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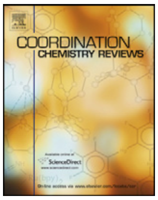

Review

Chemical equilibria in wastewaters during toxic metal ion removal by agricultural biomass

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ABSTRACT

After an overview of environmental pollution and the environmental threat posed by metals, this paper focuses on a literature survey of the different analytical methodologies and techniques used to investigate the functional groups involved in metal sorption onto biomass derived from agricultural waste. The recent literature has mainly focused on identifying the binding groups on the biomass surface through the use of different analytical techniques, from the traditional potentiometry to the most innovative and sophisticated solid surface analysis. In most of the biosorption studies, carboxylic group is the main origin for metal uptake, followed by hydroxyl group, aromatic ring and amine. The extent of the use of spectroscopic methods compared to traditional chemical analysis is being questioned. We stress that the study of biosorption mechanisms requires a multidisciplinary approach, and the efforts of analytical chemists and solution equilibrium experts really do contribute to the knowledge and to the optimization of these processes. This is the context in which we present a speciation study of the binding of various toxic metal ions by some coordinating groups on the biomass surface, which allows the classification of sorption mechanisms as a function of the pH dependence of the binding phenomena.

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1. Introduction

In a previous review [1], we took into consideration the literature on the sorption of some trace metals from agricultural by-products. In particular we laid the basis for rationalizing the adsorption mechanisms based on the coordination of the heavy metals by the functional groups on the biomass surface. In the present paper we would like to discuss this issue from a wide perspective. For this purpose, we reviewed the experimental analytical techniques used to identify the functional groups involved in the sorption mechanisms, and conducted a speciation study of the individual contribution of each group by using molecules representing the major groups involved in metal sorption and the complex formation equilibrium constants from the literature. Some other complementary aspects are also considered, such as the characteristics of the metal involved, and the geographical distribution of the potential toxic metal pollution sources in the world. Sharing the World Health Organization (WHO) political belief that all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water, we intend to build a panoramic view of whether, where and how water is polluted.

The release of acid drainage from mine-waste disposal areas, for example, is a problem of international scale: contaminated surface water from mine waste originates both as direct surface run off and, indirectly, as subsurface groundwater flow [2,3]. We also consider the potential of biomass for acting as metal ion scavengers, evaluating the application of non-living biomass, mainly those from agricultural waste, for the treatment of polluted waters. Traditional methods used for the removal of heavy metals[1] from the environment are costly and can generate potentially hazardous by-products; moreover, most of them result in solid waste that is difficult to treat or must be disposed of. Most of them are also not efficient enough as metal removers, and low concentrations of metal ions remain in the water after treatment. Ion exchange resins and activated carbon are effective in the removal of these low concentrations of metals, nevertheless, these methodologies are very costly and the reagents cannot be regenerated.

The need for a cleaner world, more enjoyable for both ourselves and the following generations, has led to the development of strategies based on the “cleaner production” concept, which refers to the continuous application of integrated preventive environmental processes in order to increase efficiency and to reduce both the quantity and the toxicity of emissions and waste [5]. Biosorption is treated as another emerging technology, which is effective in removing even very low levels of heavy metals. Biosorption of heavy metals by biomass occurs as a result of physicochemical interactions, mainly ion exchange or complex formation between metal ions and the functional groups present on the cell surface. The cell surface may contain various functional groups, such as phosphate, carboxyl, amine, amide, hydroxyl, mercapto, that are able to bind metal ions. The use of dead biomass, since sorption mechanisms are non-metabolic dependent, can eliminate problems connected with biosorption performance of live biomass, which depends on nutrient, cell age and toxicity tolerance of microorganisms [6]. In addition, the use of dead biomass is easy: they can be stored, easily regenerated and re-used [7,8]. Before their disposal metal-laden biomass can be eluted from the biosorbent by an appropriate solution to give a small, concentrated volume of metal-containing solution. Such recovery of metals must be non-destructive, so that the regenerated biomass can be re-used in multiple sorption–desorption cycles [9]. An alternative to elution is ashing of the metal-laden biosorbent. The combustion of the biomass would produce an ash with a high metal concentration, as well as providing a method of the disposal of spent biomass, after optimum cycling of the biomass has been achieved. This generally applies to biosorbents which consist of raw biomass supplied either as a waste material from industrial operations or as naturally abundant renewable material which can be cheaply harvested. A part from elution and ashing, disposal of the metal-laden biomass can be achieved by vitrification or encapsulation in concrete.

During the last decade different types of biomass have been investigated for their potential use as sorbents of metal ions. The main goal of the researchers has been to determine the most important parameters influencing metal sorption and the optimal conditions at which sorption capacity is maximum. Moreover, the mechanism by which a sorbent binds metal ions has received increased attention in the last years, as the advantages linked to better understanding of these mechanisms have become more apparent [10]. The knowledge of the mechanism is the main key that allows to modify the operational conditions under which the sorbent and the sorbate can interact in the most effective way, resulting in a more efficient performance of the biosorption process.

The mechanism of metal biosorption is difficult to elucidate, as it is the result of the particular type of biomass (fungi, vegetable, algae, etc), combined with the status of biomass (live or dead), the metal solution chemistry, and the physicochemical parameters (pH, ionic strength, temperature, etc). Biosorption may be based on one or more of the following mechanisms: ion exchange, physical adsorption, complexation and precipitation. In most cases more than one of these mechanisms can simultaneously happen, and the single steps may be hardly characterized and distinguished [11]. The structural components of biological material contain various functional groups which can interact with metal ions, though their role in metal binding is still not fully understood [12,13]. Sud et al. recently reviewed the scattered information available on various aspects of utilization of the agricultural waste materials for heavy metal removal [14]. The terms ‘absorption’ and ‘adsorption’ are often confused in the literature, and very few studies differentiate between these two mechanisms. Sorption is a general term used for both absorption and adsorption. In his review Gadd defines biosorption as the removal of substances from solution by biological material [15]. The huge variety of biological material which is defined as biomass can further contribute to the confusion, as there is no precise demarcation line between sorption and biosorption mechanisms operated by living organisms (biosorbent) [16]. On the other hand, biomass derived from plants or from some other by-product, acting in a non-metabolic way, can be surely classified as sorbents (sorption). After an overview of environmental pollution and the environmental threat posed by metals, this paper will focus on the different methodologies used to investigate the functional groups involved in metal sorption. As a conclusive step, a speciation study on the binding of various heavy metals by some coordinating groups is presented. These studies give evidence to the fact that the sorption mechanisms can be classified as a function of the pH dependence of the binding phenomena.

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[1] According to Järup [4] there is no clear definition of “heavy metal”, density is in most cases used as the defining factor. Heavy metals are thus commonly defined as those having a specific density of more than 5 g/cm^3. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic (arsenic is a metalloid, but is usually classified as a heavy metal). When publishing our review [1] one of the referees criticized us for using the expression “heavy metals” to indicate the toxic polluting elements, but we chose to retain it, even though it is not the correct chemical term, because it is employed widely in the reviewed environmental literature, and we were happy to conform with the near-universally adopted expression. The use of “light metals” for alkaline and alkaline-earth metals in environmental literature in opposition to “heavy metals” has to be remarked upon. This term should be cautiously employed given that it includes metals as Al, Ti, etc. in material sciences.

