



A review of plant metabolites with metal interaction capacity: a green approach for industrial applications

Amir Nobahar · Jorge Dias Carlier · Maria Graça Miguel · Maria Clara Costa 

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Abstract Rapid industrial development is responsible for severe problems related to environmental pollution. Many human and industrial activities require different metals and, as a result, great amounts of metals/heavy metals are discharged into the water and soil making them dangerous for both human and ecosystems and this is being aggravated by intensive demand and utilization. In addition, compounds with metal binding capacities are needed to be used for several purposes including in activities related to the removal and/or recovery of metals from effluents and soils, as metals' corrosion inhibitors, in the synthesis of metallic nanoparticles and as metal related pharmaceuticals, preferably a with minimum risks associated to the environment. Plants are able to synthesize an uncountable number of compounds with numerous functions, including compounds with metal binding capabilities. In fact, some of the plants' secondary metabolites can bind to various metals through different mechanisms, as such they are excellent sources of such compounds due to their high availability and vast diversity. In addition, the use of plant-based compounds is desirable from an environmental

and economical point of view, thus being potential candidates for utilization in different industrial activities, replacing conventional physiochemical methods. This review focuses on the ability of some classes of compounds that can be found in relatively high concentrations in plants, having good metal binding capacities and thus with potential utilization in metal based industrial activities and that can be involved in the progressive development of new environmentally friendly strategies.

Keywords Active plant-based compounds · Secondary metabolites · Metal binding · Metal interaction · Industrial applications

Introduction

Metals are pivotal in the global economy as key constituents of a vast number of products and industrial processes enabling our core societal and industrial activities from electronic devices, vehicle production, constructions to agriculture and medicine. Each metal and its alloys have unique properties that make them interesting for different applications. Currently, the majority of metals are obtained from primary sources, which have critically limited sources and disparately spread worldwide. In the last centuries, as a result of rapid industrialization and population explosion,

A. Nobahar · J. D. Carlier · M. C. Costa (✉)
Centre of Marine Sciences (CCMAR), University of the Algarve, Gambelas Campus, 8005-139 Faro, Portugal
e-mail: mcorada@ualg.pt

A. Nobahar · M. G. Miguel · M. C. Costa
Faculty of Sciences and Technology, University of the Algarve, Gambelas Campus, 8005-139 Faro, Portugal

Table 1 Some examples of recent applications of plants compounds with metal interaction potential

| Application | Plant | Reported compound | Target metal/ metal compound | Reference |
|------------------------|--|---|---|---|
| Metal insolubilization | <i>Olea europaea</i> and <i>Citrus aurantium</i> | Saponins | Pb ²⁺ , Cd ²⁺ | (Abed el Aziz et al. 2017) |
| | Spinach, Coffee, and Tea | Polyphenols, Alkaloids (Not specified) | Pb ²⁺ | (Lathan et al. 2013) |
| | <i>Ocimum gratissimum</i> | Flavonoid | Ni ²⁺ , Zn ²⁺ , Cu ²⁺ | (Louis et al. 2018) |
| | <i>Acacia nilotica</i> | Tannins | Ni ²⁺ | (Meethale Kunnambath and Thirumalaisamy 2015) |
| Nanoparticle synthesis | <i>Oldenlandia corymbosa</i> L. | Alkaloids, Saponins, Polyphenols, and Flavonoids | CuO | (Yulizar et al. 2018) |
| | <i>Ginkgo biloba</i> | Polysaccharide | Pd ²⁺ | (Cui et al. 2020) |
| | <i>Salvadora persica</i> | Polyphenols | Pd ²⁺ | (Khan et al. 2017) |
| | <i>Trianthema portulacastrum</i> and <i>Chenopodium quinoa</i> | Not reported | TiO ₂ | (Irshad et al. 2020) |
| | <i>Oscillatoria limnetica</i> | Free amino groups, sulfur containing amino acid derivatives | Ag ⁺ | (Hamouda et al. 2019) |
| | <i>Andrographis paniculata</i> | Terpenoids | ZnO | (Kavitha et al. 2017) |
| | Black tea | Polyphenols, Flavonoids | Au ³⁺ | (Alegria et al. 2018) |
| | <i>Azadirachta indica</i> | Carbonyls, alkanes and aliphatic amines, | Pt ⁴⁺ | (Thirumurugan et al. 2016) |
| Corrosion inhibitor | <i>Myrtus communis</i> | Limonene, linalool, pinene, 1,8-cineole, linanyl acetate, and terpineol (Not specified) | Copper | (Bozorg et al. 2014) |
| | <i>Corchorus olitorius</i> | (Not specified) mixed-type inhibitor | Mild steel | (Gobara et al. 2017) |
| | <i>Sapium ellipticum</i> | lavonoids, phenolics, alkaloids, tannins, terpenoids, steroids | Aluminum | (Okechukwu Dominic et al. 2020) |
| | <i>Tridax procumbens</i> and <i>Chromolaena odorata</i> | Flavanones, Persicogenin, Chalcones, Flavones and Luteoli (Not specified) | Stainless steel | (Aribo et al. 2017) |
| Biosorption | <i>Lagestroemia speciosa</i> | Tannin | Pd ²⁺ | (Choudhary et al. 2017) |
| | <i>Cladophora glomerata</i> (Algae) | Not reported | Cr ⁶⁺ | (Al-Homaidan et al. 2018) |
| | Walnut Shells | Polysaccharides | Heavy metals | (Halysh et al. 2020) |
| | <i>Rhizopus sp.</i> (Fungi) | Not reported | Cu ²⁺ | (Gomes et al. 2014) |
| | Banana peel | Compounds with nitrogen, sulfur, and carboxylic acids are responsible | Pb ²⁺ , Cu ²⁺ | (Kok Seng 2018) |

metal extraction from primary sources has tremendously increased, leading to a significant depletion of these resources. As a consequence, the necessity of resourcing metals from secondary sources by employing environmentally friendly and sustainable technologies has been emerging.

Plants are valuable resources for all living organisms existing on our planet and have evolved to survive in soils containing very low available metals (Morales et al. 2018), while others have lived in habitats with high heavy metal contents. As a result, they have developed strategies for metal uptake (micronutrients) and delivery from roots to different parts of the plant (González-Guerrero et al. 2016) benefiting from different active phytochemicals. They have also developed mechanisms to overcome the toxicity of heavy metals in their growing bed, which include exclusion, inactivation and organic ligands exudation (Choppala et al. 2014). As an example, different plants like coffee, green tea and vegetables (like spinach) are rich in different types of polyphenols, gallic acid and many other bioactive compounds (McDonald et al. 1996; Chaturvedula and Prakash 2011; Cvjetko Bubalo et al. 2018) that have different roles in plant and metal-interaction characteristics. Generally, different parts of the plant may contain distinct active ingredients. These renewable resources provide raw materials and phytochemicals, notably secondary metabolites like alkaloids, flavonoids, tannins, phenolic acids, saponins, steroids, etc., with many different mechanisms of interaction with metals that can be used for different industrial purposes. For instance, phenolic compounds have several roles in different parts of the plant, such as providing more support for the plant's structural system, protection against herbivores, pathogens, harmful solar radiations (e.g. UV) etc. (de la Rosa et al. 2019), but because of their special structure, they are also capable metal chelators (Rahim et al. 2019).

It is well-known that molecules containing atoms with lone-pair electrons, such as oxygen, nitrogen and sulfur are frequently used to interact with metals in different hydrometallurgical processes involving metal solubilization (e.g., leaching processes), extraction (e.g., liquid-liquid and solid-liquid extraction processes) and removal (e.g., via the use of sorbent materials). Hence, the search and extraction of natural compounds containing those groups of atoms from plants can be determinant to develop green and more

environmentally friendly industrial processes. Plant active compounds, depending on their nature, contain polar functional groups, such as carboxyl, phenolic, hydroxyl, sulfo and amino groups that are capable of interacting with metal ions through different mechanisms such as complex/chelate formation (Mejare and Bülow 2001; Clemens 2001; Ma et al. 2016), reduction (Sharma et al. 1998; Ma et al. 2016; Ishak et al. 2019), ion exchange (Gurung et al. 2013; Anjum et al. 2015; Li et al. 2017), sorption (Pietrobelli et al. 2009; Akpomie et al. 2015), electrostatic attraction (Yermiyahu and Kinraide 2005), covalent binding (Anjum et al. 2015), van der Waals attraction (Pietrobelli et al. 2009) and precipitation (Pietrobelli et al. 2009; Ma et al. 2016).

These compounds with desired metal interaction properties, can be used as an alternative to conventional methods in different applications relating to metals as they are renewable, eco-friendly and based on low-cost materials. They have potential to be used in different metal related industrial applications like metallic nanoparticle synthesis, metal related pharmaceuticals, metals' corrosion inhibitors, wastewater treatment, metal recovery, etc. (Table 1). The attempt to use plant based-compounds for metal recovery or removal from contaminated waters/wastewaters is a new and very promising topic, aiming the development of greener technologies in alternative to the traditional ones (chemical precipitation, ion exchange, and electrochemical removal) which are frequently non-environmentally friendly and not suitable to be applied for metal recovery from low grade minerals and secondary sources.

In the present review, the emphasis is on the most important variety of molecules of plant secondary metabolites reported as capable of specific

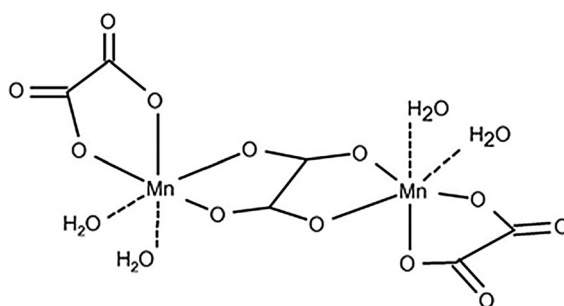


Fig. 1 Schematic view of the Mn(II) complexes with oxalate (Baran 2014)

metal(s) interaction, aiming to offer an overview of the many possible fields of application of these compounds in research, industry and health.

Plant metabolites with metal interaction potential

Organic acids

Organic acids are organic compounds possessing the carboxyl group (R-COOH) which has acidic characteristics usually associated to their ability to donate protons to water molecules (Brønsted-Lowry theory), in what is called dissociation reactions. Acids are classified as strong, if the reaction with the solvent is sufficiently complete leading to no undissociated solute molecules in the solution. Otherwise, if a partial dissociation occurs, which is the most frequent situation within organic acids, they are classified as weak, which means they react incompletely with water producing solutions containing both the parent acid and its conjugate. Different organic acids such as citric, oxalic, malic, malonic, aconitic and tartaric acids, possess at least one carboxyl group, that after losing their proton may act as oxygen-electron donor ligands (Anjum et al. 2015), thus reacting with metals and forming complexes and chelates. Organic acids possess varying negative charges (due to the dissociation degree of the carboxylic groups depending on the medium pH) responsible for complex formation with many different metal ions in the solutions.

