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Biosorbents in the Metallic Ions Determination

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Abstract

This chapter provides an overview and discusses analytical strategies for metallic ions determination using solid phase extraction. Solid phase extraction (SPE) is a much-used technique for extraction and/or concentration of complex samples, so that the analytes present in low concentration were detected mainly using chromatographic methods. However, in recent years, this technique has been widely used in the development of methodologies for metallic ions determination in the deferential samples. This technique shows simplicity and rapidity comparing with other conventional techniques, liquid-liquid extraction, cloud point extraction and others. Solid phase extraction procedures become even more interesting when commercial adsorbents are exchanged for others with higher adsorptive capacity, selectivity, flexibility, economy and low environmental impacts. For this purpose, some inorganic, organic and several natural adsorbents are used. New approaches to obtain adsorbent materials from natural sources such as fungi, bacteria, industrial residues and composting materials have received attention. These materials have been used in the development of analytical methods with varied proposals, such as preconcentration or speciation of metal ions.

Keywords: adsorbents, solid phase extraction, metallic ions

1. Introduction

Metallic ions are found in the most diverse types of samples in concentrations ranging from mg L^{-1} to those considered as trace. So, daily involuntary we contact various metallic ions,

whether in air, water, industrial products (cosmetics, makeups, remedies, deodorant, tinctures used in tattoos, etc.) and even in foods (fertilizer, packaging, pesticides, etc.).

These ions may be necessary for maintaining vital functions of organisms, since their absence can cause many diseases, as they can also be extremely toxic if ingested even at low concentrations. Mercury, cadmium, arsenic, chromium and lead, are among the metallic ions that most cause health problems [1].

Considering the toxicity or necessity of these species by the organisms, the development of analytical methodologies capable of determining and enabling their monitoring in different types of samples becomes primordial.

The atomic absorption spectrometry with flame atomization (FAAS) was utilized for many years as one of the most commonly techniques used for determining inorganic ions in the most diverse samples. However, it presents some difficulties related primarily to the detection limit and selectivity. These difficulties can be circumvented using extraction and preconcentration techniques, such as liquid–liquid extraction, co-precipitação, solid phase extraction (SPE) [2].

Solid-phase extraction (SPE) was introduced in 1976 to meet the disadvantages presented by liquid–liquid extraction and today is the most popular method of sample preparation [3]. This technique consists of the mass transfer of a liquid phase (sample) for a solid phase, called the adsorbent, and the bulk of the adsorbents used in these procedures are of synthetic origin. The main objectives of SPE are the removal of interference from the matrix, the concentration and the isolation of the analytes [3]. The state of the art of the SPE indicates that there is a tendency to develop miniaturized methods, based on flow-injection analysis systems (FIA), Sequential injection Analysis (SIA) and Lab-on-A-Valve (Lov) [4].

The adsorbents used in solid phase extraction, as ion exchangers were up to mid-1934, natural compounds called *lignitos*. After this period, several researchers were dedicated to the development of new ionic exchangers, such as polymerization resins. In the work presented by Reis and collaborators in 1996, approximately 90% of the research's involving extraction or preconcentration of metallic ions were performed using polymeric resins such as adsorbents [5].

Today, the number of scientific articles using commercial adsorbents in solid phase extraction systems continues around 90% [6]. In this sense, in the face of the ever-increasing search for methodologies that meet the principles of green chemistry, the study of alternative adsorbents in the SPE procedures, has been highlighted.

So, called alternative adsorbent materials have been applied successfully on metal adsorptive process. In its majority are considered materials of easy acquisition and in some cases, taken as by-products of industrial processes, such as sugarcane bagasse, onion skin, peanut shells, corn cobs and rice husks [7]. Therefore, the choice of an alternative adsorbing material is not only based on its adsorption capability, but also at its low cost, its ease of obtaining and abundance in nature. In this sense, this chapter makes a revision of the main absorbers used in the solid phase extraction techniques presented in recent years.

2. Adsorbents used in solid phase extraction systems

2.1. Lignocellulosic adsorbents

The lignocellulosic materials are copious renewable sources, and usually underutilized. The agribusiness, for example, generates numerous sources of biomass that are not adequately and/or properly harnessed, turning them into industrial waste [8]. Thus, the development of methods that use these wastes has been highlighted in recent years, with the lignocellulosic one of the most widely used adsorbent materials, because of its high adsorptive capacity for metallic ions and organic compounds.

The lignocellulosic biomass is the plant dry matter [9], and it is composed mainly of a mixture of lignin and holocellulose (total carbohydrate content in a plant). The typical chemical composition of the lignocellulosic materials is 48% carbon, 6% hydrogen and 45% oxygen. Proteins, organic acids and other not structuring materials are minority components [10]. In this way, it can be considered as lignocellulosic materials; rice straw, wheat straw, cotton stalk, rice hull, sugarcane bagasse, corncob, sawdust and others [9].

The ability of these materials to interact with metallic ions and organic compounds is not fully understood, however, it can be said that the adsorption capacity is related to the presence of functional groups such as hydroxyl, and amines. These functional groups are present in the pulp, hemicellulose and lignin structures. It is important to note that this process is not based on a single mechanism, the sequestration of the metal ion can occur through complex mechanisms, including ion exchange and complexation. It being probable that at least some of these mechanisms act simultaneously in varying degrees depending on the biomass and the metal ion [11].