2. An overview of environmental pollution

An impressive number of researchers all over the world are interested in chemical pollution, in chemical processes, and in analytical determination of trace elements, but our first impression is that very few chemists feature among them, the majority being process engineers, biochemists, ecologists, agricultural researchers. The mastery of issues such as solution equilibria, complex formation, influence of pH and ionic strength, speciation, hard and soft characteristics of metal ions and coordinating groups is fundamental to the understanding of the sorption mechanisms and to guide the optimal choice of sorbents and operative conditions. The need for environmental sciences to be faced with a multidisciplinary approach needs to be remarked here [15], a one-sided vision does not allow the problem to be framed in full, and provides only limited solutions. We found in the literature a huge number of papers on industrial effluents, eco-toxicity of heavy metals in plant wastewaters, removal techniques and so on. Most of these studies deal with a specific river, a specific plant and some other specificity [17–21]. Only few authors widen their observations: Zamil et al. [22] in their paper offer a panoramic view "*Environmental pollution by toxic metals occurs globally through military, industrial (especially fuel and power), agricultural processes and waste disposal that generates 5.15 million tons of As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn in total per annum all around the world*. . .*.. Near Onsan bay, Korea dissolved metal concentrations in surface seawater were 1.15 mg/l for Cd, 2.49 mg/l for Pb, 3.75 mg/l for Cu and 23.98 mg/l for Zn which were 1–2 order higher than outer regions of the Bay. In 1985, more than 500 residents (including teenage residents) of the bay area were reported to suffer from serious body pain specially back pain and knee joint pain which was medically termed as neuralgia and skin disease. Since Onsan bay was designated as Nonferrous Industrial Complex area 10 years before, it was suspected that this disease was caused due to heavy metal pollution and the disease was termed as "Onsan Public Hazard Disease" for which the government of Korea emigrated more than 10,000 inhabitants from that area*". In general, data tend to be extremely focused, so it is not able to give a real view of the whole environmental problem and of the potential overall solutions. This is comparable to demonstrations like a "no-smoking day", for instance, which can be useful to highlight the problem, and people for a day will certainly breathe better. But unfortunately this action does not contribute at all to solving the problem of pulmonary cancer!

Each industry is characterized by specific contaminant emissions, but to what extent? The toxic metal concentration in the effluent depends surely on the type and size of the industry: which raw material is treated? how many tons/day? It is not hard to understand why a vast part of the literature on ecological approaches in industrial fields (damage and remedial actions) comes from developing countries. Varying factors contribute to the fact that a large number of "potential polluting" industries are located in these countries: source of raw materials (mines, forests, . . .), water availability, ready availability of manpower and its lower incidence on cost, laws not yet as restrictive as in advanced industrial countries, due to the quite recent industrialization. Indeed, most raw matter is sourced in developing countries not only for their natural resources but especially due to the lower cost of preliminary treatment, which is not only more hazardous but also the heaviest and most polluting. People in developed nations avoid hard and dangerous labour, leading to a change in the distribution of resources and treatment of raw matter throughout the world. Various mines in Europe have been dismissed: the high incidence of labour (salary and cost of precautionary measures) and the cost of treatment to minimize the environmental impact, required by European directives, render the final product non-competitive with those from developing countries. On the other hand, to say that the more advanced nations are not involved in the low cost treatment of wastes is also false. In G8 meetings, the governments of advanced countries not only discuss environmental protocol, but also financially promote research in this ecological area. A historical vision of the various factors which determine the localization of industrial plants can be found in the work of Baron et al. [23] which puts together environmental, cultural heritage and historical knowledge. In their paper the application of modern ICP-MS technique allows the tracing of mineral sources depending on lead isotope content in the foundry wastes in Mont-Lozere, Central Massif, France. The identification of mineral sources and several factors such as wood type, water proximity and land ownership allow the mapping of metal producing locations from the medieval age up to today.

Tanneries, widely distributed in India as small-size firms, are among the most potentially polluting industries. Resulting waste water is rich in chromium which is extensively used to obtain leather of desirable quality. As far as this kind of craft industries are concerned, the environmental pollution data are not systematically collected and the related papers present only "semi-quantitative" discussions, often accompanied by superficiality or by gross inaccuracies. As examples we comment here on the difference between the total dissolved solids (4832 mg/L) and the sum of only Na^+, $SO_4{}^{-2}$ and Cl^- (6990 mg/L) [24] or the work of Rajeshwarisivaraj and Subburam [25] who report the wavelengths of absorption of different inorganic and organic salts, without any procedure description: it is unacceptable and suspicious to discuss metal element absorbance without colour developing methods, except in the case of chromium(VI). The entity of tannery pollution in India can be inferred from the work of Suthantharajan et al. [21] who wrote that "*about 30–40 m^3 of wastewater is generated per ton of raw material processed. On the whole there are 3000 tanneries in India processing 700 000 tons of hides and skins per annum, which generate about 100 000 m^3 of wastewater per day.*" The pollution of surface waters by acid mine drainage (AMD) creates different problems: besides altering the appearance of water, it destroys the living organisms in water, thus affecting the capacity of the system to remove organic pollution. The majority of mines are generally located in highly populated areas, with the highest demand for domestic and industrial water. The general mechanisms which determine the generation of AMD are well known, and produce a high amount of dissolved toxic heavy metals accompanied by low pH values and high sulfate content [26]. Acid mine drainage can have a moderate (0.35–0.55 g/L) to high (1.5–7.2 g/L) mineral content [27–28]. In some cases the amount of heavy metals transported by rivers can be impressive, as reported by Sainz et al. [29] for Tinto and Odiel rivers due to magnitude of total metal content (895.1 kg/h) and toxicity (8.7 kg/h of As + Cd + Pb). Further pollutants, not connected to mining but to domestic and agricultural activities, such as nitrates and ammonium, can also affect the fate of heavy metals [30].

2.1. The threat of metals in the environment

As a result of industrial activities and technological development, heavy metals released into the environment have been continuously on the increase, posing a significant threat to environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. The importance of controlling the concentration of toxic metal ions in waters for human use became apparent after the Four Big Pollution Diseases of Japan, a group of manmade diseases all caused by environmental pollution due to improper handling of industrial wastes by Japanese corporations [31]. Two of the Four Big Pollution Diseases of Japan, Minamata (1932–1968) and Niigata disease (1965), were due to mercury poisoning. The first one, sometimes referred to as Chisso–Minamata disease, is a neurological disease whose symptoms include ataxia, numbness in the hands and feet, general

Table 1
Sources, health effects and permissible limits of some toxic metal species.

Metal species	Main anthropogenic sources	Health effects	Limits in drinking water mg/L [33]
Aluminium	Transportation, food industries, cooking utensils, electrical transmission lines, electronics, construction, water treatment [34] http://en.wikipedia.org/wiki/Aluminium – cite_note-17.	Neurologic injuries	0.1
Cadmium	Nickel–cadmium batteries, metal alloys and electronic components additive, paint pigments, anticorrosive metal coatings, stabilizers [35]	Carcinogenic, bone softening, kidney failure, Itai-itai disease [30]	0.003
Chromium	Photography, tannery, ceramic, glass industries, catalysts, pigments, paints, fungicides, chrome alloy, metallurgic industries [36–38].	Cr(VI): genotoxic, carcinogenic	0.05
Copper	Mines, brass manufacture, electroplating industries, agriculture, water treatments [39,40].	Lung cancer [41].	2
Lead	Storage batteries, building materials, ammunitions, fuel, pigment additive [38,43].	Neurotoxic	0.01
Mercury	Mines, catalysts [42].	Ataxia, numbness, muscle weakness, damage to hearing, speech and vision, insanity, paralysis, coma, death [31,32].	0.006
Nickel	Alloy, batteries, electrolytic and welding procedures, glass, ceramic industries, catalysts [43].	Allergenic, carcinogenic [44].	0.07
Zinc	Alloy production, anticorrosion coatings, electrical devices, rubber and tyre industries, paints, pesticides [38,43].	Relatively nontoxic. Daily doses >100 mg for several months lead to different disorders [45].	3

muscle weakness, narrowing of the field of vision and damage to hearing and speech. In extreme cases, insanity, paralysis, coma and death follow within weeks of the onset of symptoms. A congenital form of the disease can also affect fetuses in the womb. Minamata disease was first discovered in Minamata city in 1956. This poisoning was caused by the release of methyl mercury in the industrial wastewater from the Chisso Corporation's chemical factory. The highly toxic mercury concentration has been bio-accumulated in shellfish and fish in Minamata Bay and the Shiranui Sea, and human and animals deaths continued over more than 30 years. As of March 2001, 2265 victims had been officially recognised (1784 of whom had died) and over 10000 had received financial compensation from Chisso [32,33]. All these severe injuries made the public opinion ecologically sensitive and extremely aware of environmental problems. Some information regarding the principal toxic metal ions are reported in Table 1.