It has been argued that organic acids complexation with metals plays a vital role in transporting the heavy metals from roots to shoots (Rascio and Navari-Izzo 2011). For instance, citrate has a strong metal ion chelation, especially in the case of Fe^{2+} (Clemens 2001), Al^{3+} (Ownby and Popham 1990), Ni^{2+} (Ferreiro et al. 2020) and Zn^{2+} (Godbold et al. 1984). Also, there are works reporting that citrate has a high affinity for other metals like Zn, Ni, Cd, and Co (Anjum et al. 2015). Higher amounts of citrate is found in different plants like in spinach leaves, Lemons and wild strawberries, containing about 8 to 15% citrate of their dried weight (Popova and Pinheiro de Carvalho 1998).

Oxalate is the smallest organic dicarboxylate ligand among low molar mass organic compounds and is also one of the most abundant low molar mass organic acids in nature (Strobel 2001). It is present in relatively

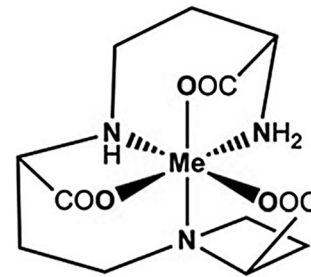


Fig. 2 Structure of nicotamine-metal complex (Kutrowska and Szelag 2014)

low amounts in most of plants but it can be found in elevated concentrations in some extreme oxalate accumulator varieties (about > 3–80% oxalate (w/w) of plants' dried weight) (Libert and Franceschi 1987) from the families of *Agavaceae*, *Aizoaceae*, *Amaranthaceae*, *Araceae*, *Cactaceae*, *Euphorbiaceae*, *Fabaceae*, *Oxalidaceae*, *Polygonaceae* and *Poaceae* (Reyers and Naude 2012). The oxalate anion is an extensively investigated and well known ligand, capable of generating expansive varieties of complexes and salts with most of the metal oxides and bases (Cotton and Cotton 1999). As oxalate can act in the form of mono-, bi-, tri- and tetradentate ligand, it has the potential to form mononuclear and polynuclear metal complexes (Fig. 1) (Baran 2014). There are many more oxalate metal (such as Mg(II), Fe(II), Zn(II), Co(II), Ni(II) and Mn(II)) complexes reported by Baran (2014). In plants, as implied by Çalişkan (2000), oxalate has an important role in balancing the high concentration of cations (like Na^+ , Ca^{2+} and NH_4^+) over anions (like Cl^- , H_2PO_4^- and NO_3^-).

Amino acids

Amino acids are a type of organic acids that contain amine and carboxyl groups coupled with particular side chains for each amino acid (Nelson and Cox 2005). These molecules have been found throughout the life science and vary tremendously in their function and complexity. Amino acids and their derivatives are compounds with metal interaction capabilities, cheap and soluble in aqueous media. These features, make them an essential part in elevating plant tolerance through metal stress. Unfortunately, the literature is scarce on information

regarding the mechanism of metal chelation by these compounds.

There are studies suggesting that these compounds may form five membered chelates with different metals through their amine and carboxylate groups (*N, O*-chelation) (Laurie 1995). They may also have other metal binding sites on the side chain of their molecules, making them able to interact with a variety of metals. Groups such as the imidazole ring (a planar 5-membered ring with the general formula of 1,3-C₃N₂) of histidine, the phenol ring of tyrosine, the β- and γ-carboxylate groups in glutamate and aspartate, the thiol group (R-SH) of cysteine and the thioether moiety (R-S-R) of methionine are often the important metal binding sites in amino acids (Laurie 1995).

Betaine is a quaternion ammonium compound containing a group of carboxylic acid. Among various types of this amino acid, glycine betaine is the most common. The role of the glycine betaine in the plants exposed to high levels of metals has been reported to be as a metal chelator, osmoprotectant and reactive oxygen species scavenger (Gill et al. 2014; Hossain et al. 2015; Ali et al. 2020).

There is not sufficient information in the literature regarding the metal specificity of amino acids and their derivatives. In plants, compounds like proline and glutamic acid, nicotianamine (non-protein amino acid) and polyamines play a major role in metal detoxification and chelation (Hasanuzzaman and Fujita 2013; Anjum et al. 2015; Delangiz et al. 2020). For example, in copper deficiency and excess conditions, nicotianamine, proline and histidine are reported to have a critical role in copper chelation in xylem sap of *Brassica carinata* (Irtelli et al. 2009). Besides metal binding capacities, proline and histidine are known to be accumulated and act as signaling and antioxidant agents in the plants exposed to heavy metals (e.g., Cd, Ni and Cu) (Richau and Schat 2009; Anjum et al. 2013; Gill et al. 2014). Histidine, as an important nitrogen donor ligand, is a crucial compound in metal

accumulator plants such as *Alyssum lesbiacum* (Krämer et al. 1996). Histidine is considered as an important metal chelator in plants through its amino, carboxyl and imidazole functional groups (Anjum et al. 2015; Seregin and Kozhevnikova 2020). Its metal chelation role in plants exposed to various metals is reported by many researchers (Richau and Schat 2009; Richau et al. 2009; Monsant et al. 2011; Seregin and Kozhevnikova 2020).

The non-proteinogenous amino acid nicotianamine is a vital component of plant metal assimilation and a homeostasis as it is a capable metal chelator; it has a key role in uptake, phloem transport and cytoplasmic distribution (Agnihotri and Seth 2019). Literature provides evidence regarding the accumulation of nicotianamine in plants upon exposure to different metals specially Zn, Cu, Fe, Ni and Cd (Irtelli et al. 2009; Mehes-Smith et al. 2013; Chen et al. 2018). The presence of six functional groups gives nicotianamine its octahedral coordination and potential for the chelation of different metals (Fig. 2) (Rellán-Álvarez et al. 2008). Finally, the pK of the metal-nicotianamine complexes along with the pH of the solution were considered to control the chelation ability of nicotianamine (Rellán-Álvarez et al. 2008).

Amino acids can also be used to synthesize other compounds with metal chelating ability; for instance, deoxyalliin (S-allyl-L-cysteine) is one of the cysteine derivatives with vegetal origination. Deoxyalliin is a strong ligand with the ability to synthesize compounds with bioactive metals such as Cu, Ni, Fe and Co (Massabni et al. 2005).

Proteins

Proteins are large natural molecules composed of one or more chains of amino acids in a specific order. They interact with different metal ions and therefore, these interactions play an important role in biological systems. Plant waste (such as soybean, corn etc.) and

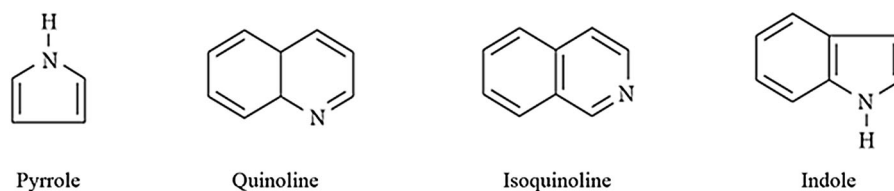


Fig. 3 Typical basic structure of alkaloids (Achilonu and Umesiobi 2015)

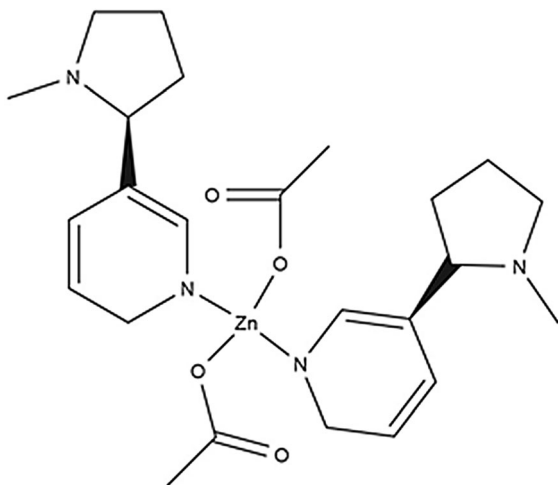


Fig. 4 Structure of zinc-nicotine complex (Mahmood et al. 2018)

waste from agricultural industries are often composed of protein-rich biomass, a part of which has been used as a source of peptides and amino acids. For example, calmodulin that can be found in plants like *Arabidopsis thaliana*, *Oryza sativa*, *Nicotiana tabacum*, *Medicago truncatula*, *Glycine max*, etc. (Ranty et al. 2006) is a calcium-binding protein (with two domains, each domain contains two Ca^{2+} binding sites) which is present in both apo- and holo-form in plant cells (Chin and Means 2000).

Moreover, among protein-based metal chelators, metallothioneins are an important class. Metallothioneins possess a thiol group ($-\text{SH}$ group) being S- an electron donor ligand. They have low mass weight and are Cysteine-rich metal-binding proteins (Cysteine (Cys) is a semi essential proteinogenic amino acid with a thiol side) that are distributed in prokaryotic and eukaryotic organisms and according to the arrangement of Cys residues are classified as Class I and II (Cobbett and Goldsbrough 2002). All the plant metallothioneins are in Class II and typically contain two Cys-rich metal binding domains in carboxy- and amino- terminal regions (Cobbett and Goldsbrough 2002). Covalent binding of metal atoms involves sulfhydryl cysteine residues. The C-terminal part (the α -domain) can bind to the four divalent metal ions, while the N-terminal part of the peptide is designated as β -domain and has three binding sites for divalent metal ions (Ruttkey-Nedecky et al. 2013). A principal feature of metallothionein complexes with metal ions

is the co-occurrence of low kinetics and high thermodynamics, resulting on a tight metal complexation along with the high availability of a part of metals for other proteins (Hassinen et al. 2011). Compounds from the metallothioneins family are a wide range of small Cys-rich proteins, with the potential of binding transitional metal ions such as Cd^{2+} , Cu^+ and Zn^{2+} (Freisinger 2011; Leszczyszyn et al. 2013). Additionally, proteins are able to adsorb precious metal ions such as Au^{3+} , Pd^{2+} and Pt^{4+} (Maruyama et al. 2007) because of the strong and specific interactions between precious metal ions and proteins (Zou et al. 2000).

Alkaloids

Among the plants' secondary metabolites, alkaloids are one of the biggest groups that are found in about 20% of plant species. They are low molecular weight compounds and are generally alkaline due to the presence of a nitrogen atom in their heterocyclic ring (Fig. 3). Indeed, the properties of alkaloids are highly affected by the precise position of N atom. The low distribution of these compounds in the living organisms is due to their negatively charged nitrogen (Pelletier 1996). Alkaloids are divided into more than 20 classes like piperidine, pyridine, pyrrolidine, tropane etc. (Yang and Stöckigt 2010; Debnath et al. 2018). Some higher plants in the families of *Papaveraceae*, *Berberidaceae*, *Fabaceae*, *Boraginaceae*, *Apocynaceae*, *Asclepiadaceae*, *Asteraceae*, *Liliaceae*, *Gnetaceae*, *Ranunculaceae*, *Rubiaceae*, *Solanaceae*, and *Rutaceae* contain high levels of alkaloids (Wink 2003). Most of these compounds can be extracted and purified through acid-base extraction, although DESs (Deep Eutectic Solvents), as a green solvent, may also be applied for the alkaloid extraction (Jiang et al. 2019).

