Biodegradable chelating agents for industrial, domestic, and agricultural applications—a review

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Abstract Aminopolycarboxylates, like ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), are chelating agents widely used in several industrial, agricultural, and domestic applications. However, the fact that they are not biodegradable leads to the presence of considerable amounts in aquatic systems, with serious environmental consequences. The replacement of these compounds by biodegradable alternatives has been the object of study in the last three decades. This paper reviews the most relevant studies towards the use of environmentally friendly chelating agents in a large number of applications: oxidative bleaching, detergents and cleaning compositions, scale prevention and reduction, remediation of soils, agriculture, electroplating, waste treatment, and biocides. Nitrilotriacetic acid (NTA), ethylenediaminedisuccinic acid (EDDS), and iminodisuccinic acid (IDS) are the most commonly suggested to replace the nonbiodegradable chelating agents. Depending on the application, the requirements for metal complexation might differ. Metal chelation ability of the most promising compounds [NTA, EDDS, IDS, methylglycinediacetic acid (MGDA), L-glutamic acid N,N-diacetic acid (GLDA), ethylenediamine-N,N′-diglutaric acid (EDDG), ethylenediamine-N,N′-dimalonic acid (EDDM), 3-hydroxy-2,2-iminodisuccinic acid (HIDS), 2-hydroxyethyliminodiacetic acid (HEIDA), pyridine-2,6-dicarboxylic acid (PDA)] with Fe, Mn, Cu, Pb, Cd, Zn, Ca, and Mg was simulated by computer calculations.

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The advantages or disadvantages of each compound for the most important applications were discussed.

Keywords Chelating agents · Biodegradability · Industry · Agriculture

Introduction

Chelating agents are widely used in many industrial, domestic, and agriculture applications due to their ability to complex metals. Over the last decades, they have been used in several applications, such as scale and corrosion inhibitors, pulp, paper and textile production, cleaning and laundry operations, prevention/inhibition of the growth of microorganisms, soil remediation, wastes and effluents treatment, agriculture, metal electroplating and other surface treatments, tanning processes, cement admixtures, photography, food products, pharmaceuticals, and cosmetics (Knepper 2003; Nowack and VanBriesen 2005). These compounds are mainly used with two different purposes: (1) to remove critical metals that can affect the efficiency of the process or (2) to avoid metal precipitation and ensure an essential amount for the good operation of the process.

Among the various chelating agents available, organophosphonates and aminopolycarboxylates (APCs) stand out as they are good metal chelators with a good quality/price ratio. APCs, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), and also organophosphonates like diethylenetriamine penta(methylene phosphonic acid) (DTPMP), hydroxyethylidenediphosphonic acid (HEDP), and nitrilotrimethylenephosphonic acid (NTMP) are the most common chelating agents used in the world (Knepper 2003; Nowack and VanBriesen 2005). In the last decades, discussion about their environmental consequences has been raised. The biodegradation of EDTA, DTPA, and organophosphonates is

very limited, and they can only be biodegraded in very particular conditions, with specific isolated bacterial strains (Bucheli-Witschel and Egli 2001; Nörtemann 2005); still, these compounds do not obey the Organization for Economic Co-operation and Development (OECD 1992) criteria for biodegradability (Knepper 2003). To reduce their concentration in industrial effluents, additional treatments such as advanced oxidation processes, which have been reviewed (Sillanpää and Pirkanniemi 2001; Sillanpää et al. 2011), are necessary.

The understanding of the chemistry of the chelates in natural waters is essential to predict the fate of these compounds in the environment (Nowack 2002). EDTA is not toxic for mammals and is used in cosmetics and pharmaceuticals with no harmful effects in human life (Nowack and VanBriesen 2005), but its strong ability to form metal complexes, together with its persistency in the environment, results in a perturbation of the natural metal speciation in the environment. The presence of chelating agents in water solubilizes heavy metals from the sediments and soils, enhancing its mobility, which can increase the presence of metals in water supply systems. The exposure of humans, animals, plants, and microorganisms to heavy metals raises concern due to their toxic effects. The metal complexes of EDTA themselves have been found to be more toxic than the free form of the ligand (Sillanpää and Oikari 1996). Mobilized metals can include radioactive ions from contaminated soils or disposal sites, with all the harmful effects associated with them (Nörtemann 2005). Chelating agents also have an effect on the liberation of phosphorous due to the dissolution of metal phosphates that contribute to an increase of microorganisms in water (Oviedo and Rodriguez 2003).

NTA (Fig. 1) was the first chelating agent to be synthesized and it is widely used. Although it is biodegradable, its usage is controversial because it is moderately toxic to humans and mammals and suspected to induce kidney toxicity and tumors (Bahnemann et al. 1998; Ebina et al. 1986). The present concentrations of NTA in the environment are lower than the thresholds determined for these effects (Bucheli-Witschel and Egli 2001), but its use cannot be increased substantially.

Other biodegradable chelating agents, such as ethylenediaminedisuccinic acid (EDDS) and iminodisuccinic acid (IDS), started to be considered and studied as alternatives in the 1980s, especially to substitute phosphonates in detergents and cleaning compositions, but also in the bleaching industry and as peroxide stabilizers. EDDS (Fig. 1) can exist in three stereoisomer forms but only the S,S-isomer is considered biodegradable according to the OECD guidelines (Schowanek et al. 1997; Takahashi et al. 1997). Most of the works concerning the application of EDDS consider the biodegradable isomer that will be only identified as EDDS throughout this work. It is commercialized by Innospec Inc., UK as Enviomet™. IDS (Fig. 1), also known as (N-1,2-dicarboxyethyl)-D,L-aspartic acid, has three stereoisomers as

well, but, unlike EDDS, all of them were proven to be biodegradable (Hyvonen et al. 2003). IDS is commercialized by Lanxess under the name Baypure CX 100, and its synthesis process is considered environmental-friendly, with no generation of off-gases or effluents (Kolodynska 2011).

The search for alternative chelating agents, more environmentally friendly, is very important, and several works concerning the various applications have been published in the last two decades. The new compounds must be biodegradable, to avoid harmful consequences for the environment, but also have good chelating abilities and be economically viable. This is a critical point since most of the biodegradable complexants have low or moderate stability constants when compared to EDTA and DTPA. For each application, the assessment of the best compounds must take into consideration the metals that need (or not) to be complexed, pH range, and compound characteristics, like solubility and stability in different conditions, protonation, and stability constants. Besides EDDS and IDS, there is a group of other APCs (Fig. 1) that are recurrently mentioned in the literature as possible substitutes of the traditional chelating agents. The correlation between the structure and respective biodegradability has been studied; most of the molecules represented in Fig. 1 have one nitrogen atom, which makes them more easily biodegraded, while the presence of tertiary amines in EDTA and DTPA molecules makes them difficult for biodegradation (Nörtemann 2005).

Methylglycinediacetic acid (MGDA) has a good stability in a wide pH range and is classified as ready biodegradable according to OECD (1992) criteria. MGDA commercial name is Trilon® M and is produced by BASF (2007).