Davis et al. [12] indicated that ion-exchange is an important concept in biosorption, because it explains many of the observations made during heavy metal uptake experiments. In this context, the term ion-exchange does not explicitly identify the mechanism of heavy metal binding to biomass, and electrostatic or London–van der Waals forces should be considered as the precise mechanism of chemical binding, i.e., ionic and covalent bonds.

Therefore, the lignocellulosic materials (due its composition, availability and low cost) are becoming widely explored in the development of new analytical methodologies for metallic ions determination in trace concentrations in various types of samples. It can be found several papers in the literature which discuss the use of lignocellulosic materials as natural adsorbents. **Table 1** shows the use of lignocellulosic adsorbents in the development of analytical methods.

The *Moringa oleifera* is one of the most widely used lignocellulosic adsorbents in the development of analytical methodologies. Native to northern India, it currently grows in many regions including Africa, Southeast Asia, the Pacific and Caribbean Islands and South America [18, 19]. Research focused on the use of *M. oleifera* seeds and fruits in water purification and

Material	Treatment	Sample	Analyte	L.O.D ($\mu\text{g L}^{-1}$)	Preconcentration factor	References
<i>Moringa oleifera</i> seeds	—	Beer	Pb	7.5	93	[13]
Rice husks	—	Water and Red Wine	Cd and Pb	1.14 and 14.1	72.4 and 46	[14]
Coffee	—	Water	Cu	0.22	—	[15]
Chinese herb Pang Da Hai	—	Water	Pb and Cd	0.0096 and 0.0032	—	[16]
Peel of <i>Citrus reticulata</i> (mandarin orange)	—	Alcoholic beverages	Ni	3.1	12	[17]

Table 1. Lignocellulosic adsorbents used in development of preconcentration and metal ion determination.

the treatment of turbid water is the best-known application [11]. It is considered a good natural adsorbent in the adsorption of trace metals; it can be used in the development of analytical methods.

The seeds were used in the determination of silver in water [20], inorganic arsenic in natural waters [21], cadmium and zinc in alcohol fuel [22, 23] and lead in beer samples [13]. Its husks were used in the selective extraction of chromium in water [24], in the copper determination in gasoline samples [25], in zinc determination in cachaça, and in the determination of lead in chicken feed [27].

For the determination of Ag(I) in aqueous solutions, Araújo and collaborators [20] describes the use of solid phase extraction on preconcentration system by flow injection, and detection by flame atomic absorption spectrometry (FAAS). In this system, 35 mg of *Moringa oleifera* seeds was used to build a mini-column. With the aim of finding the best conditions for the determination of silver, the preconcentration system of analysis by flow injection was optimized. Once the system was optimized, the analytical characteristics were estimated on preconcentration factor equals 35, detection limit of $0.22 \mu\text{g L}^{-1}$, quantification limit of $0.73 \mu\text{g L}^{-1}$, linear range between 5 and $20 \mu\text{g L}^{-1}$, and precision of 3.8% ($5 \mu\text{g L}^{-1}$, $n = 7$). Thus, showing an excellent repeatability. The method was employed in mineral and tap water samples, and the precision was assessed by the analysis of a certified reference material for water (APS-1071 NIST) and by recuperation tests which presented values between 94 and 101%. Consequently, the authors inferred that the method had satisfactory detection limits and precision.

In work developed by Alves and collaborators [22], it was made a methodology for on-line preconcentration and Cd(II) determination in alcohol fuel samples using *Moringa oleifera* seeds as bioadsorbent with detection by FAAS. The flow and chemical variables were optimized and the best values were found when using 10 mL of an enriched solution with $50 \mu\text{g g}^{-1}$ of Cd(II) on pH 9.1, 0.5 mol L^{-1} of HNO_3 as eluent, 200 mg of adsorbent to fill the mini column, sample flow rate of 6.0 mL min^{-1} and buffering solution concentration of 0.05 mol L^{-1} .

With the optimized parameters, the analytical characteristics were obtained with a detection limit of $5.50 \mu\text{g L}^{-1}$ and precision below 2.3% ($35.0 \mu\text{g L}^{-1}$, $n = 9$), linear range between 5 and $150 \mu\text{g L}^{-1}$. The developed method was successfully applied on alcohol fuel samples and the precision was evaluated through the recuperation test, which had a variation of 97.5–100%.