There are reports indicating that many alkaloids can form complexes with different metals which is the case of xanthine-based alkaloids (like caffeine) (Umale and Aswar 2015), pyridine group alkaloids like nicotine (Fazary et al. 2017), cinchona (quinoline group) (Boratyński et al. 2019), sparteine (quinolizidine group) (Jasiewicz 2009), quinoline derivatives (DiMauro et al. 2003) and isoquinoline derivatives (like berberine) (Khan et al. 2019; Neag et al. 2018) etc.

Berberine is an alkaloid from the protoberberine group of benzyloquinoline alkaloids. Mechanisms

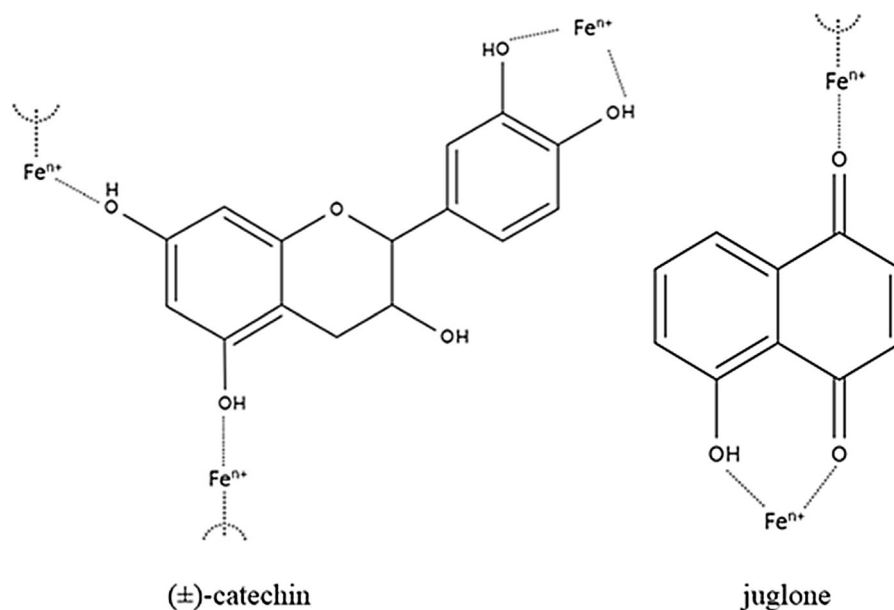


Fig. 5 A schematic view of iron chelation by two different phenolic compounds, (±)-catechin and juglone (Chobot and Hadacek 2010)

associated to its antioxidant capacity, may not only induce their metal binding potential, but can also cause an improvement in the antioxidant activity of some other endogenous compounds, like the elimination of free oxygen, oxidation of certain compounds and minimization of the destructivity of superoxide ions (Neag et al. 2018). Its antioxidant capacity is comparable with vitamin C, which is a capable antioxidant (Ahmed et al. 2015). Cinchona alkaloids are polytopic ligands capable of forming various types of complexes with many metal ions such as Pd(II), Co(III), Cu(II) etc. (Boratyński et al. 2019). Figure 4 presents the suggested structure of Zn-nicotine complex (Mahmood et al. 2018).

Besides the deep influence of sparteine and its isomers as chiral ligands in asymmetric synthesis, namely in organolithium chemistry, these have been used as ligands to form complexes with metals such as Pd, Cu and Zn (Maheswaran et al. 2006). Moreover, complexes of the sparteine-Cu(II) have been applied as a representative substance for type I copper(II) site of blue copper protein (Kim et al. 2001). A study revealed that root extract of *Ipomoea pes-caprae* rich in different classes of alkaloids such as indolizidines, ergolines and benzenoids, reduces Ag(I) to Ag(0) and effectively stabilizes the formed silver nanoparticles (Subha et al. 2015). There are many applications of

alkaloids due to their ability to bond to metal ions. For instance, different types of alkaloids have been reported to be utilized as corrosion inhibitors of various metals (Li et al. 2019).

Phenols

Phenolic compounds are mainly distinguished by the hexagonal aromatic ring bonded directly to at least one (phenol) or more (polyphenol) hydroxyl groups (–OH) and other substituents, such as methoxyl or carboxyl groups, which are responsible for the polar character of these compounds and allow their dissolution in water (Michalak 2006). They are separated into numerous diverse groups and are characterized by the number of comprised carbon atoms bonded to the main phenolic structure such as phenolic acids, flavonoids, stilbenes, coumarins, hydrolysable tannins, monolignols, lignans and lignins (Cheynier et al. 2013). Phenolic compounds are one of the most important group of secondary metabolites synthesized by plants. They comprise 0.5–5% of plants' dry weight (Swanson 2003) and are present in different plants and their wastes. They can be found in high concentrations in apple peel and flesh (Chen et al. 2012), tomato wastes (Ćetković et al. 2012), black, green and Australian fresh tea (Yao et al. 2004), spinach

(Manach et al. 2004), chestnuts (flower, skin leaf and fruit) (Barreira et al. 2008), olives (Seabra et al. 2010) and in many other plants.

Phenols have an extensive application in many industrial sectors including agricultural, pharmaceutical and petrochemical industries, pesticide and food manufacturing and iron smelters. (Stefanakis and Thullner 2016). Their functional groups provide significant capacity in scavenging free radicals, as well as hydrogen atoms or electrons donation, which is determinant for their metal ions chelating capability (Kaurinovic and Vastag 2019). However, Kulbat (2016) showed that these valuable properties of phenols can also be due to the presence of nucleophilic aromatic rings in conjunction with the occurrence of definite functional groups such as carboxyl, hydroxyl and carbonyl groups, making them able to bind to different metals (Liu et al. 2018). This ability is important for the plants, since phenols enhance nutrient uptake by forming chelates with metal ions and promotes soil porosity and active absorption sites with accelerated mobilization of different metals such as iron, zinc, calcium, magnesium, potassium and manganese (Seneviratne and Jayasinghearachchi 2003). Chobot and Hadacek (2010) for example, were able to synthesize complexes of iron ions using phenolic secondary metabolites extracted from plants, such as (\pm)-catechin and juglone as shown in Fig. 5.

Moreover, some other works suggest that peroxidases and phenolic compounds in plants are involved in some defense reactions against oxidative stress mediated by copper ions (Posmyk et al. 2009). Studies imply that in many plants exposed to heavy metals, high levels of phenolics are secreted by the roots

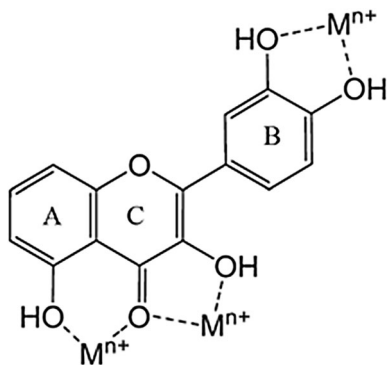


Fig. 6 Typical metal (M) chelation sites in flavonols (Pietta 2000)

(Kováčik et al. 2010; Mongkhonsin et al. 2016). To reveal the interaction of these phenolic compounds with heavy metals, Lavid et al. (2001) extracted phenols from the rhizome of *Nymphaea* and reported that the extracted phenols can directly bind and inactivate heavy metals such as Hg(II), Pb(II) and Cr(VI).

Furthermore, phenolic compounds have antioxidant properties and ability to quench free radical reactions (Bozin et al. 2008) in a number of ways. They are involved in reactions with reactive oxygen and nitrogen species in a termination reaction and are also capable hydrogen donors, preventing new radical generation (Keerthana et al. 2019). Importantly, phenol antioxidant capacity is also attributed to their chelating ability of metal ions associated with the generation of free radicals (Yang et al. 2001). There is also another mechanism described as responsible for the antioxidant ability of phenols. Milić et al. (1998) mentioned that lipid hydroperoxide (LOOH) can be decomposed by metal ions' reaction leading to the hemolytic cleavage of the O–O bond, originating lipid alkoxy radicals, which start free radical chain oxidation. Therefore, by trapping the lipid alkoxy radical, phenolic antioxidants inhibit lipid peroxidation which relies on the phenol's structure, total number and precise position of the hydroxyl groups in their molecule (Milić et al. 1998).

The most common extraction procedures that have been used in extraction and isolation of phenolic compounds from plants are liquid-liquid extraction (Garcia-Salas et al. 2010), microwave-assisted extraction (Zin et al. 2020), supercritical fluid extraction (Tyśkiewicz et al. 2018) and ultrasound-assisted extraction (Medina-Torres et al. 2017). Most suitable solvents for polyphenol extraction from plants are aqueous mixtures with polar solvents including acetone (Park et al. 2014), ethanol (Taamalli et al. 2012), methanol (Dzah et al. 2020) and ethyl acetate (Castro-Vargas et al. 2010). Ethanol is a very efficient solvent for polyphenol extraction and is not hazardous for either human or the environment. On the other hand, low molecular weight polyphenols are extracted more effectively by methanol. Aqueous acetone is a favorable solvent for high molecular weight flavanols' extraction (Do et al. 2014). Ionic liquids (ILs) and DES have been proposed as a greener alternative to the common solvents and have gained more attention in various applications, including plant extract

preparation. ILs are a combination of organic salts with low melting point and organic cations along with organic or inorganic anions. Unlike volatile organic solvents, ILs have very unique characteristics like good dissolving and extracting ability, high thermal stability, negligible vapor pressure, very wide liquidus range, good microwave absorbing ability and designable structures (Hoffmann et al. 2003; van Rantwijk and Sheldon 2007). ILs are efficient extractants of compounds with various polarities such as phenols (Du et al. 2009), alkaloids (Lu et al. 2008), organic acids (Absalan et al. 2008) and amino acids (Tang et al. 2010) from aqueous solutions. The application of ILs in association with other extraction techniques, namely ultrasonic treatment (Fan et al. 2012) and microwave (Swatloski et al. 2002) has been suggested for a more successful extraction of diverse kinds of natural compounds from solid materials such as plant biomass.