L-Glutamic acid N,N-diacetic acid (GLDA) is classified as ready biodegradable and has no toxic effect on biotic systems or human health (Borowiec et al. 2009). This ligand is marketed on commercial scale by AkzoNobel with the name Dissolvine® GL-38 (AkzoNobel 2010).

Ethylenediamine-N,N′-diglutaric acid (EDDG) and ethylenediamine-N,N′-dimalonic acid (EDDM) are two chelators, members of the same homologous series of EDDS. EDDG biodegradability was assessed by Lanham et al. (2011). Synthesis and biodegradability of EDDM were studied by Aoki and Hara (2002).

Chelating agent 3-hydroxy-2,2-iminodisuccinic acid (HIDS) is biodegradable and presents low toxicity (Nippon 2013). The compound is produced and commercialized by Nippon Shokubai.

2-Hydroxyethyliminodiacetic acid (HEIDA), also commonly referred as ethanoldiglycinic acid (EDG), has proven to be biodegradable (Lynn et al. 1975). Two companies sell this compound: Dow, as VERSENE™ HEIDA, and Akzo Nobel under the name Dissolvine® EDG.

Pyridine-2,6-dicarboxilic acid (PDA), also known as dipicolinic acid, contains a pyridine ring and is biodegradable

Fig. 1 Molecular structure of the biodegradable chelating agents: nitrilotriacetic acid (*NTA*), ethylenediaminedisuccinic acid (*EDDS*), iminodisuccinic acid (*IDS*), methylglycine diacetic acid (*MGDA*), L-Glutamic acid N,N-diacetic acid (*GLDA*), 2-hydroxyethyliminodiacetic acid (*HEIDA*), ethylenediamine-N,N′-dimalonic acid (*EDDM*), ethylenediamine-N,N′-diglutaric acid (*EDDG*), 3-hydroxy-2,2-iminodisuccinic acid (*HIDS*), and 2,6-pyridine dicarboxylic acid (*PDA*)
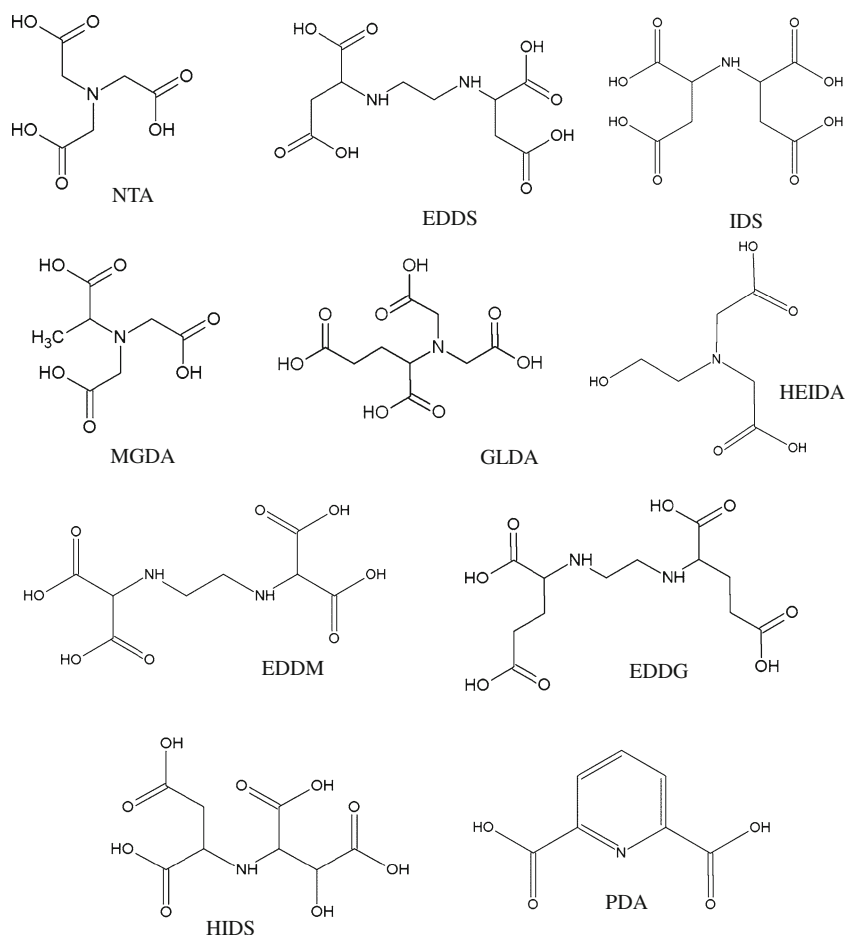
according to the OECD guidelines (Martins et al. 2014). It is a naturally occurring compound, as it constitutes ~10 % of the dry weigh of *Bacillus* species spores. Due to its structure, it tends to chelate metals in a proportion of 2:1 (ligand/metal), improving the stability of the complex.

Protonation and stability constants (as log β) for several metals of interest are presented for the APCs mentioned in Table 1.

The present work attempts to give an overview of the studies where the practical application of biodegradable chelating agents was considered and experimented. The biodegradability of the chelating agents is not considered fundamental in industries like cosmetics, food processing, and pharmaceuticals, where the compound is used in smaller quantities. Almost no studies regarding this problematic were found; therefore, these usages were not object of review in the present work. Requirements of chelation abilities differ depending on the goal of the application. For the group of compounds more recurrent in recent literature (EDDG, EDDM, EDDS, GLDA, HEIDA, HIDS, IDS, MGDA, NTA, and PDA), computer chemical simulations were performed to assess their ability to chelate metals, using conditions relevant for the applications discussed in order to make a standardized comparison between them.

Applications using biodegradable chelating agents

Oxidative bleaching processes

Chelating agents are widely used in pulp and paper as well as in textile industries and the current preference for bleaching processes free from chlorine (total chlorine-free—TCF) might increase their usage. TCF bleaching processes are usually based on oxygen chemicals, e.g., hydrogen peroxide and peroxy acids. Transition metals, such as Mn, Fe, and Cu catalyze the decomposition of peroxy compounds, thus its presence in pulp and cotton affects the efficiency of bleaching and increases process costs. On the other hand, complexation of Mg must be minimized because its presence is beneficial for the process. EDTA and DTPA are the most used chelating agents to control the presence of metals and can be applied in a pretreatment stage prior to bleaching or as stabilizers in the actual bleaching stage. The metals are then removed, as metal complexes, in the dewatering stage (Ni and Liu 2000), and discharged into the aquatic resources. The quantity of chelant used in the pretreatment stage is usually between 1 and 6 kg/ton of pulp.

EDDS and IDS are the two biodegradable chelating agents that appear more often associated to pulp bleaching processes.