Carmo and collaborators [25] describe a similar methodology [22, 24, 26] for solid phase extraction using *Moringa oleifera* husks as natural adsorbent for direct Cu(II) determination in gasoline samples, with detection by FAAS. Pure gasoline is almost insoluble in water, whilst the ethanol is completely miscible in gasoline and in water in any concentration. This is the reason why the authors used ethanol to dilute the gasoline samples in the ratio of 50% (v/v); which eases the copper ion sorption process in the sample. In this context, the parameters that influenced the adsorption/desorption of Cu(II) by the *Moringa oleifera* husks in gasoline samples were evaluated using 15.0 mL of $10 \mu\text{g L}^{-1}$ Cu(II) solution. The best conditions were found on pH 4.0, 0.5 mol L^{-1} of HNO_3 as eluent, sample flow rate of 6.0 mL min^{-1} , and 96.0 mg of adsorbent mass. After finding the best values, the analytical characteristics of the method were analyzed. The results obtained were a preconcentration factor equals 14, detection limit of $0.75 \mu\text{g L}^{-1}$, linear range between 0.75 and $500 \mu\text{g L}^{-1}$, and precision of 1.86% ($50.0 \mu\text{g L}^{-1}$, $n = 9$).

Oliveira and collaborators [27] reported a similar system to that used by Araújo and collaborators [20] for the lead determination in chicken feed samples. Metallic ions such as, Cr, Cu, Fe, Zn, Ag, Ca, Pb and Mo can be found in chicken feed [28]. Once ingested, these ions can remain in the chicken meat and be transferred indirectly to the people. Several analytical techniques can be used for determining metallic ions, however the complexity of the matrix can bring some difficulties. Thus, in this chapter, the authors applied a system of extraction/preconcentration for lead determination in chicken feed using *Moringa oleifera* husks as bioadsorbent where the detection was performed using FAAS. The off-line preconcentration system was optimized, and the best conditions were obtained on pH 9, 30 mg of adsorbent mass, $100 \mu\text{L}$ of HNO_3 0.5 mol L^{-1} as eluent, elution and preconcentration flow rate of 2.0 mL min^{-1} . The analytical performance for developed method was evaluated through the application of the optimized system. As a result, it was found a detection limit of $1.66 \mu\text{L}^{-1}$, linear range between 5.0 and $1000 \mu\text{g L}^{-1}$, and precision of 1.63%. It was found a preconcentration factor of 550 with a consume rate of 0.02 mL.

In addition to the determination of metallic ions at a trace level, the bioadsorbents have been successfully employed in the development of methods used for speciation analysis. Speciation analysis is particularly tough, due the high complexity of the matrix and the low concentration of these elements. Some matrices require a high dilution factor to minimize interference, which leads to an increased limit of detection (LOD) of the technique [29]. Alves and collaborators [21] developed a selective extraction method for inorganic arsenic in natural waters. *Moringa oleifera* seeds were used as a biosorbent for the solid phase extraction and detected by graphite furnace atomic absorption spectroscopy (GFAAS). The As(III) and As(V) species behavior was evaluated in a broad pH band. Its results showed that the As(III) had a better adsorption on pH 7, whereas the As(V) had lower adsorption values (being mainly free in solution), which allowed it to be determined directly by GFAAS. With the

aim of having an effective adsorption of As(III), the method was optimized. It was then registered that 1.0 g of adsorbent was sufficient to keep it in an agitation time of 1 hour. The limit detection for As(V) was $6.3 \mu\text{g L}^{-1}$ and its precision was below 1.23%. The recuperation results (92%) were done by the use of four different water samples, which were mixed with the determined concentration of As(III) and As(V). The precision was proven by employing the Drinking Water Standard Solution (APS 1071). As a result, the authors able to conclude that the determination method is an efficient and attractive option for the determination of inorganic arsenic in water samples.

In the study developed by Alves and Coelho [24], analytical methodology applied for selective extraction of inorganic chromium in water, using a system of analysis by flow injection like the used by the previous group [23] was evaluated. For the selective extraction and the chromium species preconcentration, the *Moringa oleifera* husks were used as biosorbent and the detection was made through the FAAS technique. The *Moringa oleifera* husks showed itself efficient in the separation of the Cr(III) and Cr(VI) species. The trivalent specie is adsorbed in the pH range between 7 and 9, whereas the Cr(VI) is adsorbed in the pH band between 1 and 2. The methodology was then optimized, it evaluated the necessary parameters for the attainment of an effective Cr(III) extraction; the optimal values were found on a 7 pH, 58.0 mg of adsorbent mass, 0.01 mol L^{-1} of HCl as eluent, and sample flow rate of 4.5 mL min^{-1} . The same conditions were applied for the determination of Cr(VI), however the pH band of the solution was between 1 and 2. For this method, the detection limits found for Cr(III) and Cr(VI) were 1.92 and 2.45 mg L^{-1} , and precision of 1.63 and 0.08%, respectively [24]. The use of lignocellulosic adsorbent presented several advantages, among them was the reduced cost analysis, since the material presents stability to 100 preconcentration/elution cycles.

In similar work, Sousa Neto [30] used *Luffa cylindrica* fibers for inorganic chromium separation. The material is positively charged surface in solutions with pH below 6.0 while above this value, the surface is negatively charged. From this evidence, a study was performed to evaluate the effect of pH on the chromium inorganic species adsorption and found that at pH 4.0 it is possible to separate the chromium species (III and VI) (**Figure 1**). The analytical performance was evaluated by the parameters, detection limit (LOD), quantification limit (LOQ), accuracy (D.P.R) and the values were 19.2; $63.99 \mu\text{g L}^{-1}$ and 0.19%, respectively, with the linear range of the method equal to $63.90\text{--}2000 \mu\text{g L}^{-1}$. Finally, the accuracy of the method was evaluated from analysis of water certificate reference material (APS-1071) and sediment (APS-1066). Recovery tests were performed on samples of water, energy and isotonic values have been found in the range from 87.60.