3. Analytical methods for identification of functional groups and of their role in metal sorption

When the biosorbent is dead, the sorption occurs via functional groups by one or more mechanisms [6]. Therefore, identification of the functional groups can help in shedding light on the mechanism responsible for metal uptake. Potentiometric titration, chemical treatment of the sorbent and spectroscopic techniques are the common procedures.

3.1. Potentiometric titrations

Potentiometric titrations measure the acid–base properties of the sorbent and the ionic exchange properties with regard to H^+ and OH^- ions. The presence of acid and basic sites determine the sorbent amphoteric properties and, depending on the pH, the groups can be either protonated or deprotonated [47]. Acidity constants in the literature can be considered as mean values, which are representative of the class of the functional groups [48]. Active site concentrations are generally determined by acid–base potentiometric titration of the adsorbent and related modeling: (a) *Spirulina* biomass was titrated with HCl and reversely with NaOH and the pK_a's determined suggested the presence of carboxylic (pK_a 2–3), phosphate and hydroxylic (pK_a 7–8) and amine groups (pK_a 11–12) [47]; (b) titration of spent waste yeast biomass was performed by using a standard solution of NaOH after preliminary addition of a known volume of HCl to lower the initial pH. The determined pK_a values indicated the presence of carboxylic and phosphate groups (pK_a 5 and 6 respectively) and saturated amines (pK_a 9.5) [49]; (c) the same titration procedure was followed to titrate olive pomace by Pagnanelli et al. [48]; in this study, titration of carboxylic acids performed by using $NaHCO_3$ solutions, following the Boehm method [50–51], revealed that the main sorption sites were carboxylic and phenolic groups; (d) Kiefer et al. [52] used NaOH and HNO_3 to titrate two algae surfaces and determined the pK_a of carboxyl, phenolic and *o*-amino groups; (e) Araújo et al. [13], by titrating a plant root material with standardized HNO_3 and KOH solutions, elucidated the functional groups, determined the pK_a's, the concentrations, and the contribution of each sorption site in metal sorption; (f) Murphy et al. [53] protonated the biomass (three different type of macroalgae) by treatment with HCl before titration with NaOH at 1 mM NaCl ionic strength: the pK_a's and the number of strong and weak acidic groups were determined; (g) base titrations with NaOH of a fungal species, performed in $NaClO_4$ media of different concentration, provided information about four different proton binding constants and the functional group site concentration [54]; (h) *Sargassum wightii* biomass was titrated in 1 mM NaCl with NaOH and two inflection points were obtained at pH 4.1 and 8.8. By comparing literature, the authors suggested the presence of two functional groups, carboxyl and saturated amines or saturated thiols [55]; (i) NaOH was also used to conduct the potentiometric titrations of citrus pectins in 0.1 M $NaNO_3$ and to observe that carboxylic groups were important contributors for negative charge on the surface of pectin biopolymers [56]; (j) $NaNO_3$ was also used as ionic strength buffer in the potentiometric titration with NaOH of algal biomass and citrus peels [57]. In the last two studies carboxylic and hydroxyl groups were the main functional groups involved. Potentiometric titrations can also be used to determine the pH at the point zero charge (pH_{pzc}) of biomass. The pH at which the sorbent surface charge takes a zero value is defined as point of zero charge (pH_{pzc}). At this pH, the charge of the positive surface sites is equal to that of the negative ones. The knowledge of pH_{pzc} allows one to hypothesize on the ionization of functional groups and their interaction with metal species in solution; at solution pH's higher than pH_{pzc} the sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pH_{pzc} the solid surface is positively charged and could interact with nega-

Table 2
The relevant parameters on the metal ion sorption literature (1997–2009) are presented: biomass, metal ions and involved functional groups.

Biomass	Species	Functional groups	Potentiometry	Chemical treatment	Spectroscopy	Light metal release	Reference
Waste tea leaves	Pb, Zn, Fe, Ni	Carbonyl, amine			X		[72]
Botrytis cinerea	Cd, Cu	Carboxyl, aromatic amino acid			X		[75]
Coconut coir pith	As(V)				X		[100]
Plant root material	Ni, Cu, Al, Fe	Amine, phenolic, carboxylic	X		X		[13]
Yeast biomass	Pb	Amide, amino		X	X		[63]
Citrus pectin	Pb	Carboxylic	X		X		[56]
Olive mill	Cr(III), Cu, Zn	Carboxyl			X	X	[64]
Lentinus edodes	Cd	Hydroxyl, carboxyl			X		[76]
Alga spirulina sp	Cr(III), Cd, Cu	Carboxyl, phosphate, hydroxyl, amine	X	X			[47]
Cork biomass	Cu, Zn. Ni	Carboxyl	X				[77]
Cork biomass	Cu, Zn, Ni	Carboxyl	X	X			[62]
Kraft lignin	Cr(III)/(VI), Pb, Zn					X	[101]
Dried plant leaves	Cu	Carbonyl			X		[73]
Yohimbe bark	Cu	Aromatic			X	X	[66]
Grape bagasse	Cd, Pb	Carboxylic, carboxyl, amino			X		[78]
Olive stones	Pb, Ni, Cu, Cd					X	[65]
Grape stalks, yohimbe bark	Cr(VI)	Aromatic			X		[90]
Exhausted coffee	Cr(VI)	Aromatic			X		[91]
Alfalfa biomass	Cr(III)	Carboxyl		X	X		[61]
Mango peel	Cd, Pb	Carboxyl, hydroxyl			X		[103]
Algae surfaces	Cu	Carboxyl, N ligands, hydroxyl	X		X		[52]
Cumin surface	Cu, Zn	Carboxylic and amino	X				[79]
Marine algal biomass	Pb	Carboxyl	X		X		[80]
Juniper fiber	Cd	Carboxyl			X		[81]
Grape stalks	Pb, Cd	Aromatic rings			X	X	[67]
Olive oil wastes	Pb	Carboxyl	X				[104]
Aspergillus niger	Cr(VI)	Hydroxyl, amine, phosphate			X		[93]
Marine macroalgae	Cu	Carboxyl, amino, sulfonate, hydroxyl	X		X		[53]
Saccharomyces cerevisiae	Cd, Pb, Sr, Zn		X				[54]
Olive stones	Cu, Ni, Cd	Lignin moieties	X		X		[97]
Cork residues	Mn(II)				X	X	[69]
Olive pomace	Pb, Cu, Cd	Carboxyl, phenolic, hydroxyl	X		X		[48]
S. natans biomass	Cu	Carboxyl, amino	X		X		[82]
Husk of lathyrus sativus	Cd	Carboxyl		X	X	X	[59]
Pine needle	Cr(VI)				X		[96]
Waste beer yeast	Pb	Carboxyl, phosphate, amine	X	X			[49]
Orange waste	Cd	Alcohol, carboxyl, aromatic			X		[83]
Green coconut shell	Cd				X	X	[70]
Aniger biomass	As(III), As(V)	Hydroxyl			X		[95]
Natural polysaccharide	Cu, Zn, Cd, Ni	Carboxylic, phenolic	X				[84]
Dealginated seaweed waste	Cd	Carboxyl	X		X		[85]
Saltbush (atriplex canasce)	Cd, Cr(III)/(VI)	Carboxyl					[86]
Citrus peels	Pb	Carboxyl	X		X		[56]
Juniper wood	Cd	Carbonyl			X		[74]
Corn by-product	As, Cu, Mo, Ni, Pb, Zn				X		[98]
Sawdust pynus sylvestris	Cd, Pb	Carboxyl			X		[87]
Alfalfa biomass	Cr(III), Ni	Carboxyl			X		[88]
White chicken feathers	As(III)	S-cysteine			X		[99]
Botrytis cinerea	Zn	Hydroxyl, amino			X		[94]
Olive mill	Cu		X		X		[48]
Sargassum wightii	Ni	Carboxyl, saturated amines o saturated thiols	X				[55]
Algal biomass	Cu	Hydroxyl, carboxyl	X		X		[57]
Cork wastes	Cu, Ni	Lignin moieties	X		X		[92]
Grape stalks	Cu, Ni	Aromatic rings			X	X	[68]
Yeast	Cd, Pb	Hydroxyl, carboxyl, amide			X		[89]