A novel class of solvents are Deep Eutectic Solvents (DES), which are prepared by combining two inexpensive and safe solid compounds (not essentially salts), such as sugars, choline and chloride with a much lower melting point than that of each of their components (Abbott et al. 2004). They have been recently used for the separation and extraction of bioactive compounds like phenols, alkaloids, flavonoids and catechins from plants (Cvjetko Bubalo et al. 2018; Huang et al. 2017; Jiang et al. 2019; Qi et al. 2015). Most of the DESs present advantages over conventional extractants such as ease of synthesis, safety, low-cost. They are also reported as energy efficient, recyclable, biodegradable and having negligible volatility at room temperature (Khandelwal et al. 2016), which are, in addition, important features. Many recent studies have applied DES and natural deep eutectic solvents (NDES) for the extraction of bioactive compounds from plants including alkaloids, flavonoids, phenols and catechins (Cvjetko Bubalo et al. 2018; Huang et al. 2017; Jiang et al. 2019; Qi et al. 2015).

Flavonoids

Flavonoids are derivatives of simple phenols with a general chemical structure based on 15-carbon skeleton (Fig. 6) consisting of two phenyl rings (A and B) and a heterocyclic ring (C) (Scotti et al. 2011). Flavonoids are one of the major group of plant

secondary metabolites and it is estimated that almost 2% of photosynthesized carbon by plants is used for the synthesis of these compounds or related substances (Robards and Antolovich 1997). Until now, more than 8000 flavonoid compounds have been identified (Yan et al. 2020). In plants, the synthesis of flavonoids is reported to increase under the microbial infection, injury, decrease in temperature and deficiency of nutrients (Michalak 2006). This class of phenolic compounds are extensively distributed in all plants and exist mainly in higher concentrations in photosynthesizing cells. Different types of flavonoids can be found in high contents in tea (López et al. 2001) and families of *Asphodelaceae* and *Euphorbiaceae* (Lopez-Lazaro 2009), *Tiliaceae*, *Leguminosae* and *Compositae* (Gupta et al. 1983), *Mimosoideae* and *Bignoniaceae* (Sannomiya et al. 2005).

Importantly, some flavonoids protect plants from heavy metal stress as they are proficient metal (such as Cu, Zn, Fe) chelators, avoiding creation of hydroxyl radicals through Fenton's reaction (Williams et al. 2004). Flavonoids can protect plants from the toxicity of high heavy metal concentrations in soils by chelating these metals (Kidd et al. 2001). Flavonol group molecules have three main sites that can be potentially coordinated with transition metal ions including the 3-hydroxyl and the 4-carbonyl groups in the C ring, the 5-hydroxyl group of the A ring and the 4-carbonyl group in the C ring and the 3'- and 4'-hydroxyl groups of the B ring (Fig. 6) (Rice-Evans 2004; Williams et al. 2004; Samsonowicz and Regul-ska 2017). Pietta (2000) suggested that the binding sites for metals in the flavonoid molecules are the 4-oxo and 5-hydroxyl groups between the A and C rings and the catechol moiety in the ring B, the 3-hydroxyl and 4-oxo groups in the heterocyclic ring C (Fig. 6). The importance of the catechol moiety in the B ring for the Cu^{2+} chelate formation has been reported by Brown et al. (1998) as the major contributory site of the copper chelation (Brown et al. 1998). Quercetin is a well-recognized compound for chelate formation and stabilization of iron ions. Due to considerably high antioxidant activity and complex formation with Cd(II) and low toxicity, sulfonic water soluble derivatives of quercetin and morin are reported as potential candidates for detoxification of cadmium (Chlebda et al. 2010).

Kostyuk et al. (2004) demonstrated that metal-flavonoid chelates display superoxide dismutase

activity. For example, Bota et al. (2011) demonstrated a correlation between flavonoid and CuSO_4 concentrations in cell cultures of *Digitalis lanata*. Similarly, this was confirmed by Kidd et al. (2001) in corn plants (*Zea mays* L.) grown on soil contaminated with aluminum ions, where high levels of catechin and quercetin in the root exudates were observed.

Flavonoids are also important molecules in metal chelation and reduction and in nanoparticles formation (Makarov et al. 2014). This ability is due to the presence of functional groups including carbonyl moiety and multiple hydroxyl groups (Maršlin et al. 2018). Moreover, the possible role in metallic ions' reduction through the transformation of internal ketones into carboxylic acids in these compounds has been discussed (El-Seedi et al. 2019). Finally, it should be noted that chelate formation of metal ions by some flavonoids can happen by the carbonyl group or π -electrons of these molecules; as an instance, extracted apiin (apigenin glycoside) from *Lawsonia inermis* was successfully applied for the synthesis of anisotropic Au nanoparticles and quasispheroidal Ag nanoparticles (Kasthuri et al. 2009).

Tannins

Tannins are a class of phenol-containing macromolecules that are synthesized by higher plants and accumulated in their tissues (e.g., making up about 30% of the dry mass of tea) (Shirmohammadli et al. 2018). They are categorized as water soluble phenolics compounds with a molar mass in the range of 300 and 3000 Da with some common features that enables the classification of these types of compounds in two main groups: hydrolysable tannins and condensed tannins (Khanbabaee and van Ree 2001). Hydrolysable tannins include gallotannins and ellagitannins that are respectively comprised of gallic acid or hexahydroxydiphenic acid esters linked to a sugar moiety, while more complicated ones can be formed by oxidative transformations that can yield macrocyclic ellagitanins (Okuda et al. 2000). However, the chemical structure of gallotannins depends on the plant species producing the compound and until now more than 8000 different tannins have been isolated and characterized and certainly, there are many more tannins that their chemical structure and characteristics have not been precisely determined yet. Condensed tannins

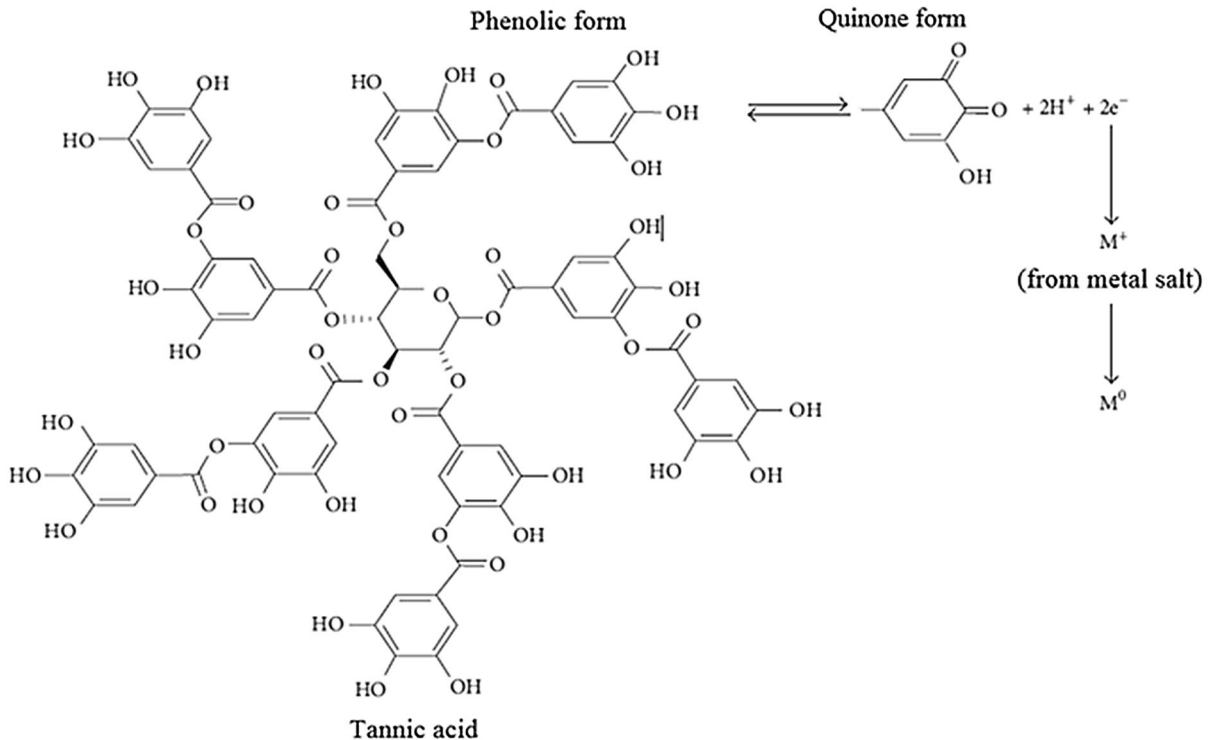


Fig. 7 Metal ion reduction mechanism by tannic acid-based compounds (Ahmad 2014)

(nonhydrolyzable), also called procyanidins, are polymers containing three ring flavanols linked with carbon-carbon bonds. Monomer units of condensed tannins are identified by the number of hydroxyl groups on the B-ring: procyanidins have a di-hydroxy B-ring, but prodelphinidins have a tri-hydroxy B-ring (Kraus et al. 2003). These monomer units might have a stereochemistry of both *cis* and *trans* C2–C3 (Schofield et al. 2001).

Tannins are cheap and widespread natural polyphenols and are well known for their biological activities including their potential to serve as antioxidants, protein precipitants and metal chelators. Following cellulose, hemicellulose and lignin, they have the highest abundance in plant biomass (Arbenz and Avérous 2015). The tissues of plant species from the families of *Theaceae*, *Vitaceae*, *Myrtaceae*, *Punicaceae*, *Actinidiaceae*, *Juglandaceae*, *Fagaceae*, *Rosaceae* etc. are rich in tannins (de Jesus et al. 2012; Smeriglio et al. 2017). Studies suggest that high tannin content can help plants to overcome the toxicity of high levels of metals in soils (Michalak 2006). Frequent catechol and galloyl groups, allow tannins to form stable chelates with some transitional metallic ions like iron among other metals (Lee et al. 2017). Yokozawa et al. (1998) reported that in tannins, the higher molecular weight and quantity of galloyl groups, as well as the existence of ortho-dihydroxy structure, significantly enhances their scavenging activity. Ellagitannins and gallotannins molecules possess many different chelating groups, which enable them to chelate efficiently ferric iron in solution and form blue-black precipitates, or to separate and extract it from alternative iron/ligand complexes rather than other low molecular weight and monofunctional phenolic compounds (Mila et al. 1996). Proanthocyanidins are capable Fe(III) chelators (Santos-Buelga and Scalbert 2000). Epigallocatechin gallate, the lowest molecular weight tannin, forms strong complexes with ferric ion at a stoichiometric ratio of 2:1 at pH 7 (Karamać and Pegg 2009).

A study by Oladoja et al., (2011) shows that tannin resins interact with metals through complex formation and ion exchange. They discussed that metal complexation occurs by two adjacent hydroxyl groups (catechols), while a third adjacent hydroxyl group (pyrogallols), enhances the stabilization of the formed complexes. Additionally, dissociation of the surface groups by the increase of the pH, increases the metal

complexation potential and electrostatic attraction by tannins (between the surface of the negative biosorbent and the positive adsorbate). These are the reasons why the patterns observed in terms of pH influence assays carried out for Cu(II), Pb(II), Zn(II) and Ni(II), which shows an increase of the adsorbed amounts with the raise of pH, in acidic range, with highest removals reached at pH 4 or 5 (Şengil and Özacar 2008; Yurtsever and Şengil 2009).