Ribeiro et al. [17] used the Mandarin peel (*Citrus reticulata*) as natural adsorbent to develop the analytical methodology using solid phase extraction for the direct determination of nickel in alcoholic beverages (whiskes and cachaça). In this work, it was used the online flow injection analysis system like that one previously mentioned in other works with detection by FAAS [17]. It was used 10 mL of a Ni(II) $30.0 \mu\text{g L}^{-1}$ solution, and the best conditions were found on 50 mg of adsorbent mass, pH 6, sample flow rate of 4.3 mL min^{-1} , and HCl 1.0 mol L^{-1} with flow rate of 2.0 mL min^{-1} as eluent. Consequently, the analytical characteristics of the methodology were linear range between 10 and 75 mg L^{-1} , detection limit of $3.1 \mu\text{g L}^{-1}$, preconcentration factor equals 12, and standard deviation of 0.9%.

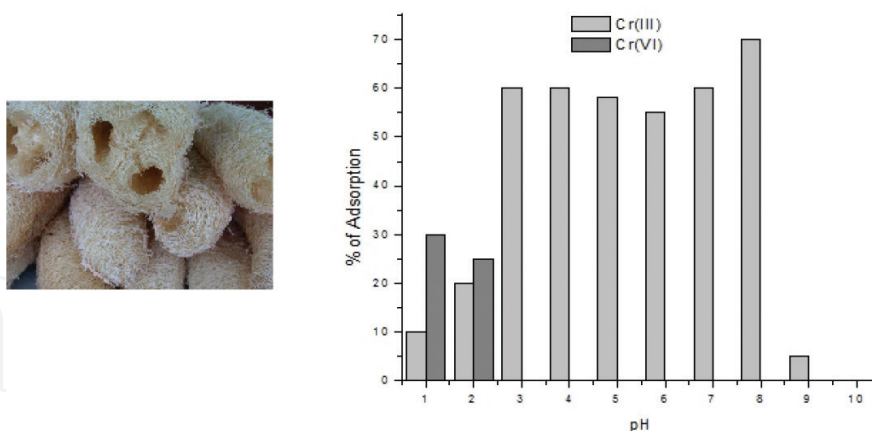


Figure 1. Inorganic chromium adsorption on *Luffa cylindrica* fibers.

Liu and collaborators [16] assessed the Chinese herb Pang Da Hai (PDH) wastes, *Sterculia lychnophora* hance seeds was used as natural adsorbent in the development of an analytical method for the determination of lead and cadmium in solid waste samples, with detection by FAAS. The parameters that influenced in the preconcentration method development were studied, and the best condition for both analyzed ions was 0.1 mol L⁻¹ of NHO₃ as eluent and pH 6.5. The adsorption capacities of PDH for Pb(II) and Cd(II) were 27.1 and 17.5 mg g⁻¹, respectively. The standard deviation related to the developed method was 10% for both metals; it was used a solution in the concentration of 100 µg L⁻¹ and 20 mg of adsorbent. The method was validated by the analysis with the certified standard (GBW 08301), and the values found in the analyzed samples comply with the values stipulated by the reference material; they have a relative error between 2.5 and 11%. The detection limits for both Pb and Cd were 0,096 and 0.032 µg L⁻¹, respectively. The method was applied in real samples of tap and river water, and the recuperation results were satisfactory for all analyzed samples.

2.2. Mineral adsorbents and humic acid

The minerals are inorganic compounds formed naturally and in general have an established chemical structure, responsible by the physical properties. Although they are produced by nature, these minerals can be synthesized in the laboratory by ensuring a higher purity and uniformity of crystalline structure. These natural resources are of great value for industrial production, and are used as raw material in different areas such as in the production of household appliances, electrical wires, jewelry, construction materials, in addition to serving as a source of energy.

Due to its chemical–physical characteristics, minerals are either natural or synthetic, have properties of ionic exchangers, which allow their use successfully in the adsorption of metallic ions and organic compounds. Among the minerals most commonly used adsorption processes are the montmorillonites, the vermiculitas, zeolites, carbon nanotubes and same oxides, such as graphene oxides, iron oxides, and titanium oxides [31–33]. Typically, the application of these minerals is in adsorption processes for environmental remediation, particularly for treatment and recovery of waters where heavy metals and other pollutants as much as organic inorganic compounds can be removed.

In the development of analytical methodologies for the determination and pre-concentration of metallic ions, few studies have been developed. However, in recent times these materials have gained a lot of attention for being a low-cost alternative and easy access since they may be found in nature in abundance and synthesized simply.