The following columns report which techniques among potentiometry, chemical treatment, spectroscopic methods or alkaline and alkaline-earth metal ion release were used.

tive species. The potentiometric mass titration technique was used to determine the pH_{pzc} of grape stalks, cork, yohimbe bark and olive stones [58].

Table 2 sums up the studies since 1997 on metal sorption by biomass that investigate the mechanisms of metal sorption. The species, the functional groups involved in metal binding and the used experimental techniques are there reported.

When potentiometric titration was used, carboxylic groups were the most involved in metal ion uptake as expected on the basis of their easiest deprotonation in the 2–6 pH range, the most suitable for metal sorption. In order to highlight the importance of each different binding group in the mechanism of metal ion adsorption, the percent incidence drawn out from 1997 to 2009 literature is presented in Fig. 1.

3.2. *Chemical treatment of sorbent surface*

Chemical treatment allows to evaluate the contribution of each functional group thanks to its blockage effect on metal sorption. It consists in carrying out chemical reactions that selectively block different functional groups on the sorbent surface [46]. The most common chemical modifications are: esterification of carboxylic

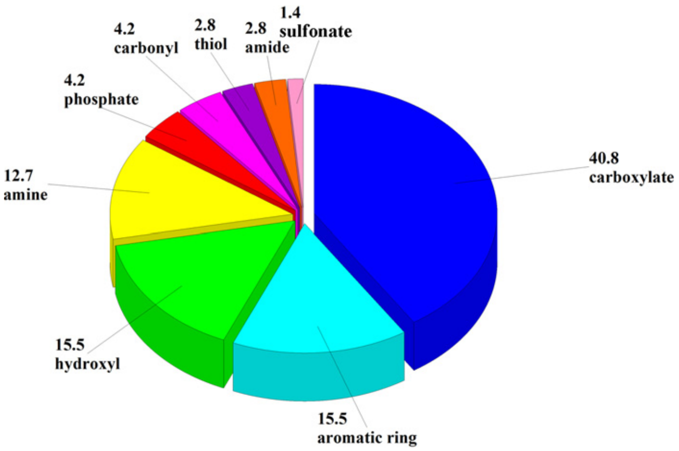


Fig. 1. Incidence of the different binding groups on biomass surface involved in metal ion complexation.

groups, methylation of amines, esterification of phosphates, and modification of mercapto groups (see Table 3).

Carboxylic groups can be alkylated by reaction with methanol or ethanol in acidic media, while amines by reaction with formaldehyde and formic acid. Alkylation of both functional groups prevents their participation in metal biosorption, thus reducing the biosorption efficiency. Panda et al. [59] blocked carboxyl and primary and secondary amines using methyl iodide and formaldehyde–formic acid to determine the involvement of these functional groups in cadmium sorption onto different biomass. The same authors investigated the involvement of phosphates in cadmium sorption, using the procedure reported by Markowska et al. [60] by treating the biosorbent with triethyl phosphate and nitromethane to esterify the phosphate groups. Esterification in acidic methanol and hydrolysis with NaOH were used by Gardea-Torresday et al. [61] to demonstrate that carboxyl groups were involved in Cr^{3+} sorption on alfalfa biomass. The effect of different physical and chemical pretreatments (acids, alkalis, sodium and calcium chloride solutions and oxidizing agents) of cork biomass on metal sorption was investigated. In particular, the effect of carboxylic group on Cu^{2+}, Zn^{2+} and Ni^{2+} sorption has been pointed out by esterification with acidic methanol [62]. This last procedure was used on algae *Spirulina* sp. to investigate Cr^{3+}, Cd^{2+} and Cu^{2+} ions sorption mechanism [46]. The Pb^{2+} uptake capacity of the sorbent was evaluated in acetone-washed yeast biomass chemically modified: (a) carbodiimide-nucleophile reaction with carboxylic groups, (b) hydroxyl and amino groups totally acetylated in acetic anhydride/pyridine, (c) amino groups modified by reaction with trinitrobenzenesulfonic acid (TNBS) and by aminosuccinylation [63]. Methylation of amines, esterification of carboxylic and phosphates groups and modification of mercapto group were carried out by Parvathi et al. [49] to investigate the role of amine, carboxylic, phosphate and thiol groups in Pb^{2+} biosorption on *S. cerevisiae*. Chemical treatments were also used to selectively extract different compounds, such as fats or polyphenols, in order to improve metal sorption [48].

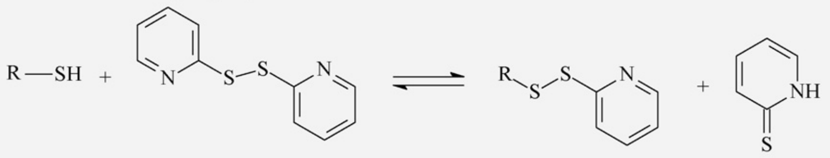
3.3. *Alkaline and alkaline-earth metal ion release*

The importance of ion exchange in biosorption has been frequently discussed. One of the common procedures to investigate whether ion exchange is the mechanism responsible for metal sorption is to determine the concentration of alkaline and alkaline-earth metal ions or protons (when the sorbent is pretreated with acid) released from the sorbent to the solution after metal uptake. The determination of the concentration of ions released into the solution (M: Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+) allows the balance of the concentration of uptake of heavy metal (M*).

$$R-M + M* \rightleftharpoons R-M* + M$$

Ion exchange was one of the mechanisms responsible for Cu^{2+}, Zn^{2+} and Cr^{3+} sorption by the organic polymeric fraction of olive mill wastewater [64], for Pb^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} sorption by olive stones [65], for Cu^{2+} sorption by yohimbe bark [66], for Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} sorption by grape stalks [67,68], and for Mn^{2+} sorption by cork residues [69]. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) can also contribute to define an ion exchange mechanism. The disappearance of alkaline and alkaline-earth metal ion peaks and the appearance of those of the sorbed metals, indicates that ion exchange takes place between alkaline and alkaline-earth metal ions on the sorbent and the metal ions in the solution. Through this method, the existence of ion exchange between Cd^{2+} and Ca^{2+} of husk of *Lathyrus sativus* [59], and K^+, Na^+ and Mg^{2+} of green coconut shell powder was demonstrated [70]. Other authors pretreated the sorbent (lignin) with Ca^{2+} and followed its release into solution during Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} sorption [71].