Table 1 Protonation and overall stability constants of EDTA, NTA, IDS, MGDA, GLDA, EDDG, EDDM, HIDS, HEIDA, and PDA with Fe, Mn, Cu, Pb, Cd, Zn, Ca, and Mg ions, at 25 °C, in $\mu = 0.1$ M

	Reaction	EDTA	NTA	EDDS	IDS	MGDA	GLDA	EDDG	EDDM	HIDS	HEIDA	PDA
H^+	$H + L \leftrightarrow HL$	9.5	9.5	10.1	10.0	9.9	9.4	9.5	9.7	9.6[d]	8.7	4.7
	$2H + L \leftrightarrow H_2L$	15.6	12.0	17.0	14.2	12.4	14.4	16.3	16.3	13.7[d]	10.9	6.7
	$3H + L \leftrightarrow H_3L$	18.3	13.8	20.8	17.5	13.9	17.9	20.5	19.0	16.8[d]	12.5	
	$4H + L \leftrightarrow H_4L$	20.3	15.0	23.9	19.4		20.4	3.3	21.1	18.9[d]		
	$5H + L \leftrightarrow H_5L$	21.8		25.3						20.5[d]		
Fe^{3+}	$M + L \leftrightarrow ML$	25.1	16.0	20.1[a]	13.9[b]	16.5[c]	15.2[d]	15.7[g]		15.0[d]	11.6	10.9
	$M + 2L \leftrightarrow ML_2$		24.0									17.1
	$M + H + L \leftrightarrow MHL$	26.4	17.0		17.8[b]		19.4[d]			18.4[d]	13.9	
	$M + L \leftrightarrow M(OH)L + H^+$	17.7	11.6	12.2[a]	8.6[b]		-3.3[d]			10.0[d]	9.2	
Mn^{2+}	$M + L \leftrightarrow ML$	13.9	7.3	9.0	7.3[b]	8.4[c]	7.6[e]	6.7	8.4	6.8[h]	5.5	5.0
	$M + 2L \leftrightarrow ML_2$		10.4								9.0	8.5
	$M + H + L \leftrightarrow MHL$	17.0		13.7								
	$M + L \leftrightarrow M(OH)L + H^+$				-4.0[b]					-3.3[h]		
Cu^{2+}	$M + L \leftrightarrow ML$	18.8	12.7	18.7	12.9[b]	13.9[c]	13.0[f]	15.5	15.9	12.6[f]	11.8	9.1
	$M + 2L \leftrightarrow ML_2$		17.4								15.8	16.4
	$M + H + L \leftrightarrow MHL$	21.9	14.3	25.0	17.3[b]		17.2[f]			16.2[f]		
	$M + L \leftrightarrow M(OH)L + H^+$	7.4	3.5	7.6	2.5[b]		3.1[f]			3.7[f]	3.1	1.6
Pb^{2+}	$M + L \leftrightarrow ML$	18.0	11.5	12.7	9.8	12.1[c]	11.6[f]	8.5	11.1	10.2[f]	9.4	8.7
	$M + 2L \leftrightarrow ML_2$											11.6
	$M + H + L \leftrightarrow MHL$	20.8	15.0	16.0			16.3[f]	14.4	15.3	14.3[f]	12.2	
	$M + L \leftrightarrow M(OH)L + H^+$						1.0[f]				1.2	
Cd^{2+}	$M + L \leftrightarrow ML$	16.5	9.8	10.9	8.3	10.6[c]	10.3[f]	8.8		7.6[f]	7.4	6.4
	$M + 2L \leftrightarrow ML_2$		14.5								12.4	10.9
	$M + H + L \leftrightarrow MHL$	19.4		14.6	13.0		15.0[f]			12.7[f]	8.8	
	$M + L \leftrightarrow M(OH)L + H^+$	3.3	-1.5				0.1[f]			-2.6[f]		
Zn^{2+}	$M + L \leftrightarrow ML$	16.5	10.4	13.6[a]	10.2[b]	10.9[c]	11.5[f]	10.2	11.1	9.8[f]	8.4	6.4
	$M + 2L \leftrightarrow ML_2$		14.2								12.0	10.9
	$M + H + L \leftrightarrow MHL$	19.5		17.3[a]	14.6[b]		16.1[f]			13.7[f]		
	$M + L \leftrightarrow M(OH)L + H^+$	4.9	0.3	2.3[a]	-1.1[b]		0.9[f]			0.8[f]	-1.1	
Ca^{2+}	$M + L \leftrightarrow ML$	10.7	6.3	4.6	4.3	7.0[c]	5.9[e]	2.6	5.4	4.8[i]	4.7	4.4
	$M + 2L \leftrightarrow ML_2$		8.8									7.4
	$M + H + L \leftrightarrow MHL$	12.8		11.5				3.6	11.7			
	$M + L \leftrightarrow M(OH)L + H^+$											
Mg^{2+}	$M + L \leftrightarrow ML$	8.8	5.5	6.0	5.5	5.8[c]	5.2[e]	3.0	4.9		3.4	2.3
	$M + 2L \leftrightarrow ML_2$											3.0
	$M + H + L \leftrightarrow MHL$	12.8		11.9				4.3	11.5			
	$M + L \leftrightarrow M(OH)L + H^+$											

Values from NIST Database (Martell and Smith 2004) unless otherwise indicated

[a] Orama et al. 2002

[b] Hyvonen et al. 2003

[c] BASF 2007

[d] Begum et al. 2012a

[e] AkzoNobel 2010

[f] Begum et al. 2012b

[g] Tak et al. 1971

[h] Hyvonen and Aksela 2010

[i] Nippon 2013

Renvall et al. (1997) and Chauveheid et al. (1999) suggest a general formula for chelating agents to be applied in the pretreatment of the pulp and both EDDS and IDS are in accordance with the formula proposed. Employing a chelant dose of 2 kg/ton of pulp, Mn concentration in the filtrate was 3.0 ppm using EDDS at optimum pH (6.5–7.0), which was 10 % below the value obtained for EDTA and DTPA (Renvall et al. 1997). For Fe, similar results were obtained for EDDS, EDTA, and DTPA, with metal concentrations of 2.0 ppm in the filtrate. For both metals, when IDS was used, the removal was 50 % below the traditional chelants. After the bleaching step, no significant differences were found for brightness; however, hydrogen peroxide consumption was usually lower for DTPA. Experiments for stabilization of hydrogen peroxide showed that in the presence of EDDS and IDS, the peroxide was mostly degraded in the first 15 and 60 min, respectively, but in the presence of EDTA or DTPA, it was still stable after 90 min.

Jones and Williams (2001) focused on the problem of finding biodegradable alternatives in the pulp and paper industry, through computer chemical simulations. The lower affinity of EDDS and IDS for Ca makes them promising alternatives for replacing EDTA.