Synthetic zeolites, for example, have been used as adsorbent material on copper ions determination and preconcentration through the formation of a chelate of copper in minicolumns of synthetic zeolite lynde type (Na-LTA) and faujasite Type X (Na-Fau). To evaluate the performance of these materials, a flow injection system was used for water samples from different sources. The preconcentration factors ranged from 35 to 125 for the LTA and 30–65 to Na-Fau. The accuracy was evaluated by recovery experiments and analysis of certified reference materials. The limits of detection, the standard deviation and relative linear calibration charts were 0.1 ng mL^{-1} , 2.6% and $2.5\text{--}30 \text{ ng mL}^{-1}$ to Na-LTA and 0.4 ng mL^{-1} , 2.8% and $2.5\text{--}40 \text{ ng mL}^{-1}$ for In-Fau respectively. The results indicate that the zeolites are promising materials for application in copper extraction preconcentration in trace levels with detection by flame atomic absorption spectrometry (FAAS) [34].

The adsorption capacity of natural zeolites was evaluated through the development of an analytical methodology for cobalt ions determination in natural waters through the formation of a neutral chelate with pyrrolidine acid ammonium diocarbamate (APDC). The neutral chelate formed was retained in a column packed with natural zeolites and then eluted with isomethyl-butyl ketone (MIBK) and detected by flame atomic absorption spectrometry (FAAS). The detection limit and the relative standard deviation (%RSD) was $1.9\text{--}2.3 \text{ }\mu\text{g L}^{-1}$ and 2.3–4.5%, respectively. The sampling frequency of 27 h^{-1} and preconcentration factor of 130–160 have been achieved, to a 6 mL sample volume, indicating a high analyte retention on natural zeolites [33].

The use of these adsorbents increases more and more, because efficient synthesis procedures, purification and characterization ensures the availability of pure materials and well characterized. Soylak and Unsal [35], have developed a separation and preconcentration procedure based on solid phase extraction for Fe(III) and Cr(III) ions, using single-walled carbon nanotubes (SWCNTs). The ions were recovered quantitatively analyzed at pH 8.0 using 30 mg of carbon nanotube. The detection limits were 2.12 and $4.08 \text{ }\mu\text{g L}^{-1}$, for iron and chromium, respectively. The method was validated by analyzing of water and food samples certificates.

For chromium speciation Tuzen and Soylak [36] used carbon nanotubes (MWNTs) multilayer in a solid phase extraction procedure and the formation of a chelate by using of ammonium pyrrolidine dithiocarbamate (APDC). The procedure had some validated analytical parameters including pH, solvent type and effects of array. The detection limit was 0.90 g L^{-1} for Cr(VI). The adsorption capacity of the multilayer carbon nanotube was 9.50 mg g^{-1} Cr(VI). The presented method was applied to the speciation of chromium in natural water showing a 95% recovery factor indicating that the proposed methodology using multilayer carbon nanotubes is more efficient in terms of selectivity, detection limit and preconcentration factor when compared to other methods of preconcentration of chrome described in the literature.

Iron oxides are found in nature in the hematite form ($\alpha\text{Fe}_2\text{O}_3$), goethite (αFeOOH) and magnetite (Fe_3O_4). In recent times, the processes involving adsorption using these oxides as adsorbent materials have attracted great interest, mainly due to the high adsorptive capacity and magnetic property of these materials. These solids can be used in preconcentration methods,

magnetic separation and molecular identification of biomolecules. Separation techniques using magnetic solids also offer some advantages over centrifugation, filtration and solid phase extraction once these steps are simplified [37]. Parham and Rahbar [38], used magnetic iron oxide nanoparticles (MIONs) as adsorbent to develop a methodology for extracting and determination of fluoride ion in water samples. The method is based on the discoloration of the Fe(III)-SCN formed with fluoride ions extracted and sequentially, monitoring by spectrophotometry at $\lambda_{\text{max}} = 458 \text{ nm}$. The detection and quantification limit were 0.042 and $0.015 \mu\text{g mL}^{-1}$, respectively. In this method the preconcentration factor achieved was 50 and the method was applied to the determination of fluoride in water samples and concentration values obtained were compared with the default values that are presenting SPADNS according to the method of the comparison. The no use of toxic compounds, the short procedure (about 8 min per sample) and a low LD are the main advantages of the proposed method.

Metal oxides such as iron oxide cited previously, zirconia oxide and titanium oxide obtained in the nanoscale have become important for various lines of research due to its special properties such as high chemical activity and mainly the good capacity to adsorb a wide variety of metallic ions. In addition, the particle size is another factor that contributes to the use of those materials in adsorption processes, because fine particles and nanoscale enable high adsorption speeds when compared the classic adsorbents [39].

Most of the nano adsorbents are used with their surfaces modified by complexing agents or microorganisms to increase the capacity to adsorb analytes. However, this modification limits the repeated use of adsorbent in adsorption processes. There are synthesized materials in the form of mixed oxides that enable their use without requiring any modification by another reagent. The nano compound of boron trioxide and titanium dioxide ($\text{B}_2\text{O}_3/\text{TiO}_2$) is an example of these mixed oxides. Kalfa and contributors [40] developed a methodology for cadmium separation and preconcentration in tap water and tea samples using this nano compound. Under the best experimental conditions, preconcentration factor and the detection limit were determined being 50 and $1.44 \mu\text{g L}^{-1}$, respectively. The precision of the method was confirmed by analysis of certified reference materials (tea leaves GBW-07605). The results showed good agreement with the certified values ($< 10\%$) relative error. Cadmium recovery in optimum conditions was $96 \pm 3\%$ at a 95% confidence level. The use of solid phase extraction enables the development of a simple method, selective, precise, fast and economical for preconcentration and determination of cadmium.