Table 3
Most common chemical treatments of sorbent surface (R stays for biomass).

Esterification of carboxylic groups	$R-COOH + \begin{cases} CH_3OH \\ CH_3CH_2OH \end{cases} \xrightleftharpoons{H^+} \begin{matrix} R-COOCH_3 \\ R-COOCH_2CH_3 \end{matrix} + H_2O$
Methylation of amines	$R-CH_2NH_2 \xrightarrow{HCHO/HCOOH} R-CH_2N(CH_3)_2 + CO_2 + H_2O$
Modification of mercapto groups	

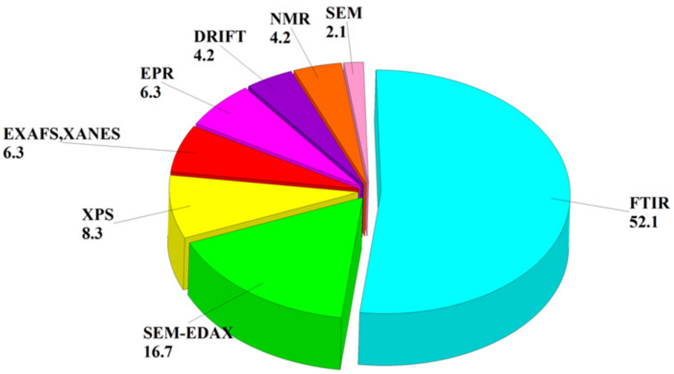


Fig. 2. Occurrence of the different spectroscopic techniques in metal ion sorption literature 1997–2009.

3.4. *Spectroscopic analysis*

Useful information on the role of functional groups on metal sorption can be reached by non-destructive spectroscopic methods, observing the modifications induced by the metal on the spectra of the pure adsorbent. The pie chart in Fig. 2 shows the kind and impact of the spectroscopic techniques used to infer the possible functional groups responsible for sorption.

3.4.1. *Fourier transform infrared spectroscopy (FTIR)*

FTIR, as can be observed in Fig. 2, is the most used technique (more than 50% of the selected papers). Infrared spectroscopy belongs to the group of molecular vibrational spectroscopies which are molecule-specific and give direct information about the functional groups, their kind, interactions and orientations. Its sampling requirements allow the gain of information from solids, liquids and gases, and in particular from solid surfaces. Even if historically IR has been mostly used for qualitative analysis, to obtain structural information, nowadays instrumental evolution makes non-destructive and quantitative analysis possible, with significant accuracy and precision. The shift of the bands and the changes in signal intensity allow the identification of the functional groups involved in metal sorption. Using this technique, carbonyl [72–74], carboxylic [47–48,52–53,55–57,59,64,75–89], aromatic [48,66,68,69,83,84,90–92], amine [47,49,53,55,63–64, 78–79,82,93–94], and hydroxyl groups [47–48,52–53,57,77,89,95] are involved in metal uptake by different biosorbents.

3.4.2. *X-ray photoelectron spectroscopy (XPS)*

XPS, introduced by the Nobel prize winner Siegbahn in 1949, is the main technique used for qualitative and quantitative elemental analysis of surfaces. It provides significant information on the chemical bonding of atoms. The absorption of high energy electromagnetic radiation (X-ray or UV) by surfaces leads to the emission of photoelectrons; those generated in the outermost layers emerge from the surface into the vacuum and can be detected. The measure of the kinetic energy of the emitted photoelectrons allows the determination of the binding energies of electrons and the intensity function (number of photoelectrons vs. kinetic energy), and quantitative results are obtained from the knowledge of the number of atoms involved in the emission process. Ashkenazy et al., using X-ray photoelectron spectroscopy (XPS) pointed out the involvement of nitrogen in lead sorption and the lead–oxygen interaction at the carboxyl group on the basis of the decrease in nitrogen concentration and of the shift of oxygen peak [63,80]. The same technique confirmed that chromium was sorbed onto grape stalks in both its trivalent and hexavalent forms [91], and allowed the derivation of the oxidation state of chromium bound on pine needles [96]. Furthermore it was used to explain the increase of cadmium and lead sorption onto baker's yeast after modification of sorbent surface by cross-linking cystine [89].

3.4.3. *Scanning electron microscopy (SEM)*

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope which provides images of the sample surface by scanning it with a high energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface. The samples must be electrically conductive, at least on their surface, for conventional SEM imaging. Nonconductive samples are coated with an ultra-thin layer of electrically conducting material; this coating prevents the accumulation of static electric charges on the sample surface during electron irradiation. Magnification of the imaging can be controlled over a range of up to 6 orders of magnitude from about ×25 to 250,000 times. Farinella et al. [78] used it to observe the surface porosity of grape bagasse. When coupled with energy dispersive X-ray analysis (EDAX), the atom concentrations on the sorbent surface can be determined. This enables the confirmation of a mechanism of ion exchange, generally investigated by determining the concentration of alkaline and alkaline-earth metal ions released from the sorbent after metal sorption. It thus confirmed the ion exchange between alkaline and alkaline-earth metal ions and Cd^{2+} and Cu^{2+} on *Botrytis cinerea* surface, Pb^{2+} and Cd^{2+} on grape stalks and Cd^{2+} on coconut shell [67,70,75]. SEM-EDAX gave evidence both of the presence of metals on the sorbent surface and of metal microprecipitation [59,87,90,94].

3.4.4. *X-ray absorption spectroscopy (XAS)*

XAS specifically examines the local structure of elements in a sample. The structure of a material is deduced on theoretical basis, but usually the interpretation of XAS spectra utilizes databases of known structures. This technique is useful in the case of heterogeneous samples and a wide variety of solid materials can be examined directly and non-destructively. Also the structure of amorphous phases can be easily achieved, as the local structure does not depend on long-range crystalline order. The application of XAS varies from the trace element concentration up to that of major elements. So it is useful to speciate trace elements adsorbed on the surface of biomass. X-ray absorption spectroscopy consists in the absorption of high energy X-rays by an atom in a sample. This absorption takes place at the energy corresponding to the binding energy of the electron in the sample. The interaction of ejected electrons with the surrounding atoms produces the observed spectrum. (XAS) and extended X-ray absorption fine structure (EXAFS) were used to ascertain the ligands involved in metal binding and the coordination environment for Cr^{3+} bound to *alfalfa shoot* biomass [61,88].

3.4.5. *Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)*

DRIFTS occurs when light strikes on the surface of a material and is partially reflected and transmitted. The light that penetrates the material may be absorbed or reflected out again. The diffuse reflectance (radiation reflected from an absorbing material) is thus composed of surface-reflected and bulk re-emitted components, and contains information relative to the structure and composition of the sample. DRIFTS was used to verify the enhancement of cadmium sorption capacity by juniper wood when carbonyl groups were substituted by sulfonic groups [74]. It was also used to determine that Cr^{3+}, Cu^{2+} and Zn^{2+} were sorbed onto the organic polymeric fraction of olive mill wastewater by ion exchange between alkaline and alkaline-earth metal ions and protons bound to carboxylic groups [64].