Giles and Dixon (2009) proposed a bleaching pretreatment, at pH 4–7.5 with a mixture of biodegradable and nonbiodegradable chelating agents. According to this work, the mixture of chelating agents resulted in a better brightness than it would be expected from the results using similar amounts of each chelating agent alone. For instance, DTPA and EDDS, when used alone under the same experimental conditions, resulted in a brightness of 66.0 and 63.9, respectively, after the peroxide stage. When applied together in a ratio of 30:70, the obtained brightness was 66.9. The biodegradable compounds suggested are EDDS, MGDA, GLDA, and IDS and can be combined with DTPA, EDTA, or DTPMP. Even though these formulations still contain nonbiodegradable chelating agents, the combination of both types of chelants can be a solution for obtaining good chelating and bleaching results combined with a more environmentally friendly process since lower amounts of nonbiodegradable chelating agents are used.

Recently, PDA and MGDA were tested experimentally in a pretreatment of paper pulp, at pH 5–7 (Pinto et al. 2014). In these experiments, a consistency of 70 kg of dried pulp/m^3, followed by a bleaching sequence with hydrogen peroxide and peracetic acid, was used. Mn was totally removed from the pulp with both ligands studied and EDTA, but MGDA at 3.7×10^{-3} M also solubilized up to 70 % of Mg. On the other hand, PDA at 2.0×10^{-3} M was more selective and a removal of only 37 % of Mg was achieved. Similarly, NTA (7.0×10^{-4} M) and EDDM (4.5×10^{-4} M) removed Mn efficiently with a good selectivity over Mg (Neto et al. 2014).

Detergents and cleaning compositions

Chelating agents found in detergents, both used for laundry or dishwashing, are frequently added to the composition to soften water by inactivating Ca and Mg ions, which are the major metal ions that contribute to hardness. Hard water has negative effects in cleaning applications due to precipitation of minerals that accumulate in the washing machines or in other objects. Chelating components inactivate Ca and Mg ions by sequestration, leaving them soluble. Phosphonates have been extensively used in detergents, but they pose some environmental concerns. There are also cases where compounds are added to laundry detergents with peroxy-based bleaching agents to chelate heavy metals in order to stabilize the solution (Baillely et al. 1994).

The target metal ions must be complexed between pH 7 and 12, which is the typical pH of cleaning and washing operations. Considering the large quantity of chelating agents used in cleaning compositions, which can be up to 30 wt.%, this is a crucial application where biodegradable alternative chelating agents should be used.

PDA was added as a builder in dishwashing (De Ridder 1983; Frankena 1988) and laundry (Boskamp 1990) compositions due to its ability to sequester Ca ions. In the experiments performed by De Ridder (1983), the capacity of sequestering Ca, using 0.15 g/L of chelating agent, was measured by weighting the insoluble Ca deposit in glass slides. EDTA and NTA had better performances with formation of 4.1 and 3.6 mg of solid deposit, respectively. PDA was also effective (formation of 4.5 mg of deposit) when compared to the situation where no chelating agent was used (7.4 mg of deposit). These results could still be improved by changing the concentration of other components in the detergent. The addition of 2.0 % of PDA in a laundry detergent had a significant effect on avoiding the reduction of the fabrics reflectance after 10 washes (Boskamp 1990).

In recent years, MGDA and GLDA studies in cleaning applications became more frequent. MGDA alone showed a good ability to inhibit scale formation due to calcium or magnesium carbonate precipitation (Dailey et al. 2011). When different compositions of the builder were tried, it was verified that this parameter can be more or less affected depending on the compounds and quantities present. MGDA or GLDA can be present in a detergent composition together with citrate and carbonate. Citrates are weaker chelants, but mixed with a stronger chelating agent, can also sequester hardness metals as they act as an alkaline buffer (Jefferis and Zack 2011).

Another purpose for the addition of chelating agents to cleaning compositions is to chelate heavy metal ions (Fe, Mn, Cu) present in stains to enhance their removal (Palladini 2007; Pike 1996). Palladini (2007) suggested detergent formulations containing one biodegradable chelating agent (IDS

or GLDA) pointing out the importance of both sequestration of hardness and heavy metal ions.

The presence of EDDS and EDTA in a laundry detergent composition at two concentrations (3.3 and 6.7 %) was studied for the removal of organic stains at pH 9.8 (Hartman and Perkins 1987). For some types of stains, the addition of chelant does not make any difference; grape juice and tea were better removed in the presence of EDDS while grass and bacon removal was higher with EDTA. In general, higher concentration of chelating agent led to better removal of the stains.

For the rinse aid composition, proposed by Pike (1996), the compounds must chelate heavy metals, preferentially at pH lower than 7 to improve the removal of stains. In fact, these pH conditions usually enhance bonding with heavy metals instead of Ca and Mg for the majority of the chelating agents. EDDG and hydroxypropylenediamine disuccinic acid (HPDDS) were used, but since the purpose of using chelants was the complexation with heavy metals during the rinsing cycle of the dishwasher, phosphonates were also present to soften water.

HEIDA salts have been compared to EDTA salts in a composition with 3.2 % of chelating agent for hard surface cleaning (Crump and Wilson 2011). The cleaning of soiled tiles, where the soil contained Fe, Ca, and Mg was measured by the number of strokes necessary to remove 90 % of the soil. Even though HEIDA stability constants are significantly lower, HEIDA and EDTA potassium salts showed similar cleaning efficiency (with 19 strokes each).

The use of HEIDA was also proposed by Giles and Dixon (2012) in a dishwashing composition mostly free of bleaching agents and phosphate builders. A second chelating agent, biodegradable or not, could be added maintaining the total concentration at 15 %. Compositions with mixtures of chelating agents gave better results on the removal of tea stains than compositions with just one chelating agent, with an increase of the cleaning score value up to 30 %.

Scale prevention and removal

The hardness ions present in the water used in industrial processes lead to the formation of scale in metallic surfaces of equipments, especially in heat exchanging processes. These incrustations decrease the efficiency of heat transmission, increase pressure drop, and promote the corrosion of the equipment (Simpson et al. 1999). The removal of these deposits can be very costly, time consuming, and harmful to the environment due to the use of strong acids and alkalis (Zack et al. 2012). Chelating agent solutions can be used to prevent and/or remove scale from the equipments.

In circulating aqueous systems for steam generating and cooling, chelating agents can be added to the water. The stability of GLDA (at 13 % in the treatment solution) and EDDS (at 9.3 % in the treatment solution) and their ability to avoid metals precipitation were tested at high temperatures (216–235 °C) and pressures (21–31 bar) to assess their use in water systems (Charkhutian et al. 2004, 2006). The stability of both compounds decreases for higher temperatures and pressures. The anti-precipitation effect was tested, at pH 10, for Ca, Mg, and Fe separately and with the three metals together. When the three cations were mixed and tested at 216 °C and 21 bar, the results were similar between both ligands, with more than 80 % of Mg and Ca and around 50 % of Fe remaining in solution instead of precipitating. GLDA showed better results for the solutions containing only one metal, especially for Mg and Fe, while Ca showed a good stability in solution with both compounds.

Aqueous solutions containing biodegradable chelating components, such as MGDA and GLDA, can be used as oil field chemicals. In this case, the solutions are preferentially acidic or neutral and the main goal is to dissolve calcium carbonate scale and other subterranean carbonate formations to increase permeability and enhance the withdrawal of oil or gas (De Wolf et al. 2009, 2012). In the case of very acidic solutions, GLDA showed a better solubility in aqueous acids than other chelants.