Some hybrid materials based on silica (SiO_2) have been synthesized by mixed metal oxides form as the titanium dioxide (TiO_2) and used to preconcentrate a large quantity of metallic ions the trace level. Lima and contributors [41] describe the analytical performance of a hybrid composite material of SiO_2 , Al_2O_3 and TiO_2 . The material was prepared by a sol-gel process to act as adsorbent in copper preconcentration system. The retention capacity was 1.4 mg g^{-1} in dynamic conditions. The detection and quantification limits were of 0.50 and $1.4 \mu\text{g L}^{-1}$, respectively, and the calibration curve is linear in the range of 5.0–245.0 $\mu\text{g L}^{-1}$ ($r = -0.999$). The relative standard deviation is 3.20 (for $n = 7$ to a concentration of Cu(II) of $10 \mu\text{g L}^{-1}$). The method was applied to the determination of copper ions in water, vegetables and alcohol fuel using flame atomic absorption spectrometry (FAAS).

Among the wide variety of materials that can be used as adsorbents, humic acid, although little reported in the literature has a good application in the area of analytical chemistry. Humic substances are natural materials and called major components from the decomposition of organic matter. This decomposition is subdivided into three parts: humic acid, fulvic acid and humina [42]. These substances have a high capacity of cationic exchange for different species due to the presence of carbonyl groups, phenolic hydroxyl, and alcohols in their structure as well, metals to interact with the humic substances, are retained by active sites of adsorption.

Pereira & Arruda [43] used vermicompost, humic substances produced from the metabolism of organic residues in the soil by earthworms, and humic acid commercial for Cd(II) and Pb(II) preconcentration using flow systems coupled to the flame atomic absorption spectrometry (FAAS). The Cd(II) ion was preconcentrated for 4 minutes (flow rate of 4.0 mL min⁻¹) and eluted with 220 mL of nitric acid 3.0 mol L⁻¹. Under these conditions, the preconcentration factor obtained was 46 and 27 to vermicompost and humic acid, respectively. Except when used nitric acid 1.0 mol L⁻¹ (for humic acid), all conditions of Pb(II) preconcentration were identical to those of Cd(II), and the preconcentration factors obtained were 62 and 83 to vermicompost and humic acid, respectively. This method was applied in mineral and tap water samples.

Bianchin and collaborators [44], evaluated the Cd(II) determination using vermicompost in a solid phase extraction methodology with a system of flow injection analysis and was detected by flame atomic absorption spectrometry. Optimal extraction conditions were obtained using the sample pH in the range of 7.3–8.3, buffered with tris (hydroxymethyl) aminomethane the 50 mmol L⁻¹, a sample flow rate of 4 mL min⁻¹, and 160 mg of adsorbent mass. With the optimized conditions, the preconcentration factor, the detection limit and the analytical frequency were estimated as 32; 1.7 µg L⁻¹ and 20 samples per hour respectively. The analytic curve was linear to 5 at least 50 gL⁻¹, with correlation coefficient of 0.998 and a relative standard deviation of 2.4% (35 µg L⁻¹, n = 7). The method was applied in ethanol fuel samples and the accuracy was assessed by testing of recovery, with a 94% recovery varying from 100% indicating that the worm compost is an efficient and stable material on cadmium preconcentration in complex samples.

2.3. Fungi and bacteria

The process that employs biological materials as microbial biomass for the accumulation of organic and inorganic substances from diluted solutions is the biosorption. Initially research on biosorption described the use of biological materials for the metal removal [45]. However, today, algae, fungi, bacteria and yeast are considered an important part of the natural adsorbents used in the development of analytical methodologies.

Depending on the metabolic activity, the bioadsorbents can be divided into two classes: the one where there is only a rapid interaction of the metallic species with the surface of the material and the one where the metallic species initially exert a rapid superficial interaction with the bioadsorbent alive. Subsequently, a slower and more complex process is established, initiated by the connection of the metallic species with the cellular membrane, followed by the transport through this and, finally, resulting in intracellular reactions such as methylation, reduction and oxidation [46].

Industrial processes for the production of antibiotics, enzymes and fermentation processes in general generate a large amount of biological material as by-products that are normally discarded and can be used in the adsorption process [47].

The microbial biomass has in their cell walls several chemical groups: polysaccharides, proteins or lipids that link by means of the functional groups (hydroxyl, sulfhydryl, carboxyl, amine and phosphate), and is responsible for attracting and retaining your metals biomass, therefore they possess mechanisms responsible for biosorption, and can be one or a combination of this, such as ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation [48].

Several micro-organisms have been studied in determination of metal ions. Fungi are micro-organisms considered to be good bioadsorbents, since they are easily reproduced by producing a high amount of biomass, besides being microorganisms capable of adapting in extreme environments [48].