3.4.6. Nuclear magnetic resonance (NMR)

NMR has been used to elucidate the role of functional groups in the binding of metal ions: by ^{1}H NMR the functional groups involved in Ni^{2+}, Cu^{2+}, Al^{3+} and Fe^{3+} sorption onto plant root material were determined; by ^{13}C NMR those involved in Cd^{2+} and Pb^{2+} onto grape bagasse, those in Cu^{2+}, Ni^{2+} and Cd^{2+} onto olive stones and those in Cu^{2+} and Ni^{2+} onto cork waste [47,78,92,97].

4. Speciation of some toxic metal ions

The pie chart in Fig. 1 shows the incidence of the different binding groups on biomass surface involved in metal ion complexation, as results from the literature overview (Table 2).

This pie chart reveals that carboxylate, aromatic rings, hydroxyl groups and amines are those most involved in metal binding, while phosphate, carbonyl, thiol, amide and sulfonate contribute to a minor extent. In the work of Gadd and of Wang and Chen [15,102] the binding of metal ions is discussed taking into account the hard/soft classification of metals and binding groups (class A and class B). Beside this classification of great importance for evaluating the real contribution of each coordinating group toward each given metal ion, we present here a speciation study, assuming that each biomass particle suspended in a solution containing the toxic metal ions behaves as a ligand characterized by given binding groups. The term speciation here means distribution of an element amongst defined chemical species in a system, according to the IUPAC Recommendations 2000, as reported by D.M. Templeton et al. [103]. Such species distribution in a given metal–ligand system depends on such factors as concentration, stoichiometry, pH, and ionic strength. The complete set of stability constants for a system defines the species distribution of the system as a function of pH at the concentrations of metal(s) and ligand(s) studied. Extensive compilations of stability constants as well as numerous speciation programs are available; in this work the IUPAC database [104] for the stability constants and the program HYSS [105] for species calculation were used. Hence we used the methods of solution equilibria taking into consideration the binding properties of –COOH, $–NH_2$ and –SH groups from the 1:1 complex formation constants of carboxylic acids, amines and mercaptans towards different metal ions (Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) chosen from the IUPAC database. Complexes of higher stoichiometry were not considered, as they are not allowed for steric reasons in binding groups anchored on a flat surface. The availability of stability constant databases offers an excellent opportunity to obtain the numerical values of complex formation constants of ligand classes, characterized by given coordinating groups, to be used as input parameters for speciation programs. The distribution curves of the complexes for any given set of experimental conditions allow the observation of the behavior of the various metal ions toward different coordinating groups. In the present work the speciation study was limited to the coordinating groups –COOH, $–NH_2$ and –SH and to some of their combinations. The speciation study was based on the availability of meaningful literature stability constants. Actually for the carboxylic group it was possible to find data of a single representative ligand (acetic acid) for all the metal ions. In the case of NH_2 group, the differences of complex formation and of protonation constants among different primary amines with the same metal ion are negligible, indeed they are not greater than the discrepancies for the same metal ion with the same ligand found among various authors. Moreover, even if very little data is available for the SH group, it is enough to make some proper considerations and the above statements for NH_2 apply. The dependence of stability constants on the binding groups has been observed with ligands bearing multiple binding groups too; therefore we will report the speciation curves for the binding groups irrespective of the ligand and, for simplicity, the ligands taken into account will be represented only by the sequence of the binding groups (mercaptosuccinic acid COOH–CHSH–COOH will be reported as COOH–SH–COOH).

After discussing the simplest cases, we will deal with the quantitative effects of two or more coordinating groups on the same molecule on the metal binding. The formation of the various complexes calculated in solution 1 mM of both the ligand and the metal ion together to the protonation constants reported as dotted lines are plotted in Figs. 3–5. In what follows, we will discuss the observation that catches one's eye in these figures.

4.1. One coordinating group

For acetic acid (Fig. 3 COOH), Cr^{3+}, Hg^{2+} and Fe^{3+} complex formations occur at acidic pH values (2–4) in the amount of ~80% Cr^{3+}, ~70% Hg^{2+} and ~50% Fe^{3+}; as far as the other metals are concerned, their complex formation is always less than 10% and takes place only when acetic acid loses its proton, as clearly shown by the formation curves centered around the dotted line of CH_3COOH protonation constant (Fig. 3 COOH zoom).

For the $–NH_2$ group the literature gives complex formation constants for some metal ions. The complex formation in the pH range 4–6 is achieved only by mercury, while the other metal ions undergo hydroxide precipitation at pH values lower than those necessary for their complexation at 1 mM concentration [1]. Very few experimental results can be found for a single mercapto group, which strongly binds lead and cadmium in the pH range 5–7 and nickel in a lower amount.

4.2. Two vicinal groups

While the formation of 1:2 or higher stoichiometry complexes is not a realistic hypothesis for binding groups on a surface, on the contrary the binding by two vicinal groups is surely consistent.

This situation, in the case of two vicinal carboxylate groups, can be well represented by the distribution curves of oxalate complexes (Fig. 4 COOH–COOH). The cooperative effect drastically increases the percent formation of all metal complexes and shifts the formation range to lower pH's. The complexation by two amino groups totally alter the pH distribution plots (Fig. 4 $NH_2–NH_2$) and, besides mercury, copper and nickel are quantitatively bound before pH 6 and 8 respectively, and a certain amount of complexation of the other metal ions is attained before their precipitation. The presence of two vicinal –SH groups, as in dimercapto succinic acid (Fig. 5 COOH–SH–SH–COOH), strongly affects the coordination capacity: the complete complexation of lead, cadmium, and zinc is attained in the pH range 3–5 and at higher values (5.5–7.5) that of nickel. These observations are for a large extent in line with the hard-soft characteristics of metal ions and binding groups, and light on the role of a second vicinal group. This second group gives an effective and synergic contribution, by increasing the stability of the 1:1 formed complexes and by drastically lowering the pH range of complexation. The observed cooperative effect projected onto biomass can play a very important role in the binding of metals. In this instance, to simulate the biomass surface on which different chelating groups are present, the complexation by mixed vicinal coordinating groups was taken into account. The strong binding of mercury by $COOH–NH_2$ and, above all, by COOH–SH has to be noted, and in a second instance the strong binding of the hard Fe^{3+} and Cr^{3+} by both couples containing the –COOH group. The couples containing the –SH group favour instead Cd, Pb and Zn complexation, and Ni in limited amounts (Fig. 4).