For control and removal of Ca and Mg deposits at alkaline pH in a steam generator, NTA and EDDS were suggested as biodegradable alternatives, along with some nonbiodegradable compounds (Richardson et al. 2012). Zack et al. (2012) tested MGDA at pH close to neutrality, with the addition of different acids, to dissolve calcium carbonate. In the presence of methanesulfonic acid, the increase of MGDA concentration from 0 to 8.7 % improved the scale dissolving capacity from 26.6 to 43.7 %.

The formation of Ca scale is also a major problem in the pulp and paper industry, both in pulping and bleaching stages. The presence of Ca in alkaline bleaching stage can lead to precipitates, mainly oxalate and carbonate that accumulate in the equipment, forming scale that is hard to remove. The presence of chelating/sequestering agents, such as EDTA and DTPA, can help to increase the solubility of calcium oxalate (Elsander et al. 2000; Moore et al. 2012). Biodegradable alternatives must be good Ca chelators forming soluble and stable complexes. Pinto et al. (2014) considers PDA as a possible Ca chelator to prevent the formation of scale during pulp bleaching, since about 90 % of the Ca present in the pulp is removed during the pretreatment.

Remediation of soils

The presence of toxic metals in the soils has become a major concern due to industrial and agricultural practices, inappropriate waste disposal, and increasing urbanization. Heavy metals cannot be mineralized or decomposed; therefore, human intervention is needed to remove them from the soils.

Soil washing and flushing

In situ and ex situ remediation techniques have been studied (Lestan et al. 2008), and chelating agents can be applied in both techniques. In situ techniques include phytoremediation and soil flushing. Ex situ methods usually consist of soil washing to separate contaminants and the use of chelating agents is less disruptive for the soils than acid washing. According to some authors, the chelating agents must have low biodegradability to allow recycling and reuse of the washing solution (Dermont et al. 2008; Lestan et al. 2008), thus reducing treatment costs. Nevertheless, a fast biodegradation rate of the ligand in this application is not convenient because removal of metals from the soil cannot occur or be inefficient. EDDS biodegradation studies in soils showed a lag phase up to 11 days and proved that degradation was effective even in polluted soils (Tandy et al. 2006). Meers et al. (2008) compared the biodegradability of EDDS in three different soils and concluded that the time of degradation differed significantly due to different durations of the lag phase. The type of soil is important in biodegradation and can be related to EDDS recovery and reuse in remediation of soils.

Chelants must also have low toxicity to soil microorganisms, which is not observed for EDTA (Epelde et al. 2008; Kos and Lestan 2003), and the metal complexes should not adsorb on the solid surfaces (Dermont et al. 2008). The ligand/metals ratio must be higher than 1, to maximize the metals removal, especially due to interferences of other cations present in the soil (Fe, Mn, Ca, Al and Mg). The low selectivity of EDTA caused by strong chelation with interfering cations is a disadvantage in this process (Dermont et al. 2008).

In the middle 90s, PDA was considered for soil remediation applications (Pb and Cd extraction and recovery), although it was not mentioned as a biodegradable alternative in the respective studies (Macauley and Hong 1995; Hong and Chen 1996). The extraction of Pb from soil with PDA 1 mM was above 80 % in four consecutive experiments using reused PDA (Macauley and Hong 1995). Efficiency of extraction was comparable to EDTA, but PDA has the advantage of forming weaker chelates, which makes the release of extracted Pb easier.

Heavy metals extraction from soils was studied using an ex situ washing procedure (Vandevivere et al. 2001). EDDS achieved extraction efficiencies of Pb, Zn, Cu, and Cd between 70 and 90 % as long as the contact time was sufficient (1 to 6 days, depending on the metal) and pH higher than 7 in order to avoid Fe interference.

Tandy et al. (2004) studied EDDS, NTA, IDS, and MGDA for the extraction of Cu, Zn, and Pb and verified that the best time for the experiments was 24 h; longer times only enhanced Fe extraction without improving the other metals efficiency. Although extractions of Cu and Pb were better using EDTA (values above 80 % of extraction), EDDS, at pH 7, was considered the best compromise between extraction of Cu,

Zn, and Pb (>60 % at chelant/metal=10) with reduced loss of Ca and Fe.

Studies performed by Polettini et al. (2006) were focused on the efficiency of the extraction of Cd, Cu, Pb, and Zn from soils using different treatment durations. NTA, citric acid, and EDDS were compared with EDTA. EDDS showed extraction efficiency of target metals comparable to EDTA. EDDS also had the advantage of reducing the co-extraction of metals from the soil matrix, like Ca, Mg, and Fe to values below 10 %.

Yang et al. (2012) concluded that pH 5.5 led to better extraction than pH 8.0, using EDDS, especially for Zn (64.4 vs. 53.3 % at 1.26 mol EDDS/kg soil) and Cd (52.2 vs. 37.2 %). These conclusions are contrary to the work of Vandevivere et al. (2001), where pH above 7 evidenced better results. These facts suggest that the optimal pH is dependent of soil characteristics, namely the quantity of interfering metal cations and the way how metals are coordinated to the soil.

Comparison between batch and column experiments on the efficiency of EDDS for extracting Cu, Zn, and Pb showed that Zn and Pb are equally extracted while Cu was affected in column leaching (Hauser et al. 2005). The importance of performing experiments in column is that this method is more practical and economical to upscale. It was observed that short-time experiments were more adequate for EDDS to maximize the recovery and reuse of the ligand because longer processing led to loss of compound due to biodegradation. For simulating an in situ soil flushing situation, Mancini et al. (2011) used column tests, comparing EDDS with EDTA for Pb, Cu, Ni, Cd, and Zn mobilization. EDDS presented a better mobilization capacity for Cu, Ni, and Zn, while EDTA gave better results for Cd and Pb.

Several chelants (EDDS, IDS, MGDA, GLDA, and HIDS) in 0.05 M solutions were compared in the treatment of a soil (1:10 w/v) contaminated with Cd, Cu, Ni, Pb, and Zn at pH 4, 7, and 10 (Begum et al. 2012c). In general, extractions were enhanced at pH 4. At this pH, the metal extraction performance of GLDA for all metals studied was better (Cd 84 %, Cu 94 %, Pb 54 %, Zn 62 %, and Ni 39 %) than for the other biodegradable options and even better than EDTA for Ni and Cu. At pH 7, metal extraction efficiencies decreased but GLDA was still the best biodegradable option. These results cannot be explained by the stability constants of the metal complexes but probably by the way how metals are coordinated to the soil. In order to guarantee homogeneous conditions in the study, the same research group compared EDDS, GLDA, and HIDS with EDTA on the treatment of artificially contaminated reference soils (Begum et al. 2013). Chelant/metal molar ratio and solution pH were varied, and results showed that GLDA had the better extraction efficiency for the lower chelant concentration (0.01 M). A better performance of GLDA than EDTA was obtained, at pH 4, except for Pb, which is consistent with a previous work of the same authors (Begum et al. 2012c). At higher pH, EDDS performance is

better than GLDA but none of the biodegradable chelating agents is able to achieve the same efficiency as EDTA on the extraction of Pb.