Mendil et al. [49] developed a preconcentration system using *Penicillium italicum* to determine Cd(II), Mn(II), Pb(II), Fe(II), Ni(II) and Co(II) in trace levels. The adsorption occurs in pH range 8.5–9.5. After optimizing the method, the detection limit was 0.41 and 1.60 $\mu\text{g L}^{-1}$, for cadmium and iron, respectively. The method was successfully applied for the determinations of analytes in natural water, cultivated mushroom, lichen (*Bryum capillare Hedw*), moss (*Homalothecium sericeum*) and refined table salt samples. The proposed method is safe, fast and handy.

The fungus *Penicillium* was used by Baytak and collaborators [50] to determine copper, zinc and lead in the dam water, waste water, spring water, parsley and carrots. The fungi were immobilized in pumice stone, and the ideal conditions for adsorption, such as solid phase mass, pH, solution flow rate and elution solution was studied. The analyte was determined by flame atomic absorption spectrometry (FAAS). The preconcentration factor obtained was 50 and the detection limits of detection were 1.8; 1.3 and 5.8 for copper, zinc and lead, respectively. Already the accuracy of the method was evaluated in samples of tea standard reference (GBW-07605).

To determine arsenic in drinking water samples, Shahlaei and collaborators [51] used dead fungal biomass (*Aspergillus niger*) in a solid phase extraction (SPE) system. We evaluated the effects of parameters such as time of biosorption, sample volume, pH, type and concentration of the eluent and effect of interfering ions. The recovery was evaluated by precision between 99 and 102%. The detection limit found for the method was of 1 mg mL^{-1} .

Alpodogan and collaborators [52] also used dead fungal biomass from *Aspergillus niger* loaded into TiO_2 nanoparticles for copper, nickel, cadmium, manganese, and chromium preconcentration in milk samples, with determination by flame atomic absorption spectrometry (FAAS). The preconcentration factor was 600, detection limits for copper, nickel, cadmium, manganese, chromium and lead were 0.21; 0.34; 0.18; 0.08; 0.53; 0.61 g L^{-1} , respectively.

Among the fungi, yeasts are the most exploited scientifically, due to the fact that eukaryotic organisms are easier to manipulate, serving as an excellent model for studies. Ohta and collaborators [53] evaluated a preconcentration method for copper determination in trace level in river water, using yeast *Saccharomyces cerevisiae*.

Another microorganism fairly used in the metallic ions adsorption is the bacteria. Bacteria have adsorptive capacity due to the presence of nitrogen (N) and oxygen (O) ligands in their cell walls, where mechanism of micro precipitation between metal and bacteria, in addition to presenting also an electrostatic attraction and exchange by ion groups in your cell wall [54]. Pagnanelli and collaborators [55] analyze the adsorption capacity of biomass of *Sphaerotilus natans* for lead, copper, zinc and cadmium in aqueous solutions. The bio-sorption was tested in different pHs, experimental results showed the positive effect of the increase of pH on the uptake of metals analyzed, showing that biomass had significant capacity to adsorb the ions studied.

2.4. Functionalized biosorbent

The functionalization of supporting materials with bio-organic species of sorption capacity for metallic ions has attracted extensive attention in the field of analytical chemistry. The purpose of this procedure is to improve the preconcentration of metallic ions commonly found in food, vegetables, drinking water and/or river samples at concentrations considered trace and ultra-trace.

This functionalization can be accomplished by structural modifications of biomass surfaces or by immobilization of bio-organic species on the surfaces of biosynthetic, inorganic, polymeric materials and biomass itself. In addition, the surfaces of these bio-organic compounds can be treated with acid and base solutions or organic and inorganic solvents which in many cases increase the adsorption, selectivity and recovery capacity of those metals ions. In this context, several bio-organic systems functionalized and/or immobilized on solid supports will be discussed that are used in the processes of adsorption of metal ions [56].

Yang and contributors [57] described in their article that various efforts have been made to generate selectivity and adsorbent capacity through chemical modification and genetic engineering, due to the low selectivity of biological cells towards certain metal species and a low capacity for anionic metal species in neutral pH. In this section, we will describe some methods that have been used with great success in metal ion analyzers after functionalization or immobilization of the biological cells and other biosorbents on a support material.

The main biological organisms used as functionalizing agent on supporting material in analytical chemistry for trace metal determination are shown in **Table 2**. They offer several advantages, such as ease in immobilization on the surface of supporting material, their biodegradability, natural abundance, low cost, and simple production.

Bathocuproine (BCP) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline is well-known reagent that respond selectively to Cu by forming a colored 2:1 complex with copper. It was successfully used to determine the Pb(II), Fe(III), Co(II), Cr(III) and Zn(II) in water and food samples after preconcentration [59]. Teodoro and collaborators [60] in their study, functionalized bamboo fiber with bathocuproine for determination of copper in foods using FAAS. Copper preconcentration was performed in an off-line system consisting of a glass column containing bamboo fiber functionalized with bathocuproine and peristaltic pump. This method made it possible to separate, preconcentrate and determine the copper ion in wine, cassava flour, corn flour, oregano and coriander with concentrations much lower than mg L^{-1} , that is, in the $\mu\text{g L}^{-1}$ for liquid samples and $\mu\text{g g}^{-1}$ for solid samples.