Tannin gels have a high tendency to interact with heavy metals including lead (Yurtsever and Şengil 2009; Şengil and Özacar 2009), chromium (Nakano et al. 2001; Inoue et al. 2010; Alvares Rodrigues et al. 2015), copper (Şengil and Özacar 2008, 2009), and zinc (Şengil and Özacar 2009; Arasaretnam and Karunanayake 2010) in aqueous solutions. In addition, different works with wattle tannins, obtained from the bark of black wattle (*Acacia mearnsii*) trees that are commercially available, revealed precious metal complex formation with metals such as Pd(II) (Kim et al. 2007), Pt(IV) (Morisada et al. 2011), Au(III) (Ogata and Nakano 2005) and Ag(I) (Cataldo and Angelini 2013).

In tannic acids, through the oxidization of phenolic groups to quinones, electrons are released which may consequently get involved in the reduction of metallic ions (Fig. 7). Phenolic and polyphenolic compounds are electron rich and strong antioxidants, which comprise their ability to release free reactive hydrogen atoms (Aromal and Philip 2012).

Different industrial applications of tannins or tannin-based compounds rely on the complex formation with metal ions. Humans have taken advantage of the coordination complex of Fe(III) ions with tannins (Lee et al. 2015; Park et al. 2017) throughout history, such as iron gall ink, which has been used since the Middle Ages in Europe (Han et al. 2019). Other applications of tannins in industry include their use as: corrosion inhibitors for steel (Rahim et al. 2011; Rahim and Kassim, 2008) and non-ferrous metals (Kusmieriek and Chrzescijanska 2015), modifiers of rheological properties of minerals and clays (Chang and Anderson 1968) for applications in mineral flotation, ceramic, cement and drilling industries, agents for heavy and precious metal recovery from wastewaters (Nakano et al. 2001).

Only strong oxidants are able to oxidize tannins. However, the formed phenoxyl radical is able to interact with metals (Jovanovic et al. 1998). The

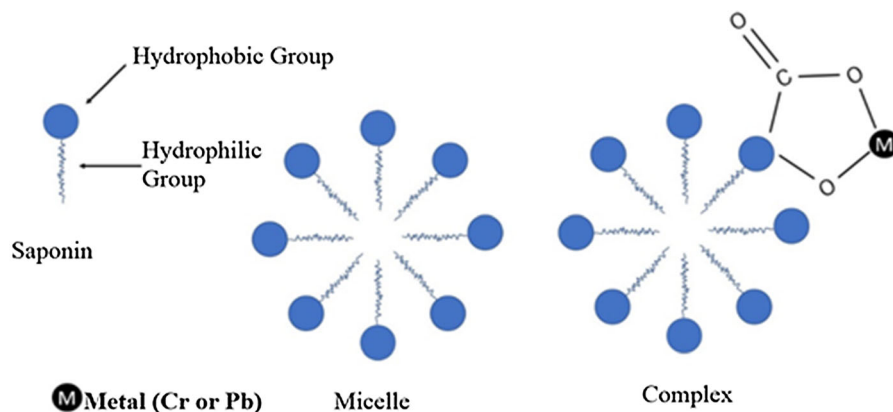


Fig. 8 Reaction mechanisms of metal ions with hydroxyl and carbonyl groups of saponins (Tang et al. 2017)

existence of several phenolic groups in the structure of tannic acids, which participate in the redox reactions through electron donation and quinone formation, makes these strong reducing properties (Ahmad 2014).

Saponins

Saponins are natural glycosides of steroids, or triterpenoids (sapogenins) and a carbohydrate moiety by ester or ether linkages with foaming characteristics. They are a class of non-ionic biosurfactants found in more than 500 kinds of plants with high surface activity, biodegradability, eco-friendly and low toxicity (Tang et al. 2017). They are included in a large group of protective molecules named ‘*phytoprotectants*’ or ‘*phytoanticipins*’ (Francis et al. 2002) and can make up to 30% of the plants’ dry mass (Fenwick et al. 1991). Saponins are divided in eleven main classes including dammaranes, cycloartanes, tirucallanes, oleananes, lupanes, taraxasteranes, ursanes, lanostanes, hopanes, cucurbitanes and steroids.

Saponins are present in different plants mainly in legumes and some medicinal herbs. Alfalfa (*Medicago sativa*), sarsaparilla (*Smilax regelii*), licorice (*Glycyrrhiza* species like *Glycyrrhiza glabra*), soapwort (*Saponaria officinalis*), soap bark tree (*Quillaja saponaria*), *Gypsophila* genus (like *Gypsophila paniculata*), horse chestnut (*Aesculus hippocastanum*), fenugreek (*Trigonella foenum-graceum*) and Mojave yucca (*Yucca schidigera*) are the most important non-food saponins sources that are being used in different applications (Hostettmann and Marston 1995;

Balandrin 1996). Because of the existence of a lipophilic aglycone (sapogenin) and hydrophilic sugar chain, saponins have amphiphilic properties resulting in foam formation (with liquid-gas phases), dispersion abilities (with liquid-solid phases) and emulsifier effect (with liquid-liquid phases) (Kregiel et al. 2017), and thus have been used as a detergent (Vincken et al. 2007).

Saponins are also reported as important agents for the heavy metal removal from aqueous wastes aiming for the remediation of contaminated sites due to their ability to form chemical complexes with metals (Abed el Aziz et al. 2017). In fact, different studies describe saponins as naturally occurring chelating agents that can be used for the elimination of contaminants caused by several heavy metals including Cd, Pb, As, Cr, Cu and Zn from contaminated waters and soils (Kiliç et al. 2011). It is reported that saponins can remove and retain heavy metals from their original solutions by complex formation with their carboxyl group (Gao et al. 2012a). Saponins are very suitable compounds for remediation of very low concentrations of heavy metals due to the presence of hydroxyl and carbonyl groups in their structure (Fig. 8) (Chen et al. 2008). During the heavy metal (like Pb, Cr, Cu, Ni, Zn) removal through different procedures such as sequential sludge washing, Huang and Liu (2013) described saponins’ capability in complex formation with the mentioned heavy metals. Moreover, Zhou et al. (2011), applied saponins to extract heavy metals and hydrophobic organic compounds (HOCs). From a chemical point of view according to El-Aziza (2018), heavy metal-saponin biochemical reactions can be

considered as a contemporary process in decontamination of industrial and other metal contaminated effluents and the synthesis of new organometallic complexes. Furthermore, there are studies suggesting that saponins can extract heavy metals from contaminated soils even more effectively than with conventional surfactants (Gusiati and Klimiuk 2012; Maity et al. 2013). Metal removal from soil and aqueous solutions by saponins must be due to strong bond formation between the metal ions and saponin as a complex (Munichandran et al. 2016). The most important chemical factors that may affect the reactions between metal bearing solutions and saponins are metal concentration, pH of the solution and the amount of saponin.

Saponins are usually extracted by liquid-liquid extraction or column chromatography. Also, saponins can be extracted by DES (Zainal-Abidin et al. 2017). During the storage or processing, specially by acid/base treatments or microbial/enzymatic transformations, the main structure of saponins can change due to the hydrolyzation of links between sugar chains and aglycones, or between sugar residues, resulting in the formation of aglycones (sapogenins), sugar residues and partially hydrolyzed saponins (prosapogenins) (Oleszek and Hamed 2010). Accordingly, plant substances must be stored using suitable techniques based on the target compound as in every efficient technology.

Polysaccharides

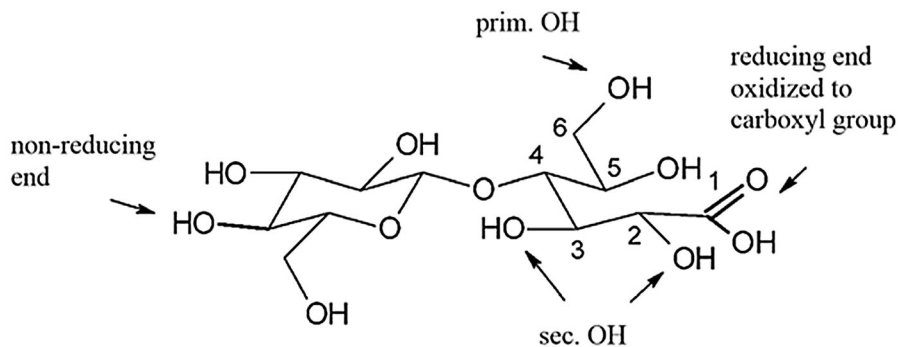
It is well known that polysaccharides are chain carbohydrate molecules originating from plants and therefore are abundant, renewable and biodegradable resources with the capacity to be interacted by chemical and physical mechanisms to an extensive

number of molecules (Ciesielski et al. 2003). During the last few decades many studies were focused on the synthesis of cost-efficient biosorbents from the biomass of different resources (Won et al. 2014). Between different materials, plant polysaccharides (like cellulose) were found to be very suitable candidates for the adsorption of various metal ions (Gurung et al. 2014).

In their polymeric chain, polysaccharides possess several functional groups (carboxyl, hydroxyl and amino), which gives them their high and selective metal adsorption capacities (O'Connell et al. 2008; Liu et al. 2013). Hence, due to their metal binding capacity and high availability, polysaccharides and their derivatives-based adsorbents could be considered as an economically viable approach in metal extraction and remediation of water sources. Because of the protonation and deprotonation of polysaccharides' functional groups (especially amine groups in amino sugars), their adsorption behavior for metal ions is influenced by the pH and because of this, they can be positively or negatively charged with varying metal sorption mechanisms. Biosorption is a combination of different mechanisms including complexation, ion exchange, electrostatic attraction, adsorption, Van der Waals attraction and covalent binding (Montazer-Rahmati et al. 2011; Witek-Krowiak 2012).

Polysaccharides such as starch (Yuryev et al. 2002) and their derivatives (cyclodextrin) (Del Valle 2004) are effective natural metal adsorbent polymers. However, natural forms of polysaccharides have inadequate chemical resistance and structural strength, making them unsuitable for a direct application as biosorbents. Therefore, these natural compounds need some chemical modifications by cross-linking and surface grafting to be more efficient biopolymeric adsorbents. For example, there are works suggesting

Fig. 9 Functional groups present in processed cellulose (Wurm et al. 2020)



that the modifications could be applied to starch in order to make it a good adsorbent for heavy metals and dyes by the introduction of active groups like carboxylate, xanthate, amine phosphate, acrylate and many other groups that have chelating abilities (Kweon et al. 2001). Crini (2005) showed that several hundred ppm of divalent metal ions (Cu, Pb, Cd and Hg) could be extensively removed from water by dispersing 1% of the modified starch in a few minutes. It is suggested by Kim and Lim (1999) that starch, after the crosslinking with carboxymethylation and POCl_3 , could be a good sorbent for the different heavy metal ions.