Phytoremediation

Plants have the ability to uptake metals that have no biological function (Rahman et al. 2011). Since the remediation of large areas by soil washing can be very costly, the use of plants to accumulate heavy metals arises as a possible solution to extract contaminants and restore the fertility of the soil. The metals must be uptaken from the soil, transported from roots to shoots, and accumulated in aboveground parts of the plants (Rahman et al. 2011). After harvesting, the plants are burned to produce energy and metals are recycled from the residues (Kos and Lestan 2003). Chelating agents are used to increase the solubility and mobilization of the metals, making them bioavailable for plants (Nowack and VanBriesen 2005). The main concern of using nonbiodegradable chelating agents is their persistence in the soils that leads to the leaching of heavy metals into underground waters.

EDDS has been the most studied alternative for EDTA in phytoextraction. Studies performed with EDDS by Kos and Lestan (2003), Luo et al. (2005), Epelde et al. (2008), and Evangelou et al. (2007) for different plant species showed that EDDS is more efficient than EDTA for Cu and Zn uptake but less efficient for Pb. However, plant growth was affected by EDDS, evidencing some toxicity. EDDS toxic effects were not observed in other studies (Komarek et al. 2010; Meers et al. 2005), which means that EDDS toxicity is dependent on plant species and experimental conditions, such as, pH, type of soil, presence of other metals, etc. The study performed by Meers et al. (2005) also showed that metals mobilization decreased with time when EDDS was used. This behavior was not observed for EDTA and can be explained by the higher biodegradability of EDDS.

Shilev et al. (2007) studied NTA and EDDS to enhance the accumulation of Cd, Pb, and Zn in maize and sunflower. The results revealed that the efficiency depends on the plant species. For instance, Cd was more efficiently accumulated in the leaves of sunflower in the presence of NTA (5 mmol/L) and EDDS was better for maize. In addition, no negative effects in soil bacteria and fungi were observed, which is an advantage over EDTA. Freitas and Nascimento (2009) and Araújo and Nascimento (2010) concluded that NTA toxicity to the plants was significant but lower than EDTA, while Pb leaching results showed that NTA caused no environmental effects, unlike EDTA (Araújo and Nascimento 2010).

Cao et al. (2007) compared Pb and Zn phytoextraction by ornamental flowers using EDDS and MGDA in dosages of 4 and 8 mmol/kg of soil. Both of the ligands showed an effective increase in Pb accumulation in leaves as well as a benefic contribution for bacterial activity in the soil. In the case of Zn,

metal accumulation was independent from the use of chelating agents. EDDS and MGDA showed some toxicity to the plant causing death at maximum dose. The application of MGDA to a primrose species showed an effective Cu extractions and increase in foliar concentration and plant growth (González et al. 2011).

Iron-chelating agents for agriculture

Iron is an important nutrient for plant growth, and its deficiency is one of the causes of chlorosis in plants. Chlorosis leads to loss in the fruit quality and yield, lack of the green color in the leaves, and in extreme cases, the death of the plant (Rodriguez-Lucena et al. 2010). The deficiency of Fe in plants is caused by Fe poor bioavailability, especially in calcareous soils (Shenker and Chen 2005). Above pH 7, Fe species are mainly insoluble and cannot be taken by the plants; thus, chelating agents can be added to the soil in order to make the Fe already present bioavailable or supplied to the plant as Fe-chelates in fertilizers solutions (Lucena et al. 2008; Villen et al. 2007). EDTA and DTPA complexes are often used in liquid formulations; however, for calcareous soils, ethylenediamine-N,N′-bis(1-hydroxyphenylacetic) acid (EDDHA) is the most used because of its even higher stability constant of the FeL complex, which allows complexation at higher pH (Lopez-Rayo et al. 2009; Shenker and Chen 2005).

The use of IDS chelates (Fe, Mn, Zn and Cu) in fertigation and hydroponics formulations resulted in healthy plants (Lucena et al. 2008). The same compound was tested in a foliar spray composition though this technique was not as effective.

The ability of the chelating agents to improve the mobility of Fe in the soil is important to increase the bioavailability of Fe for a plant. HIDS and EDDS showed a higher apparent mobility followed by GLDA, EDTA, MGDA, and IDS at pH 10 (Hasegawa et al. 2011). Results were related to the growth of radish sprouts that showed the same trend. Authors claim that stability constant of the FeL complex influences the movement of Fe in the growth medium but the stability constants in Table 1 do not show the same trend.

At pH<7 and 0.25 M of chelant, HIDS was more efficient on the Fe uptake and plant growth than EDTA, EDDS, and IDS (Rahman et al. 2009). HIDS is considered an effective option to replace nonbiodegradable chelating agents in agriculture and Fe uptake due to the good experimental results as an iron chelator and plant growth and its stability in severe conditions (Hasegawa et al. 2011). The very fast biodegradation is also shown as an advantage by some authors (Hasegawa et al. 2011, 2012). However, this property can be seen as a disadvantage for agricultural purposes since the ligand should have some resistance to degradation in order to increase the period of action of fertilizers and fulfill its purpose as metal chelating agent (Shenker and Chen 2005).

EDDS was compared with DTPA and EDTA as a Fe-chelate source in a liquid fertilizer for the production of marigold and extractant of metals from peat medium. Plants treated with Fe-EDDS solution showed enough Fe in the leaves for a normal growth (Albano 2008).

Other applications

Electroplating Electroless deposition of Cu into metallic surfaces can be done in the presence of complexing agents to stabilize the metallic ions in solution by avoiding its precipitation as metal hydroxide in the alkaline baths. The most common complexants used in plating industry are EDTA and tartrate salts. Performance of biodegradable chelating agents, such as EDDS and NTA, has been also tested in electroplating of Cu (Macmillan 1996; Pauliukaite et al. 2006; Simpson et al. 1999; Wilson and Crump 1994). The stability of the electroless plating solution containing EDDS was comparable to the situation where EDTA was used and the rate of Cu deposition was very favorable (Macmillan 1996). From this study, it could be concluded that the use of EDDS fulfilled the requirements for the industry and can replace EDTA in existing plating systems.

Waste treatment Sewage sludge can be recycled as fertilizer for land because of its large content of organic substances and also nitrogen and phosphorus content. However, the toxicity of the heavy metals present in the sewage is a risk to human health and plants (Zhang and Zhang 2012). Heavy metals in sewage sludge can be removed by chelating agents, before its reuse as a fertilizer. Zhang et al. (2008) and Zhang and Zhang (2012) studied the use of EDDS to extract Cu and Zn from sewage sludge. Zhang et al. (2008) observed that, within the pH range of 4–10, both EDDS and EDTA had a good and equivalent performance for extracting Cu from the sewage sludge. Zhang and Zhang (2012) showed that the extraction efficiency of Zn, using EDDS, was comparable to the extraction efficiency obtained with EDTA at pH between 5 and 9.

