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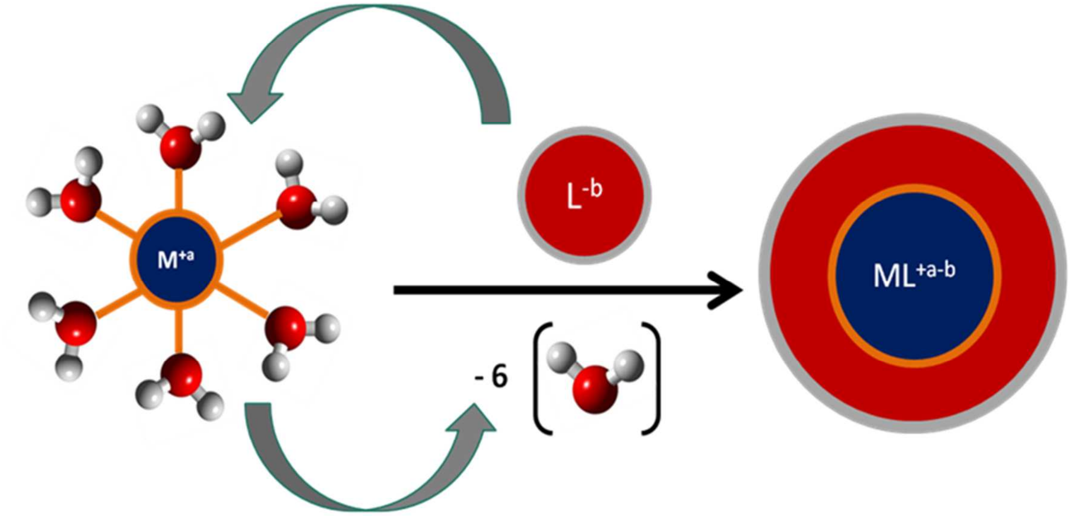
This review covers technical applicability of chelation technology for metal extraction from contaminated sites, recent research trends and future opportunities to spring up this process as a Green Chemical Engineering Approach.



Chelation Process—A Ligand Substitution mechanism

Environmental Impact Statement

Heavy metals are present in industrial wastes in significant amount and may become a threat to ecosystem and human health which. Chelation-dechelation technology was coined by our research group for extraction of heavy metals from spent catalysts. Nearly “closed loop” green technology has also been developed in order to extract metals from multimetallic spent catalyst using biodegradable chelating agents. The present review article explores all the aspects of this technology to spring up the chelation process as a Green Chemical Engineering Approach. This manuscript covers the interaction mechanism of ligands with metals, ecotoxicological risk associated with increased bioavailability of heavy metals and technical applicability of chelation technology in different research areas. Emerging trends and opportunities have also been suggested to carve-out the new territory of Green Chelation Technology.

Chelation Technology: A Promising Green Approach for Resource Management and Waste Minimization

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Abstract

Green chemical engineering perceives the concept of developing innovative environmental benign technologies to protect human health and ecosystem. In order to explore this concept for minimizing the industrial waste and for reducing the environmental impact of hazardous chemicals, new greener approaches need to be adopted for extraction of heavy metals from industrial wastes. In this review, a range of conventional processes and new green approaches employed for metal extraction are discussed in brief. Chelation technology, one of the modern research trends, has shown its potential to develop a sustainable technology for metal extraction from various metal-contaminated sites. However, the interaction mechanism of ligands with metals and the ecotoxicological risk associated with increased bioavailability of heavy metals due to formation of metal-chelant complexes is still not sufficiently explicated in literature. Therefore, a need was felt to provide a comprehensive state-of-art review of all aspects associated with chelation technology to spring up this process as a Green Chemical Engineering Approach. This article elucidates the mechanism and thermodynamics associated with metal-ligand complexation to have better perceptivity of metal extraction process. Effects of various process parameters on formation and stability of complex have been discussed elaborately in order to optimize the chelation efficiency. Non-biodegradable attribute of ligands is another important aspect which needs a sincere concern these days. Therefore, biotechnological approaches and computational tools have been assessed in this review to illustrate the possibility of ligand degradation which will help the readers to look for new environmentally safe mobilizing agents. In addition, emerging trends and opportunities in the field of chelation technology have been summarized and diverse applicability of chelation technology in metal extraction from contaminated sites has also been reviewed.

Keywords: Green Engineering**,** Chelation technology, Biodegradability, metal-ligand complex, contaminated sites

Introduction

Sustainability is the primary obligation for process industries in the present competitive era where energy resources are consuming at much faster pace than ever. Brundtland communicated the most widely adapted definition for sustainability which suggests that “Sustainable development is development which meets the needs of the present without compromising the ability of future generations to meet their own needs”[1]. Necessity of energy resources sprang up to prominence in recent decades due to rapid urban and industrial growth. It is projected that world energy consumption will grow by 56%, from 132 quadrillion kilocalories (kcal) in 2010 to 207 quadrillion kcal in 2040[2]. A strong conjunction of energy utilization with industrial growth can also be substantiated by the data reported in IEO2013[2] survey which indicates that industrial sector is the largest energy consuming sector with 52% of global delivered energy utilization in 2010. This increasing rate of energy dependence is inciting the world towards resource scarcity, price inflation and degraded ecosystems. Therefore, innovative processes are required within an eco-friendly framework that should realize the global necessity of resources (metals) and significantly reduce the hazardous emission to environment without compromising economics of the process.