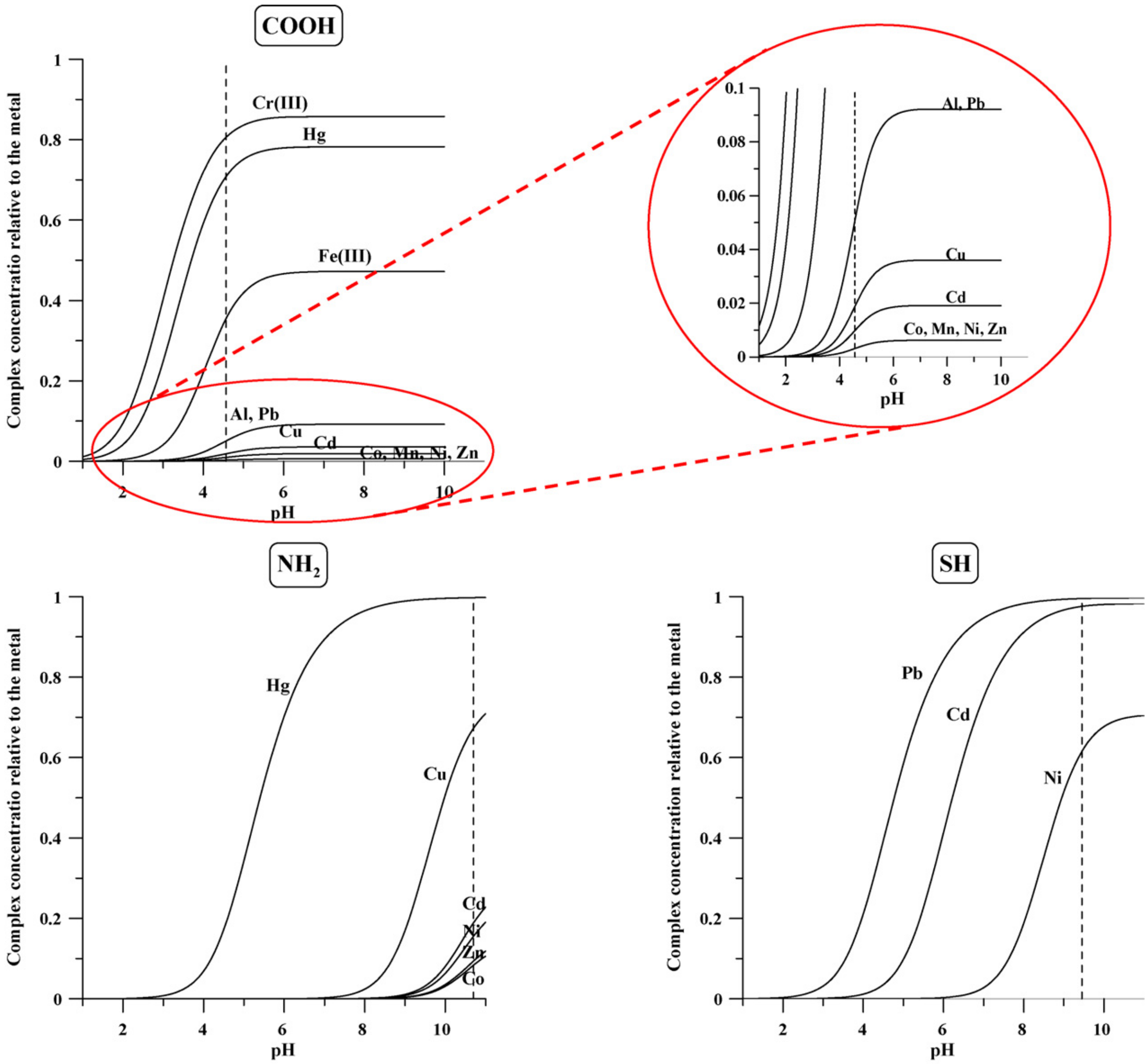


Fig. 3. Formation curves for complex formation among different toxic metal ions and various ligands bearing a –COOH, –NH2 or –SH group calculated for 0.001 M solutions in both ligand and metal ion, using complex formation and protonation constants (dashed vertical lines) from the IUPAC database. The title on the top of each plot indicates the coordinating group on the involved molecule.

4.3. Multiple coordinating groups

The presence of a third coordinating group brings forward further considerations (Fig. 5). In the case of NH_2–CH_2–CH(SH)–COOH we can observe:

1. the complexation of Fe^{3+} and Cr^{3+}, similar but occurring to a minor extent than that for SH–CH_2–COOH, marks the coordination by –SH and –COOH groups;
2. the coordination of Cd, Ni, Pb, and Zn, occurring like and to same extent as NH_2–SH, points out the complexation by only –NH_2 and –SH groups.

The above remarks imply that in the presence of multiple coordinating groups on the biomass surface, the metal ions prefer given sets of coordinating groups according to their hard/soft character. More difficult however is the case of mercaptosuccinic acid (COOH–SH–COOH) which resembles the behavior of COOH–SH but with a stronger stability for many metal ions (Co, Ni, Pb and Zn) to be ascribed to a possible coordination by all the three binding groups. The increase in stability for these metal ions from mercaptosuccinic acid to dimercaptosuccinic acid (COOH–SH–SH–COOH) marks the involvement of both –SH groups in coordination. The SH groups, besides coordinating metal ions, can also give oxido-reductive reactions with metal ions as long as their reduction potential (Cu^{2+}/Cu^{+} and Fe^{3+}/Fe^{2+}) allows the formation of sulfur bridges –S–S–. In this instance different and not easily forecasted phenomena can happen on the biomass surface. Furthermore the reality can be more intricate than the implication of only two binding groups anchored on a flat surface, and a multiple coordination can be favoured by steric conformation, as in the case of proteins and other biomolecules

4.4. Further considerations

The distribution plots in Figs. 3–5 were calculated without considering the hydrolysis of metal cations, that in many instances takes place at pH values lower than those necessary for metal coordination leading to hydroxide precipitation.

Other considerations can be drawn from the analysis of the distribution plots. The complex formation is in all cases pH dependent,