Spent hydrodesulphurization catalysts, used in petroleum refineries, contain metals that must be extracted and recycled to avoid their deposition in the environment. This is commonly done by acid or alkaline leaching but EDTA has also been used (Goel et al. 2009; Pinto and Soares 2013). EDDS (Chauhan et al. 2012) and NTA (Pinto and Soares 2013) have been studied in the removal of Mo and Ni from these catalysts; however, the metal recoveries were not as high as with EDTA due to the lower stability constants of these ligands.

Indium is a rare metal employed in the fabrication process of liquid crystal display (LCD) panels. The quantity of spent LCD panels is increasing worldwide and they can be a secondary source of indium (Hasegawa et al. 2013a, b). Hasegawa et al. (2013a) studied the use of NTA, IDS, and HIDS to extract indium from spent LCD. NTA showed to be comparable with EDTA at optimal conditions (acidic medium, temperature ≥120 °C, and the pressure of 50 bar).

Biocides Some specific metal ions possess biocidal properties and can be used for stabilization, inhibition, or reduction of the growth of microorganisms when associated to a chelating agent (Borkow et al. 2010). Several formulations containing various biodegradable chelating agents, such as citric acid, salicylic acid, NTA, EDDS, MGDA, and GLDA, have been reported in the literature for cleaning and disinfection (Back et al. 2003; Ploumen and Borgmann-Strahsen 1991; Romano et al. 2000), herbicidal, fungicidal, or algaecide purposes (Samarajeewa and Taylor 2011). Back et al. (2001) described a method to control microbial growth in the water of climate control systems where salicylic acid and NTA were found to be effective.

Assessment of potential application of chelating agents by computer calculations

In order to better understand the ability of the biodegradable chelating agents for the applications described in this review, computer simulations were performed and major conclusions are pointed out in Figs. 2 and 3 and in the supplementary data found in online resources 1 and 2. For assessing the potential of each chelating agent for a specific application, the target metals to be chelated and the pH range should be considered in the computer simulations. Briefly:

1) In paper pulp and textile TCF bleaching processes, there is a need to form strong complexes of Fe, Mn, and Cu while leaving Ca and especially Mg uncomplexed. In the case of a pretreatment process before bleaching, the pH range might vary between 4 and 8. Additionally, during the bleaching stage, chelants are also useful in the stabilization of the peroxide solution itself; this process is typically performed between pH 9 and 12.

2) To avoid scale formation in industrial cooling or heating systems, as well as for using in the detergents, it is important to complex Ca and Mg ions between pH 6 and 12.

3) The remediation of metal-polluted soils implies the solubilization of contaminant metals, usually Pb, Cd, Cu, and Zn, while reducing the extraction of cations that are important for plant growth and soil quality (Fe, Mn, Ca, and Mg). In ex situ remediation, pH might be varied between 4 and 10 while for phytoremediation, a narrower interval is preferred (6–8).

4) In the case of agricultural practices, the main goal is to increase Fe uptake by plants mainly in calcareous soils; so, ligands must complex Fe to enhance its mobility at pH higher than 7.

Fig. 2 pH range, calculated by chemical simulations, for which there is at least 80 % of metal complexed. Chemical simulations were performed assuming the simultaneous presence of one chelating agent (L) at a [L]/∑[M] ratio of 5 (*solid color line*) and 10 (*dashed color line*) and the presence of all metal ions ([Cd]=[Cu]=[Fe]=[Mn]=[Pb]=[Zn]=2×10^{-5} M) with an excess of Ca and Mg ions ([Ca]=[Mg]=1×10^{-3} M)
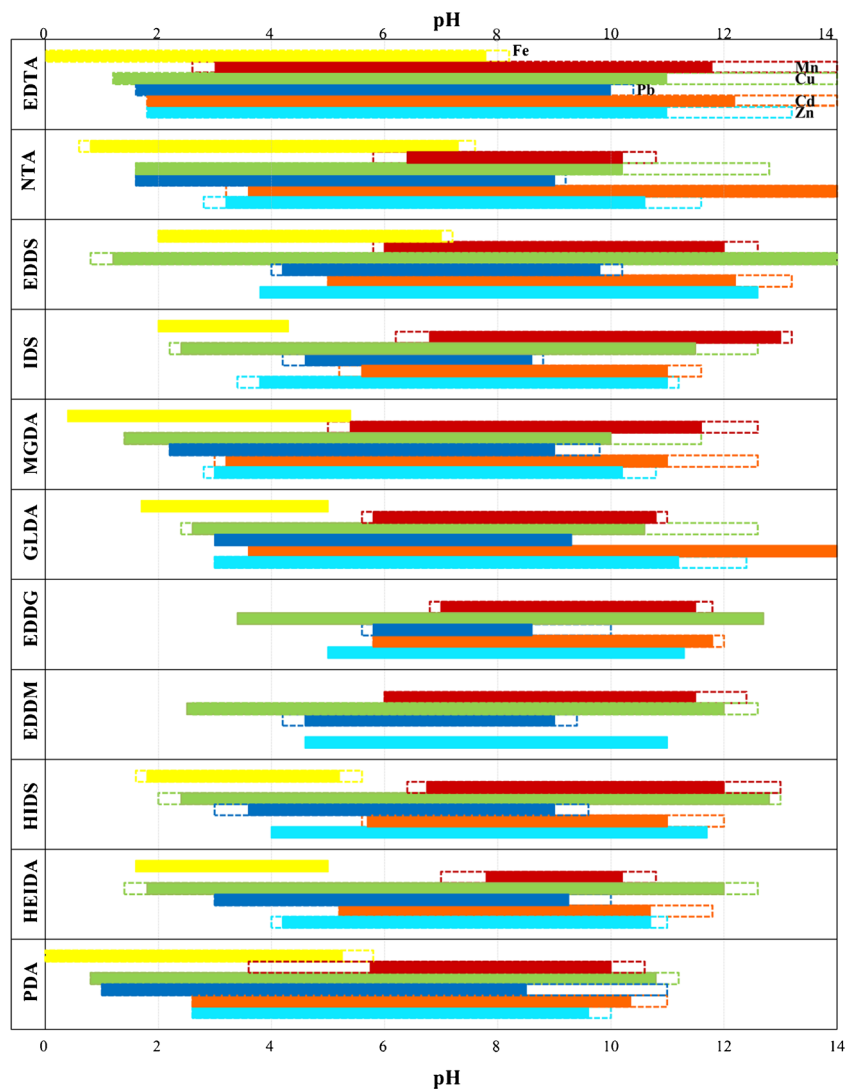
According to the aims to be fulfilled when chelating agents are used in these major applications, two different computer