Many of the cellulosic-based sorbents have high metal ion interaction potentials and a part of them present better selectivity towards some precious metals in highly acidic conditions (Pangeni et al. 2012; Dwivedi et al. 2014). In a related work, in order to improve biosorption performance, cellulosic based sorbents underwent some modifications with sulfonic, sulfhydryl or amino groups (Dwivedi et al. 2014). Many different studies used powdered plant containing cellulose or alginate and they were successfully used as biosorbents (Vijayaraghavan et al. 2011; Jain et al. 2016; Wang et al. 2021). Precious metal recovery by polysaccharide-based biosorbents has been the main focus of many studies for a long time. Amongst different types of polysaccharides, cellulose and alginate could be efficient base matrices for the recovery of heavy and precious metals (O'Connell et al. 2008; Abdolali et al. 2014).

The main mechanisms known for metal and dye adsorption on cellulosic biosorbents is chelation and ion exchange, which frequently results in H_3O^+ being released into the aqueous solution (Abdolali et al. 2014). As depicted in Fig. 9, a free hydroxyl group is present at one end of the cellulose chain and is referred as the non-reducing end, whilst an aldehyde group at the other end of the chain is called a reducing end, which can simply get oxidized to carboxylic groups (Wurm et al. 2020). Ionic exchange is a process including electrostatistical interchanges among cations and negatively charged groups of plants' cell walls (Fiol et al. 2006).

Applications of the plant-based compounds with metal interaction ability

Strict environmental regulations applied to contaminants discharged from industrial operations are being introduced in most of the developed and developing countries (Abdel-Aty et al. 2013). Commonly used methods of metal recovery/removal from solutions and soils are ion exchange/chelation, precipitation, solvent extraction/liquid membrane and electrolytic recovery (Li et al. 2009; Hong-Bo et al. 2010). These procedures are frequently not economically viable and there is a lack of efficiency in metal recovery or removal especially when the concentration of metals in wastewaters is low (Hammami et al. 2003). Beside this, the chemical compounds being used in the metal industries and then released into the environment in wastewaters could be harmful to both ecosystems and human. Thus, in recent years, more attention has been paid to biological methods for the treatment of heavy metal bearing effluents aiming to reduce their concentrations in the environment to acceptable levels. For this reason, utilization of plant-based compounds can represent a promising alternative that deserve to be explored.

Some of the most important biological methods based on active compounds obtained from plant materials have been previously tested in research studies and thereafter introduced for industrial purposes. Additional applications of plant-based compounds benefiting from their metal interaction capacity are also reviewed. These methods are supposed to be more cost effective, attractive from an environmental point of view and efficient in terms of metal interaction efficiency.

Metal insolubilization

Chemical precipitation of metals is one of the most widely used methodologies applied for metal/heavy metal removal from different metal contaminated effluents. However, conventional methods like chemical precipitation that are being used for the treatment of wastewaters polluted with metals have some limitations. These methods present weak aspects such as slow metal precipitation and partial metal removal (Aziz et al. 2008), the creation of huge amounts of metal polluted sludge (Ayangbenro and Babalola 2017), high costs, energy and reagent requirements

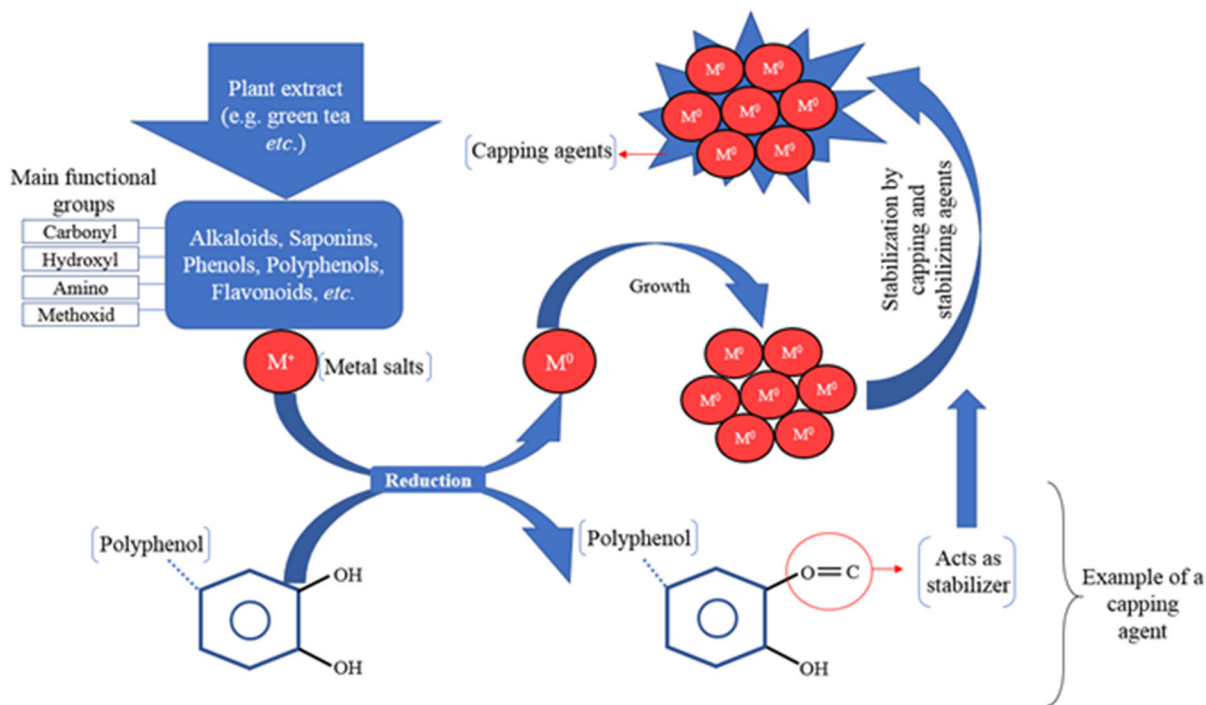


Fig. 10 Suggested mechanism for metal reduction and metallic nanoparticle synthesis

and problems related to precipitates solubility and the clogging (Kanamarlapudi et al. 2018).

Plant compounds such as phenols, saponins, alkaloids etc. extracted from plants have potential to precipitate metals depending on their nature and this ability usually relies on complex/chelate formation and the reduction of metals by these compounds. As an example, these compounds could be utilized to precipitate or separate different metals from metal bearing solutions. For instance, McDonald et al. (1996) reports the successful precipitation of zinc and copper using tannins and low molecular weight phenols extracted from plants. Gatew and Mersha (2015) used *Moringa stenopetala* seed powder extract to remove chromium from tannery wastewater which results in 99.86% of chromium removal. In addition, Agwaramgbo et al. (2012) described the successful lead (Pb) precipitation from an aqueous solution by aqueous extracts of some plants. In another work, (Lathan et al. 2013) Lathan et al. (2013) used some plant extracts rich in polyphenols to remove lead from a solution (with initial concentration of 1280 mg/l) and reported that spinach, tea and instant coffee extracts efficiently precipitated more than 90% of the lead in the solution. These results proved the metal bio-

reduction methods assisted by plant extracts rich in phenols/polyphenols is very effective to remove and recover metals from wastewater.

Moreover, some researchers suggested that saponins could be applied as natural chelating agents to solve the problems caused by different heavy metals like Cd, Cr, Zn, Cu, As and Pb from wastewater and soil (Kiliç et al. 2011; Gonzalez-Valdez et al. 2013). The presence of strong bonds in saponin-metal complexes is considered to be the reason for metal removal from soils and solutions (Munichandran et al. 2016). Abed El-Aziz et al. (2017) have successfully prepared heavy metal saponin complexes by combining water extract of *Citrus aurantium* and *Olea europaea* and heavy metal bearing solutions.

Metal precipitation by plant extracts depends on some operational factors like settling time, type of plant compound in plant extract, metal/heavy metal type and concentrations, extract concentrations, pH and temperature which can affect the metal precipitation process.

Synthesis of metal nanoparticles

Nanoparticles are a special group of materials with a dimension below 100 nanometers that due to their small size have unique features and extensive applications in miscellaneous fields (Mohamad et al. 2013). Metallic nanoparticles are nowadays widely used compounds with many applications such as degradation of dyes (Vomáčka et al. 2016), catalysis (Yang et al. 2010), antibacterials (Naika et al. 2015) and gas sensors (Su et al. 2015). Nanoparticles are usually synthesized through physical and chemical procedures, that are mostly expensive and non-environmentally friendly (Makarov et al. 2014).

In parallel with growing consciousness of the necessity of green chemistry and sustainability, environmentally friendly methods for biosynthesis of nanoparticles are gaining more attention. One of the methods to synthesize nanoparticles is the green synthesis technique which is ecological friendly, simple, cheap and very fast (Mittal et al. 2013). Biosynthesis of nanoparticles by plant extracts is a way to reduce the use of hazardous chemicals compounds, avoiding the environmental pollution and therefore the biological routes for synthesis of nanomaterials are getting more popular. Nanoparticles synthesized using plants are reported to be highly stable and more variable in shape and dimensions (Irvani 2011). It is shown by many research studies that plants containing high amounts of active metabolites including phenols, flavonoids, saponins, steroids, alkaloids that can act as reducing, capping or stabilizing agents, have substantial capabilities to reduce and maintain metals into their respective nanoparticles (Ajitha et al. 2016; Mystrioti et al. 2016; Sigamoney et al. 2016; Martínez-Cabanas et al. 2016; Devatha et al. 2016; Siddiqi and Husen 2017). Utilizing plant extracts as reducing, capping and stabilizing agents obviates the need to use different chemical reagents for all those purposes (El-Seedi et al. 2019).

Capping agents are biological or chemical components (Fig. 10) that naturally restrict the reaction and the particle growth in the nanoparticles synthesis; the reduced metals form nanostructures like nanoparticles or nanocrystals, which needs to be capped appropriately to be stable, biocompatible and functional against aggregation in different biological systems (Vadlapudi 2015). Capping agents follow different mechanisms such as steric and depletion stabilization,

electrostatic, hydration and van der Waals forces (Kim et al. 2004). Usually, the H-donating ability of polyphenols are associated to the metal ion reduction capacity. Due to the redox reaction that leads to the reduction of metal ions, the OH group in the reduced form of polyphenols is converted into a carbonyl group (C=O), that electrostatically stabilizes the metal nanoparticles (Fig. 10) (El-Seedi et al. 2019).