Biological organisms	Types
Bacteria	Bacillus sp., Streptococcus sp., Streptomyces sp., Escherichia sp., Enterobacter sp., Klebsiella sp.
Fungi	Filamentous fungi (<i>Aspergillus niger</i> , <i>Alternaria</i> sp., <i>Rhizopus oryzae</i>), unicellular yeasts (<i>Saccharomyces</i> sp., <i>Yamadazyma</i> sp.), <i>Pleurotus</i> sp., <i>Helvella</i> sp., <i>Coriolus</i> sp., <i>Agaricus</i> sp.,
Plant-derivatives	<i>Musa paradisiaca</i> , <i>Citrus reticulata</i> , <i>Glycine max</i> , <i>Zea mays</i> , <i>Sorghum bicolor</i> , <i>Agave sisalana perrine</i> , <i>Bambusa vulgaris</i>
Other biological organisms	Algae (<i>Chlorella</i> sp.), resting eggs, sea sponge, eggs shell membrane

Source: Adapted from Escudero and collaborators [58].

Table 2. Types of biological organisms used as functionalizing agent on surface of supporting material.

In the study developed by Baytak and collaborators [61] the fungus *Rhizopus oryzae* functionalized on the almond bark (natural cellulose) was used to preconcentrate and determine the Cu(II), Fe(III), Mn(II) and Zn(II) in water, fish and vegetable tissues samples. The glass column (150 mm × 8.0 mm i.d) containing the *Rhizopus oryzae*-loaded almond shells was used during the preconcentration of the analytes. Analyte detection was based on high resolution continuous source atomic absorption spectrometry. According to the author, the proposed method presented several advantages, such as precision, accuracy, preconcentration factor, reuse, environmental friendly material and did not require chelating or complexing agents during ion analyzes.

Boas and collaborators [62] used macadamia nuts waste to investigate the adsorption of copper ions. They proved that by chemical modifications of the residues of macadamia nuts was treated by NaOH solution and citric acid, and other residues treated by NaOH solution showed a better adsorption of Cu²⁺ ions compared to “in natura” residues. The adsorption process consisted of the addition of 0.5 g of the “in natura” and modified residues in a solution of Cu²⁺ ions at 100 mg L⁻¹ at optimized pHs and after 24 hours the supernatants were analyzed with flame atomic absorption spectrophotometer (FAAS).

Studies have shown that sisal fiber, obtained from the plant *Agave sisalana perrine* of Mexican origin, can be used for preconcentration of metals. In a recent study by Dias and collaborators [63] first used the sisal fiber functionalized with 3-aminomethylalizarin-N,N-diacetic acid or Alizarine Fluorine Blue (complexing reagent) to preconcentrate and determine the copper ion in tobacco leaves. According to these results, the concentration of copper in tobacco leaves was very low.

According to Chen and collaborators [64], the eggshell contains on its surface carboxylic groups that reduce the adsorption of arsenic ions on the surface of the shell. They performed a chemical modification of the eggshell by methyl esterification to improve the bioadsorption efficiency of the arsenic ion and verified a high selectivity for these ions.

When using the key words sorghum and bioadsorption, in search engines of different journals, we can find several researches where sorghum is used as adsorbent material to preconcentrate, determine and remove heavy metals present in natura. A recent work has used the sorghum agricultural residue in natura and chemically modified with phosphoric acid to determine the cadmium, copper, manganese and lead ions in samples of

black tea and river water using flame atomic absorption spectrometry (FAAS) as detection device [65]. In this work, the authors verified that the agricultural waste of chemically modified sorghum obtained an adsorption capacity 4.5 times greater when compared to the in natura waste. After this observation, they used the modified residue as solid phase for preconcentration and determination of the Cd, Cu, Mn and Pb ions present in tea and river water samples. According to their results, the chemically modified sorghum presented great potential in the separation and preconcentration of the metallic ions in real samples.

Passive sampler disks based on diffusion in thin films by concentration gradient were prepared with *Saccharomyces cerevisiae* yeast functionalized in agarose gel (polysaccharide extracted from red seaweed) to preconcentrate and determine Cd(II) with ICP-OES [66]. These disks were prepared with different proportions of gel and yeast that aimed at an optimized composition for the determination of the Cd(II) ion in river and sea water. In the study the yeast *Saccharomyces cerevisiae* was chosen due to previous works that found an excellent ability to separate and preconcentrate metal ions.

3. Conclusion

Considering the constant presence of metallic ions in people's daily lives, it is extremely necessary to develop methods capable of determining these, even at low concentrations. In recent years there has been increasing interest in developing methods that seek to comply with the terms of chemical "green", these methods involve the use of materials leading to a more clean, healthy and sustainable environment.

The development of methods that use alternative adsorbents has been highlighted in recent years, because of its high adsorptive capacity for metallic ions and organic compounds. In this sense, the study and development of new materials with low cost and the possibility of reuse has been an interesting area in analytical chemistry.

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Conflict of interest

The authors declare there is no conflict of interest.

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