simulations were performed. In the first case, the selectivity of each chelating agent to transition metals in medium with
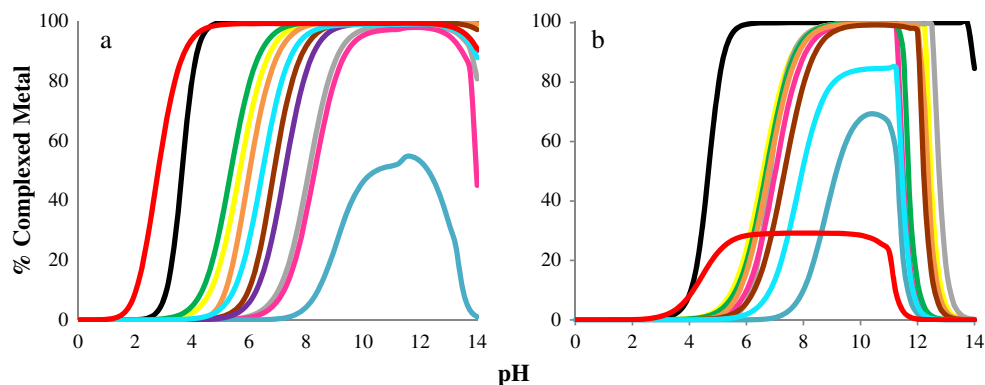

Fig. 3 Amount, in percentage, of Ca (**a**) and Mg (**b**) complexed with NTA (*yellow*), EDDS (*gray*), IDS (*pink*), MGDA (*green*), GLDA (*orange*), EDDG (*blue*), EDDM (*brown*), HIDS (*violet*), HEIDA (*light blue*), PDA (*red*) and EDTA (*black*). Chemical simulation were performed assuming the simultaneous presence of Ca, Mg and each chelating agent, with a [L]/([Ca] + [Mg]) ratio of 2, [Ca]=[Mg]=1×10^{-3}M

excess of Ca and Mg ions was evaluated. In the second case, the ability of compounds to complex Ca and Mg ions at a high concentration was assessed. Metal chemical speciation calculations were performed using MINEQL+ Version 4.5 (Schecher and McAvoy 2003), a computer program that generates chemical equilibrium concentrations of all species being considered in the model by the program reactions. Computational simulations were performed in aqueous medium in the pH range between 0 and 14 and the studied chelating agents were EDDS, EDDG, EDDM, EDTA, GLDA, HEIDA, HIDS, IDS, MGDA, NTA, and PDA. The first simulation was performed in the presence of all transition metals (M–Fe, Mn, Cu, Pb, Cd, and Zn), and one chelating agent (L), in a situation of excess of Ca and Mg ions. Two different conditions were tested, [L]:$\sum$[M] ratios of 5 and 10 with [M]=2×10^{-5} M for each transition metal, except Ca and Mg. The concentration of Ca and Mg ions was 1×10^{-3} M for each metal ion.

In the second simulation, the presence of Ca and Mg with one chelating agent was assessed. The concentration of chelating agent was twice the sum of Ca and Mg ions, [L]= 2([Ca]+[Mg]), where [Ca]=[Mg]=1×10^{-3} M. The main results taken from the first and second computer simulations are represented in Figs. 2 and 3, respectively.

Figure 2 shows the pH range at which the chelating agent complexes more than 80 % of the respective transition metal (Fe, Mn, Cu, Pb, Cd, and Zn) in a medium with Ca and Mg in excess. The results for EDTA are also shown to allow an easy comparison with the most usual situation. Despite the good ability of all compounds to complex transition metals, EDTA chelates most metals in a larger pH range, especially Fe, Mn, and Pb.

For paper pulp and textile bleaching process, considering only the pH range and the metals to be chelated, we can conclude that NTA, EDDS, MGDA, and PDA could be used, which is in line with the literature (Chauveheid et al. 1999; Moore et al; 1997; Neto et al. 2014; Pinto et al. 2014; Renvall et al. 1997; Seccombe and Dournel 2007). For EDDM, although stability constants for Fe were not found, a recent study showed that this compound could be a potential alternative to this process (Neto et al. 2014). As Giles and Dixon (2009) suggested, a mixture of biodegradable and nonbiodegradable chelating agents can be an interesting option. The combination of GLDA, IDS, or HIDS with EDTA can override the lack of affinity of GLDA, IDS, and HIDS to Fe ions.

In soil remediation process, NTA and EDDS could be used; however, these ligands can only be used at alkaline pH to avoid the removal of Fe, as it was mentioned by Vandevivere et al. (2001) and Tandy et al. (2004). Also IDS, HIDS, HEIDA, PDA, MGDA, EDDG, and GLDA could be used and experimental studies have already been performed (Arwidsson et al. 2010; Begum et al. 2012c, 2013; Cao et al. 2007; Macauley and Hong 1995; Tandy et al. 2004). The conclusion obtained from these studies is that none of the

biodegradable options has a good performance for removing Pb as EDTA. This fact is justified by the evident stronger ability of EDTA to complex this metal.

According to the speciation simulations, only NTA could be an interesting option to increase Fe bioavailability in agriculture using the higher [L]:[M] ratio simulated. Despite the poor chelation ability evidenced by the computer simulations, different researchers described that some of these chelating agents could be possible options (Albano 2008; Hasegawa et al. 2011, 2012; Lucena et al. 2008).

Figure 3 shows the percentage of Ca (Fig. 3a) and Mg (Fig. 3b) complexed over the pH range in a solution with only Ca and Mg and one chelating agent. These simulations were performed in order to understand the possibility of using the chelating agents to avoid scale formation or to be applied in detergents. The computer simulations suggest better results with the use of NTA, MGDA, and GLDA. Both MGDA and GLDA are frequently suggested in the literature for these applications due to their high potential to complex with Mg and Ca ions (Charkhutian et al. 2004, 2006; De Wolf et al. 2009; Palladini 2007; Zack et al. 2012). PDA and HEIDA could also be used when only Ca ions complexation is required.

Conclusions

The search for more environmentally friendly chelating agents to replace traditional EDTA and DTPA resulted in numerous studies in the last two decades. Most of the research regards areas where there is a large consumption of chelating agents, such as paper pulp bleaching, detergents and cleaning, scale prevention, soils remediation, and agriculture.

Many biodegradable compounds, like NTA, EDDS, IDS, MGDA, GLDA, EDDG, EDDM, HIDS, HEIDA, and PDA, have been suggested as potential alternatives and some of them are now marketed to be used at industrial scale. EDDS has been widely studied in different applications and, in some cases (e. g. detergents), used at commercial scale. In the last decade, the various papers and patents, where MGDA and GLDA were studied, pointed out the use of these compounds as biodegradable substitutes in main industries.

Computer simulations, based on stability constants of complex formation, show the difficulty of finding an alternative biodegradable compound with chelation ability as good as EDTA. However, the requirements depend on the purpose and, in some cases, a more selective chelation is preferred, which can be an advantage for the biodegradable options.

With the aim of replacing nonbiodegradable chelating agents in industrial and agriculture applications, the need to find efficient and low-cost alternatives and optimize processes still remains.

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