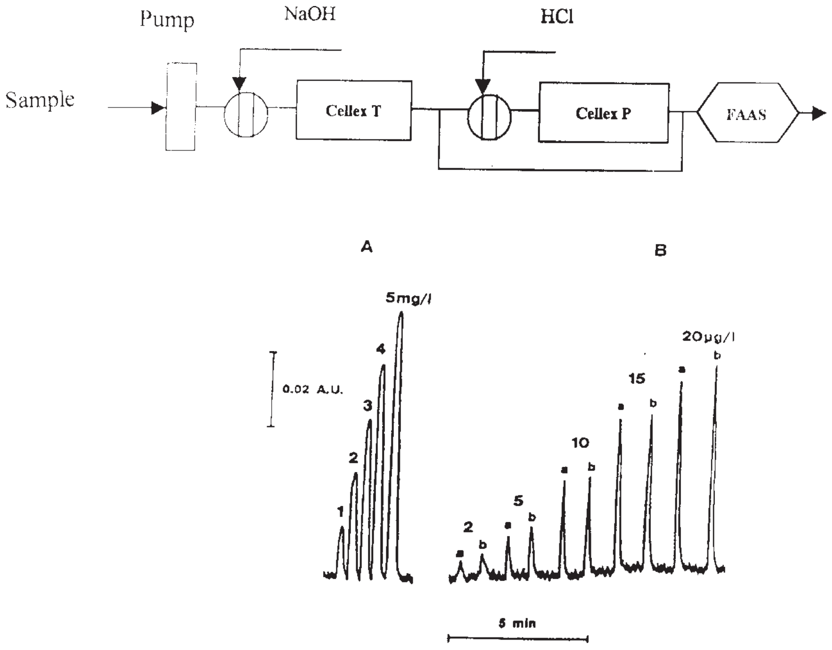

FIGURE 2. Schematic diagram for system used for speciation of chromium and comparison of recordings obtained with conventional aspiration and FI-AAS system with preconcentration of (a) Cr(III) and (b) Cr(VI). Aspirated sample volume, 100 ml; flow rate, 5 ml/min.[9]

In addition to the fast sorption and desorption properties of Cellex P toward Pb(II), it was found,[20] that ionic alkyllead compounds behave similarly to inorganic lead, for example, can be completely eluted by 1 *M* nitric acid, while the neutral tetraethyllead retains on the column. Elution first with nitric acid and then with ethanol obtains two signals corresponding to the sum of inorganic lead and di- and trialkylead and to tetraethyllead, respectively.

In most natural matrices free metal ions occur in only a small fraction of cases as simple, hydrated cations. Trace metals are mainly present in ion pairs or complex compounds with inorganic and organic ligands. In a series of recent studies[40-42] cellulose sorbents have been applied as discriminators for the lability/inertness of metal ions associated with humic substances. Applying cellulose sorbent Hyphan in batch procedure (96 h) the following reactivity order was obtain:[41] Mn. > Zn > Co > Pb > Ni > Cu > Al > Fe. In the column procedure with cellulose-immobilized triethylenetetra-amine-penta-acetic acid the lability order of Cd [a] Mn > Zn > Pb > Co > Ni > Cu was revealed.[42]

VI. CONCLUSION

Although the solid-phase extraction is commonly used for the preconcentration of trace elements in environmental analysis, the advantages of cellulose-based sorbents are not yet widely recognized. They can be synthesized with complexing groups incorporated into the cellulose structure or loaded with the ligands on the surface of cellulose beads. Fast kinetics of sorption and desorption, minimum swelling, chemical resistance, and wide availability make them very useful sorbent for trace analysis.

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