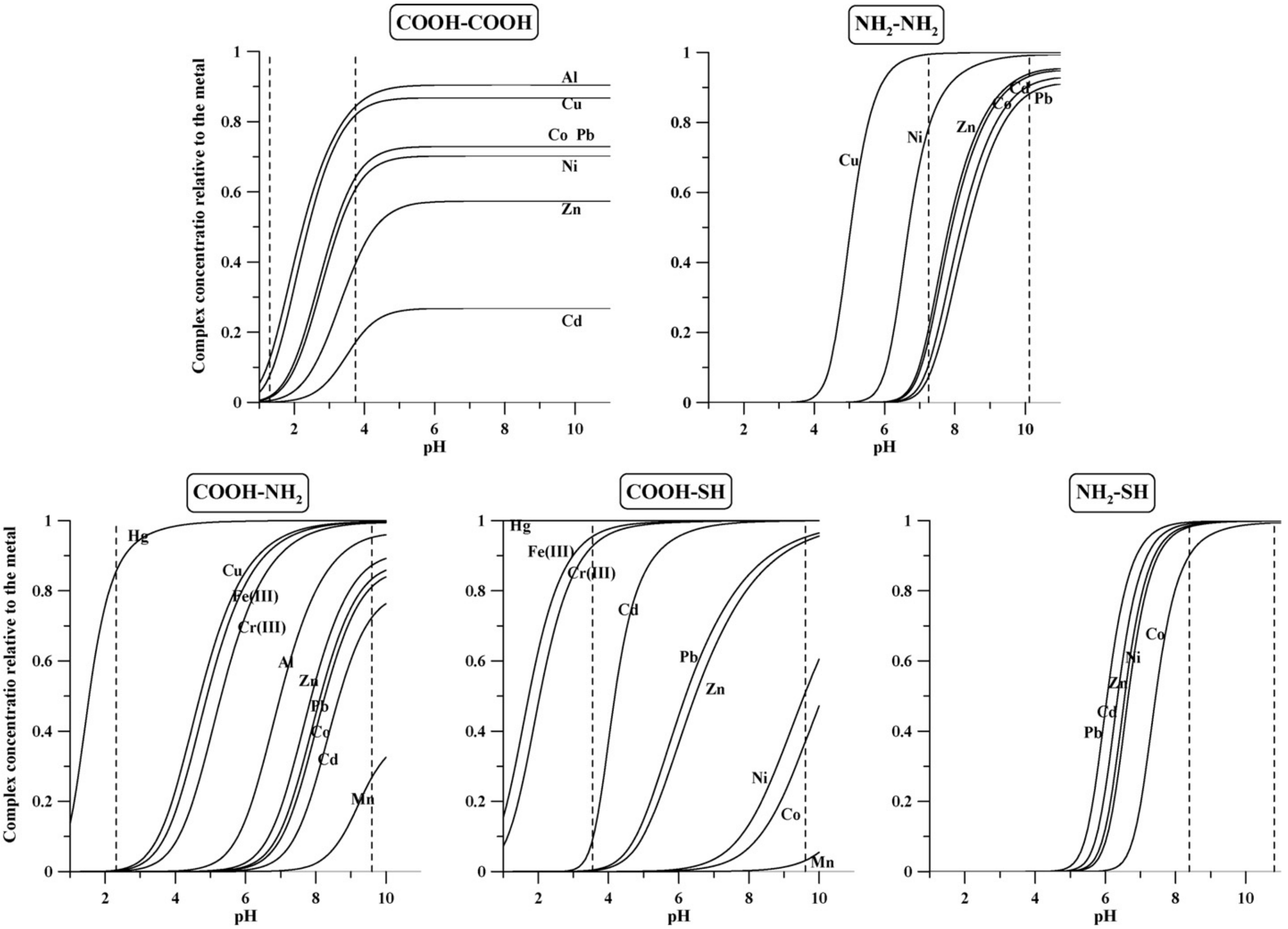


Fig. 4. Formation curves for complex formation among different toxic metal ions and various ligands bearing two vicinal groups, calculated for 0.001 M solutions in both ligand and metal ion, using complex formation and protonation constants (dashed vertical lines) from the IUPAC database. The title on the top of each plot indicates the two coordinating groups involved.

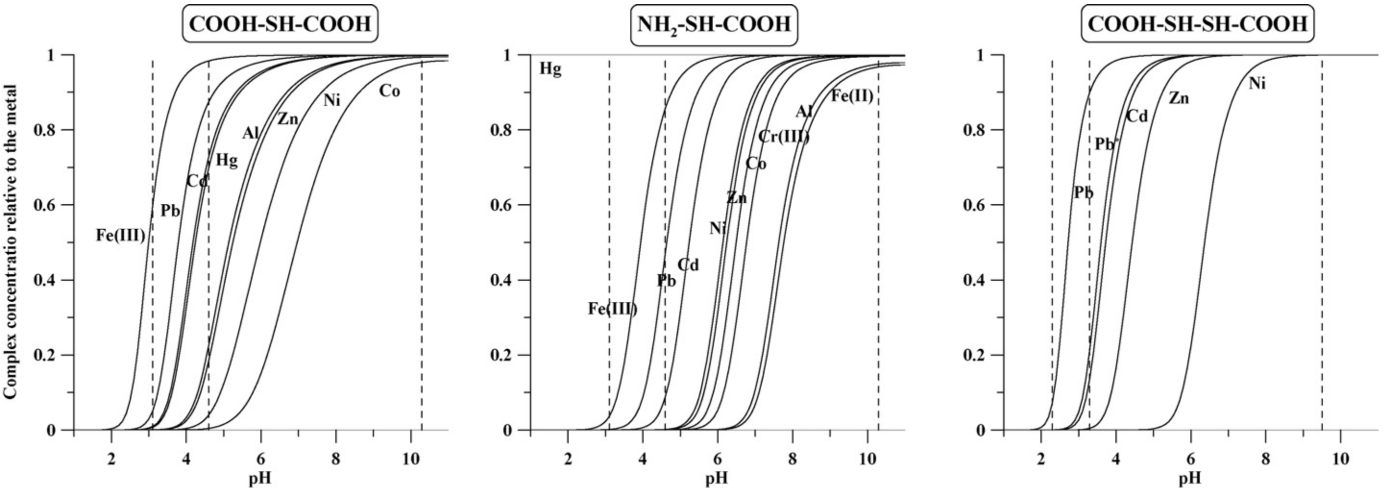


Fig. 5. Formation curves for complex formation among different toxic metal ions and various ligands bearing multiple coordinating groups calculated for 0.001 M solutions in both ligand and metal ion, using complex formation and protonation constants (dashed vertical lines) from the IUPAC database. The title on the top of each plot indicates the coordinating groups involved.

and the complex concentration increases to a constant value with an S-shaped trend in a narrow range (about two pH units) characteristic both of the metal and of the ligand. The formation of stable complexes favours the proton release, that takes place at lower pH values as the complex stability is stronger. Only the complexes of lower stability need for their formation the previous ligand deprotonation, as in the case of Al^{3+}, Pb^{2+} Cu^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} with acetic acid, of Mn^{2+} with the $–NH_3{}^+$ deprotonation of glycine ($COOH–NH_2$) and of Ni^{2+} and Co^{2+} for the deprotonation of –SH group in COOH–SH. On these basis we can distinguish different mechanisms by which the metal ions are sorbed on the biomass surface. All of them are characterized by a different bonding strength: we can speak first of all of coordination by the groups on the biomass surface, when the binding takes place at pH values lower than the pK of deprotonation of the groups characterizing the biomass, and before any metal hydroxide precipitation. We can then speak of electrostatic bonds when the binding takes place only after the deprotonation of surface groups, i.e. at pH equal or greater than the pK, the biomass surface thus being negatively charged. Depending on the pH value, the kind of cation and its concentration, microprecipitation can also occur at the biomass surface. In such real biphasic systems the dielectric constant of the medium near the surface can be drastically different from that in solution, thus favouring the precipitation phenomena. The competition of different cations towards a given biomass can be roughly approximated on the basis of distribution plots: metal cations which are bonded with the same mechanism on the same groups surely will be competitive, otherwise if they bind preferentially different groups they can be simultaneously sequestered on the surface.

5. Conclusions

Recent literature focuses on identifying the binding groups on the biomass surface through different analytical techniques, from the traditional potentiometry to the most innovative and sophisticated surface analysis. In our work, we reviewed this literature in order to both identify the main functional groups involved in metal binding (Fig. 2) and classify the principal analytical procedures used in their identification. Some important points must be conclusively remarked upon. The first observation we would like to make concerns the large use of solid state spectroscopic methods. Using these highly sophisticated and extremely expensive apparatus enables one to obtain structural information on the sorbent morphology and indirect knowledge of the implied sorption mechanisms by comparing some physical properties of the sorbent material before and after metal sorption. Little importance is given to the classical chemical methods such as potentiometry and alkaline and alkaline-earth metal ion release, which on the contrary offer a lot of advantages: they are easily available in all the laboratories, they are widely used by chemical researchers, they are fast, cheap, friendly and above all they give quantitative results, i.e. they allow the evaluation of the amount and the kind of functional groups involved (potentiometry) or the amount of exchanged metal (alkaline and alkaline-earth metal ion release) [106,107].[2]

Metal removal from waste waters by biomass requires a multidisciplinary approach (as do environmental sciences in general) and the efforts of analytical chemists and solution equilibrium experts can give an important contribution to the knowledge and optimization of these processes. The study of the characteristics of binding groups on the biomass is of paramount importance to identify the mechanisms of metal sequestration, and to predict the selectivity towards the different cations, the strength of binding and the influence of pH on the sorption processes. The use of speciation methods can lead to the best definition of the binding mechanisms. In this instance we simulated the speciation of different toxic metal ions as a function of the groups on the biomass. Speciation studies are based on the knowledge of the complexation properties of the various binding groups toward each metal ion. They allow to quantitatively simulate to what extent the surface characteristics of the sorbent affect the interaction with any metal ion, the selectivity, and the competition among different metals. These speciation studies can furthermore highlight the relationship between the coordinating properties (complex formation and protonation constants) of the binding groups and the sorption mechanisms.

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