Biosynthesis methods for metallic nanoparticle production are obviously more cost-efficient and environmentally friendly than other physical or chemical procedures. Even though the biosynthesis of metallic nanoparticles by plant compounds has been extensively studied, the exact mechanisms of the process are not clearly understood (Punjabi et al. 2015). However, the main functional groups present in different plant compounds such as carbonyl, hydroxyl, methoxide and amino are known to bind to metal ions through electrostatic interactions and reduce them (Küüinal et al. 2018). Hydroxyl groups and other substituents, such as methoxyl or carboxyl groups in the phenolic compounds are key groups for the metal chelation potential of those plant-based compounds.

There are many reports regarding different metallic nanoparticle synthesis using plant compounds; for instance, *Ambrosia maritima*, *Callicarpa maingayi* and *Coleus aromaticus* extracts were used for the synthesis of metallic Ag nanoparticles (Shameli et al. 2012; Vanaja and Annadurai 2013; El-Seedi et al. 2016). Polyphenols extracted from the leaf of *Tabebuia berteroi* (Vellaichamy and Periakaruppan 2016) and flavonoids, tannins and phenolics extracted from *Withania coagulans* are shown as responsible compounds for the reduction of lead and iron ions into their metallic nanoparticles, so along with graphene oxide (rGO) the respective nanocomposite is formed (Atarod et al. 2016). The flower extract of *Anthemis xylopoda* (Nasrollahzadeh and Sajadi 2015a, b), leaf extract of *Ziziphus ziziphus* (Aljabali et al. 2018), extract of *Garcinia mangostana* fruit peels (Xin Lee et al. 2016) and many others were reported for Au(III) reduction into Au(0) nanoparticles. Also, Nasrollahzadeh and Sajadi (2015a, b) used the quercetin (flavonol) rich leaf extract of *Ginkgo biloba* to reduce Cu(II) to Cu(0) nanoparticles in a two-step process, without requiring any additional agents for capping or stabilizing the particles.

Some other examples of metal oxide nanoparticle synthesis using plant extracts include CdO using

Parkia speciosa (Permana and Yulizar 2017), Fe_3O_4 using *Graptophyllum pictum* (Sari and Yulizar 2017) and ZnO using *Imperata cylindrica* (Saputra and Yulizar 2017). It is reported that *Euphorbia peplus* extract containing high levels of flavonoids and rare disaccharides, reduces AgNO_3 in the presence of Fe_3O_4 and stabilize the formed silver nanoparticles with enhanced catalytic activity (Sajjadi et al. 2017). In another work, Pd/CuO nanoparticles were effectively synthesized by seed extracts of *Theobroma cocoa*, which contains phenolic antioxidants (Nasrollahzadeh et al. 2015). There are also other reports about the synthesis of CuO nanoparticles, using extracts of *Thymus vulgaris* (Nasrollahzadeh et al. 2016), *Gloriosa superba* (Naika et al. 2015), *Citrus lemon* (Mohan et al. 2015), *Euphorbia tirucalli* (Ravikumar et al. 2014), *Tamarindus indica* (Ankamwar et al. 2005), *Azadirachta indica* (Shankar et al. 2004) and *Cinnamomum champora* (Huang et al. 2007). Nasrollahzadeh et al. (2015) synthesized very stable TiO_2 nanoparticles using *Euphorbia heteradena* extract, reporting phenolic compounds present in the extract as key factors for the reduction of the metallic ions and capping the ligands on the nanoparticle surfaces, as evidenced via FTIR (Fourier-Transform Infrared) spectroscopy. FTIR studies reported the

frequent association of terpenoids with biosynthetic metallic nanoparticles (Kavitha et al. 2017).

Other studies also suggest that proteins are effective compounds in the biosynthesis and stabilization of metallic nanoparticles (Balaji et al. 2009). Durán et al. (2015), throughout the biosynthesis of nanoparticles reports a great number of molecules, comprising amino acids and proteins with exposed disulfide bridges and thiol groups, acted as non-enzymatic capping and reducing agents. Moreover, Jain et al. (2011) identified two extracellular proteins and illustrated their roles in the biosynthesis and stabilization of silver nanoparticles.

The type and concentration of compounds present in plant extracts have high impact on the morphology of the synthesized nanoparticles, whilst the size of the particles is mainly affected by the pH and temperature of the medium (Sankar et al. 2014). Moreover, the concentration of metal ions controls the shape and size of the formed nanoparticles (Huang et al. 2007; Makarov et al. 2014). Furthermore, to synthesize nanoparticles with a controlled size and morphology, proteins and peptides can be added as biomatrices (Makarov et al. 2014). The biosynthesis of the nanoparticles allows the size and shape of the particles to be controlled due to the extremely specific reactions

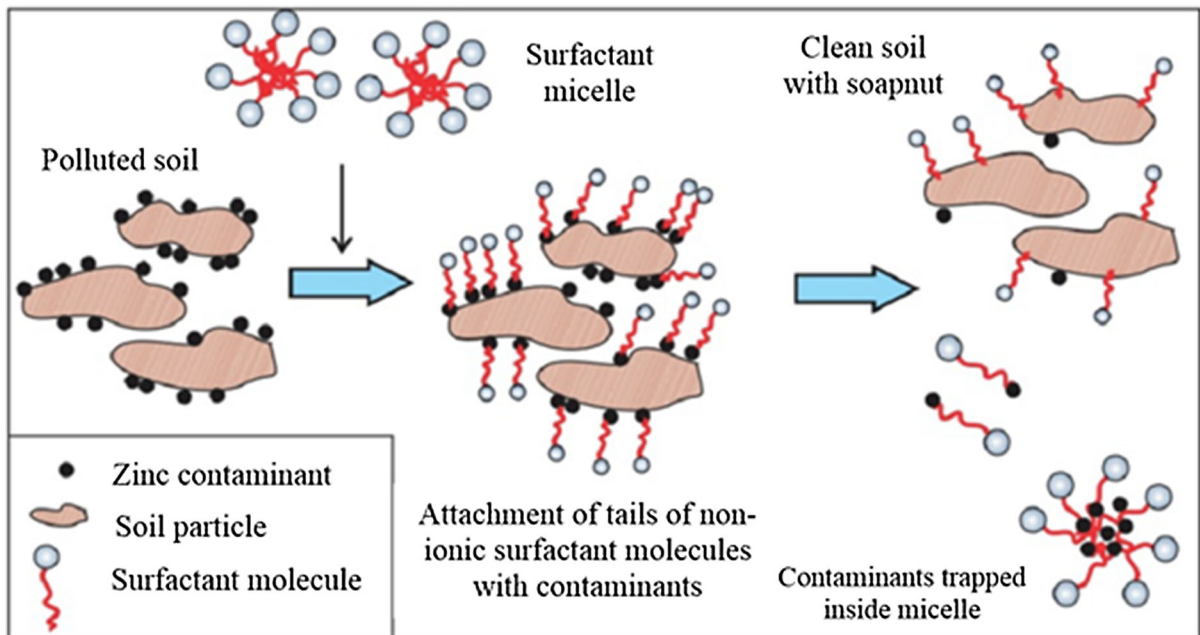


Fig. 11 Biodegradable plant-based surfactant (saponin) (Mukhopadhyay et al. 2018)

among the biomolecular templates and inorganic compounds (Das et al. 2012).

Biosorption

Biosorption is explained as the ability of a biomass to bind and concentrate metals from an aqueous solution to its structure. It is the most widely studied mechanism of metal removal that in comparison with other metal recovery/removal procedures, has high-rate kinetics, high capacity and metal selectivity balanced by the synthesis method, which makes the mechanism suitable for the complex metal polluted water streams in high volumes and low concentrations (Wang and Chen, 2009). Ideal biosorbents need to be abundant and easily accessible, stable in different conditions, have great potential for the target metals, highly selective and present simple separation from the solutions (Wang and Chen, 2014). However, one of the most important disadvantages of biosorption is that the reutilization of the sorbent material is frequently difficult, usually due to low recovery of the metal from the sorbent material. Metals biosorption on the surface of biosorbent may occur through several mechanisms including complexation or chelation, ion exchange, reduction, electrostatic interactions and microprecipitation. Different active functional groups presented on biosorbents like carboxyl, hydroxyl, amine and phosphoryl are determining for these interactions (Won et al. 2014).

A wide variety of agricultural by-products and fruit wastes such as sugarcane bagasse, banana cortex, soya bean hulls, lemon and orange peel, walnut hulls, cotton seed hulls, corn cobs and carrot residues (Kelly-Vargas et al. 2012) were used for metals biosorption. Phenolic and carboxylic functional groups present either in the cellulosic matrix or in materials related to cellulose, such as hemicellulose or lignin, can be the reason of the cation exchange properties in these residues (Nasernejad et al. 2005).

Even though the emphasis of this review is the plant-based compounds, it is worth mentioning the potential of different algal species as biosorbents and their application to the treatment of metal polluted wastewaters and/or metal recovery, because of their high sorption potential and availability.

Bioremediation of heavy metals in soils

Washing the soils using natural surfactants is a suitable alternative for the heavy metal contaminated soil remediation (Fosmire 1990). Mainly, there are two technologies to remediate the metal contaminated soils (Dermont et al. 2008). One is to immobilize heavy metals through tightly bounding the metals to soil compounds in order to minimize migration. The other consists of metal mobility by moving them to a solution by solubilization and elution in a washing solution (Pathak et al. 2009; Zhang et al. 2010a). The second process usually employs wash solutions that contain chelating agents (Zhang et al. 2010b; Zou et al. 2009), acids (Wen et al. 2009), or other suitable compounds such as surfactants (e.g. saponins) (Arwidsson et al. 2010; Guo et al. 2010) as shown in Fig. 11.

Different studies regarding the application of saponins from sources other than soapnut show heavy metal (e.g. Zn, Ni, Cd and Cu) removal from soil and a removal up to 90%, depending on the soil type and contaminant level (Song et al. 2008; Gusiatin and Klimiuk 2012). Desoky et al. (2019) supplemented saline soils contaminated with heavy metals with root extract of *Glycyrrhiza glabra* through irrigation water and analyzed its effect on the growth of *Capsicum annum*. Their results revealed a significant reduction in the content of the contaminant metals', such as Cd, Pb Ni, Cu, and Na in the plants. They hypothesized that some proteins with low molecular mass such as metallochaperones or chelators like nicotianamine, phytochelatins, spermine, mugineic acids, putrescine, metallothioneins and organic acids, or extracellular compounds including phenolics and flavonoids, heat shocked proteins, protons and some particular amino acids like proline and histidine, are possible plant compounds present in the extracts that immobilized/washed metals and reduced the negative effect of these contaminants.

Corrosion inhibitors

Metal corrosive inhibitors are usually organic compounds with an abundant number of oxygen, nitrogen and sulfur atoms with aromatic compounds (Moura et al. 2013; Felipe et al. 2013); the lone pair of electrons present on these atoms is transferred to the metal surface thus, avoiding the loss of electrons by the metal, since their molecules form bonds on the

metal surface, blocking the active corrosion site. Frequently, many of these compounds are highly hazardous for the environment and organisms and therefore, substitution of naturally produced compounds as environmentally-safe and non-toxic corrosion inhibitors has become popular (Raja and Sethuraman 2008; Prabha et al. 2012). Plant based corrosion inhibitors can be used as an effective substitute for the currently exploited organic inhibitors, due to the presence of significantly better inhibitive properties than the currently employed organic inhibitors (Baban and Milind 2011).

Recently, green corrosion inhibitors are becoming more popular because of the increase in environmental awareness that has led to restrictions and regulations of toxic corrosion inhibitors. Consequently, many studies regarding alternative and less toxic inhibitors have been reported (Li et al. 2008). Green corrosion inhibitors form a layer on the metal surface through adsorption and create a protective layer (Hefter et al. 1997). That protective barrier interacts with anodic or cathodic reaction sites and decreases the corrosive reactions (Singh et al. 2016). Green corrosion inhibitors have adsorptive characteristics that are recognized as site blocking substances (Sanatkumar et al. 2012). Studies suggest that plant extracts of *Piper nigrum* rich in phenolics, alkaloids, terpenoids or other biomolecules (such as proteins, carbohydrates and lipids) can act as corrosion inhibitors (Raja and Sethuraman 2008). There are many recent studies regarding the efficiency of different plant extracts like *Ficus tikoua* (Wang et al. 2019), olive leaves (Ben Harb et al. 2020) and *Celtis tournefortii* fruit (Sedik et al. 2020) as steel corrosion inhibitors, *Idesia polycarpa* fruit extracts as copper corrosion inhibitor (Zhang et al. 2020), *Bagassa guianensis* as zinc corrosion inhibitor (Lebrini et al. 2020) and *Sapium ellipticum* as aluminum corrosion inhibitor (Okechukwu Dominic et al. 2020).

Kundu et al. (2016) reviewed the effects of the green corrosion inhibitors in rebar embedded on concrete in pH conditions between 12 and 13. In this review, they explained the effect of *Bambusa arundinacea* extract as being due to its strong hydrophobic effects, which helps the development of a two-faced layer of iron oxides (Fe_3O_4 and Fe_2O_3) adsorbed to the steel surface (Asipita et al. 2014), or as spinel α - Fe_3O_4 - γ - Fe_2O_3 solid solution that forms an inactive layer on the steel (Abdulrahman and Ismail 2011).

Rosaline Vimala et al. (2012) explained that the inhibition efficiency of *Annona muricata* L. acid extract may be due to the adsorption of an alkaloidal compound named 6-hydroxyundulatin and other alkaloids on the metal surface, thereby blocking the surface and protecting the metal from the aggressive atmosphere.

Pharmaceutical applications

It is well known that heavy metals (e.g., Cr, Cd, Pb and Hg) and also the accumulation of essential heavy metals (Zn, Cu, Fe, and Co) may cause different disorders in the human body. Metal ions can have some interactions with different cellular units like DNA or nuclear proteins causing apoptosis, harmful carcinogenic structural changes (Mehrandish et al. 2019), initiation of reactive oxygen and nitrogen species resulting from the peroxidation of lipids in the plasma membrane (Kim et al. 2019) and also, catalysis the generation of hydroxyl radicals via Fenton like reactions (Valko et al. 2016). The use of compounds able to chelate metals are in the origin of several treatments regarding the above-mentioned diseases and the search for natural and less toxic chelating agents for such purpose is a topic greatly investigated.

Antioxidants

Nowadays, antioxidants with a significant potential role in pharmaceutical and agri-food industries are getting increasingly popular. They are known as compounds with potential to interact with oxidizing agents, inhibiting their consequent damage to other molecules or cellular components as well as substances with abilities to repair a system such as iron transporting proteins (Brewer 2011).

Flavonoids have antioxidant properties due to their potential to chelate iron which can damage protein and lipid on cell membrane and regulate many signaling pathways such as the inhibition of xanthine oxidase which is considered as a source of reactive oxygen species that causes the oxidative stress (Cos et al. 1998). Tannins are well known to have the ability to interfere with cell-based activity assays and also to display antioxidative effects (Zhang et al. 2010a, b).

Various studies have shown that green tea and epigallocatechin gallate significantly avoid misregulation of iron metabolism, preventing the

neurodegenerative diseases in animal models (Levites et al. 2001). In addition to their well-established metal-chelating properties, polyphenolic compounds like catechins are known as radical scavengers of oxygen and nitrogen species and therefore, regulate the cellular redox state (Higdon and Frei 2003). Their chelating potential may interfere with iron and neutralize the ferric iron to form redox inactive iron, providing a protection for cells against oxidative damages (Grinberg et al. 1997). Natural antioxidants like phenolics present in dietary resources such as resveratrol in peanuts and grapes, catechins, and theaflavins in tea, curcumin in turmeric and anthocyanins in berries are able to form adducts with metals and thus reverse ROS generation (Uttara et al. 2009; Ratheesh et al. 2017).

Ascorbic acid serves as an antioxidant that is essential for the preventing and treatment of scurvy. It has been shown that vitamin C reduces transitional metals, as an instance, Cu^{2+} into Cu^+ and Fe^{3+} into the Fe^{2+} (Satoh and Sakagami 1997).

Chelation therapy

Interest in utilization of plant extracts and plant-derived compounds for metal chelation is increasing and a new field recognized as ‘natural chelation therapy’ in medical sciences is arisen. Chelation therapy is defined as a treatment method for the reduction of unnaturally accumulated essential heavy metals (like Cu, Fe and Zn), or other inessential toxic metals (like Al, Cd and Pb) (Andersen 2004). In fact, chelating agents form complexes with metallic ions and enhance their discharge through urination and fecal excretion and finally a reduction of their body concentrations (Hegde et al. 2009). Some natural polymers with the potential of heavy metal absorption such as chlorella and citrus pectin, algal polysaccharides alginate and also fibers in foods, like cereals and fruits are also potent compounds for chelation therapy besides the main treatment processes (Mehrandish et al. 2019).

It has been shown that modified citrus pectin, a linear polysaccharide with 10% rhamnogalacturonan II has improved the As removal through urination by chelation for the reduction of the As in the body (Eliaz et al. 2006). Mehrandish et al. (2019) also reported medicinal plants including *Ginkgo biloba* (gingko), *Coriandrum sativum* (cilantro), *Allium sativum*

(garlic), *Curcuma longa* (turmeric), *Silybum marianum* (milk thistle) and *Chlorophyta* (green algae) containing phytochelatin, herbal fibers, triphala and other compounds, which chelates the metals and could be a suitable potent treatment method for heavy metal poisoning.

Neurology related disorders

It is a well-known that with normal ageing, bio-metals (Fe, Zn, Cu) are accumulated in the brain (Kastenholz and Garfin 2009). There is growing evidence regarding the role of the disruption of cerebral bio-metal regulation in the etiology of Alzheimer’s disease, Parkinson’s disease, Wilson disease and other neurological disorders (Dusek and Aaseth 2016).

Alzheimer’s disease Among other features, neurodegeneration in Alzheimer’s disease (AD) is distinguished by the accumulation of metals (usually Fe, Al, Zn and Cu) in different parts of the brain (Speziali and Orvini 2003; Molina-Holgado et al. 2007) and the disruption of the metabolism of these metals leading to their modified transport and accumulation in plaques and other parts of the brain resulting in Alzheimer’s disease (Bishop et al. 2002).

Therapeutics that prevent biological damage from intra and extra-cellular metals by forming stable complexes with the metals, with less toxicity for the body, originating from natural sources have gained attention from most drug designers (Flora and Pachauri 2010; Lawson et al. 2016). Natural based flavonoids, sterols, carotenoids and phenolics as potent metal chelators, scavengers of free radicals, inhibitors of Fe^{2+} induced lipid peroxidation and protein oxidation (Pangestuti and Kim 2011). These chelators are useful for treating AD by protecting the cells from oxidative and nitrosative damage (Olasehinde et al. 2017).

Parkinson’s disease Studies discuss the role of iron metabolism dysregulation as an important pathological characteristic of Parkinson’s disease (Mandel et al. 2004). Iron chelation has been introduced as a favorable therapeutic method for the treatment of neurodegenerative diseases with features of iron overload including Parkinson’s disease. Epigallocatechin gallate with its strong iron chelating capabilities is known as having a

neurodegenerative protection role and other associated disorders (Mandel et al. 2004).

Gao et al. (2012b) after 20–22 years of follow-up on more than 130,000 people concluded that it is less likely to develop Parkinson's disease with higher intakes of dietary flavonoids and their subclasses like anthocyanins, quercetin, epicatechin and some proanthocyanidins. Ginkgetin, which is a natural biflavonoid present in *Ginkgo biloba* leaves, can effectively chelate ferrous ions and subsequently avoid the enhancement of intracellular iron concentrations, contributing to neuroprotection used in the therapy for Parkinson's disease and other iron metabolism related disorders (Wang et al. 2015).

Conclusions

The threat of the application of hazardous materials in the metal related industry and finally the release of these materials in the environment is raising the importance of innovative environmentally friendly methods for different applications related to metals utilization, removal, recovery, etc. This paper reviews the most important plant metabolites with the capacity of binding to metals. Some of these compounds are present in considerable concentrations in plants and are usually grouped as phenols and polyphenols, alkaloids, saponins, proteins, amino acids, polysaccharide and organic acids. They have the capacity to interact with metals usually due to the possession of hydroxyl, carboxyl, carbonyl, amino groups, thiol groups, which contain atoms with lone pair electrons, that make them able to bind to different metals.

One of the most important characteristics of these compounds, that are supposed to be used for industrial applications, is their specificity and selectivity to interact with a certain type of metal. Although, some plant compounds have been identified with this feature, most of them lack selectivity, binding to a variety of metals. Some modifications of these compounds may increase their metal specification, or some of them can raise their metal interaction potential. There are several applications of plant-based metal interaction compounds in the industry, and other possibilities are still under research. Nevertheless, more investigation in this area is required to introduce suitable and safe compounds and their bearing plants for different industrial purposes. Additional research

is also needed to modify the plant compounds, making them more metal-specific and to increase their efficiency and reusability. On the other hand, metal binding capacity, structure and characteristics of these compounds, can also inspire scientists to design and manufacture artificial compounds more selective in their interaction with metals.

Finally, it should be taken into account that extraction and purification of plant-based compounds can be difficult and very expensive as well as requiring relatively high quantities of organic solvents that may have negative effects on the ecosystems. The revised methods can be considered low-cost if they require few processing steps and/or the use of easily accessible plants abundant in nature, or plant wastes/by-products from other plant-based industries. Moreover, the stability and efficiency of these active constituents at high temperatures, high or low pH conditions and also in the presence of some chemical compounds may be decreased/inactivated. In severe conditions these compounds may be decomposed and thereby their relative efficiency may decrease. For these reasons, further studies are required in order to broaden and potentialize their application.

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