Though, numerous efforts are being made worldwide to call for sustainable industrial processes in order to conserve resources, relatively little has been emerged on a practical level so far. The reason behind this lack of practical applicability may be due to complexity of process industries where it is difficult to manage economics, ecology and resource need, all at one platform. Green chemical engineering perceives the concept of developing innovative environmental benign technologies in order to overcome this complexity and to flourish new trends in sustainable process development. Several green research efforts[3-9] are being made in process industries to conserve resources and minimize pollution possibility.

In context of conserving resources, heavy metals are one of the major natural resources which need a sincere concern. Inconceivability of having economic and industrial development without concomitant increase in resource consumption has now stepped up the necessity of metals which are considered as ‘key of industrialization’. Heavy metals are extensively used in preparation of various catalysts in petrochemical and fertilizer industries in form of metal oxides and metal sulphides. Recovery of these metals from industrial waste is an essential issue to consider for the aid of industrial and economic benefits. The increasing demand of metals in industrial activity evokes them as an ineluctable contributor in process industry however, negative strikes of heavy metals can also not be disregarded. Heavy metals are bioaccumulative into the ecosystem and their removal from soil-plant-atmosphere continuum is a tedious objective. Waste generated from industrial and manufacturing processes can be considered a substantive source to release heavy metals into environment. Waste water treatment sludge, distillation bottom sludge and spent catalyst generated due to organic chemical manufacturing have been classified as potential hazardous waste by the environmental protection agency (EPA), USA[10]. Spent catalysts from petroleum refining dual process reactors (spent hydrotreating catalyst (EPA-K171) and spent hydrorefining catalyst (EPA-K172)) have also been listed in hazardous waste due to presence of toxic metals[10]. Wastewater treatment sludge from circuit board manufacturing operations (EPA-F006) and spent pickle liquor generated by iron and steel industry (EPA - K061, K062) are also considered major source of environmental pollution[10].

In this review, a range of conventional processes (basic inspiring technologies) and green approaches (new modern trends) employed for metal extraction are discussed in brief. Positive and negative strikes of each process have been briefly reviewed in order to understand the current and future process design necessity. Chelation technology, one of these modern approaches, has been increasing affinity to environmental sciences for extraction of heavy metals from soils[11,12] and industrial wastes[13-15] in recent years. Therefore, the core of this article is a deep review of what has been done in the field of chelation technology so far and what can be done in near future to illustrate this technology as a Green Chemical Engineering Approach (Zero waste technology). Efforts have been made in present review to summarize the important aspects associated with metal-chelate complex formation including its chemistry and interaction mechanism with metals. Ecotoxicological issues associated with conventional chelating agents as well possibilities to degrade the chelating agents in environment have also been reviewed in detail. Diverse applications of chelating agents in various research fields have been summed up and metal extraction from soils and industrial wastes using chelation technology have been emphasized particularly. In addition, pertinence of new computational tools in the field of chelation technology has also been considered to illustrate the future possibility in designing new biodegradable chelating agents.

2. Available methods for metal extraction from contaminated sites

2.1. Conventional Approaches

Numerous approaches have been reported in literature for recovery of heavy metals from contaminated sites. Adsorption has been considered a good alternative for efficient extraction of metals from industrial waste water[16,17]. Membrane separation[18], electrotreatment[19], photcatalytic processes[20] and absorption by aquatic plants[21,22] have also been employed to remove metals and other pollutants from water. Toxic metals may also present in soils which may exhibit chemical interaction mobility and potential toxicity. Therefore, various techniques such as vitrification, excavation, removal of contaminated soil layer, phytoremediation[23,24] and soil washing using surfactant, acids, alkalis and chelating agents[25,26] have been investigated for soil remediation. Spent catalysts generated from refineries and fertilizer industries are also considered potential sources of heavy metals and therefore research on metal extraction from spent catalysts is being conceived by researchers. Various pyrometallurgical processes such as calcination followed by leaching[27,28] or roasting at high temperatures[29,30] have been employed for extraction of heavy metals from spent catalysts. Hydrometallurgical approaches (leaching[31,32], solvent extraction[33,34] and biological methods[35,36]) have also been reported to recover metals from spent catalysts, soil and other industrial wastes. Table 1 summarizes different studies performed to extract heavy metals from contaminated sites using hydro and pyrometallurgical approaches along with positive and negative strikes of each process. Experiments were performed under batch mode for all the references listed in Table 1.

Table 1 : Studies performed to investigate recovery of heavy metals from spent catalyst using different hydro/pyro metallurgical methods.

All these processes have shown potential in removing metals from industrial wastes however, use of hazardous chemicals, secondary pollution possibility by these chemicals, less acceptance of biological processes in the environment and high process cost restrict their use on large scale. Thus, health and environmental issues associated with these traditional methods are drawing researcher's attention to look for a sustainable alternative for metal recovery from industrial wastes.

2.2. Recent Trends

Globally, there is an urgent need to look for new green reagents for metal extraction. This excogitation is now assisting researchers to move towards ionic liquids (ILs), novel resins and polymeric composites, chelating agents and other green extractants. ILs have been efficiently used in the extraction of lanthanides and actinides. Recently, Methylimidazole (1-MIM) and 2-methylimidazole (2-MIM) with imidazolium-based ILs was employed for the solvent extraction of lanthanides and yttrium[53]. Quaternary phosphonium- and ammonium ILs Cyphos(R) IL101 (Cytec) and Aliquat(R) 336 (Henkel) were also demonstrated to remove Pt from aqueous solution by replacing chloride anion with functionalized aromatic anions[54]. Liquid phase micro extraction with phosphonium- and ammonium-based ILs bearing sulphur functionality in the form of thiosalicylate and 2-(methylthiobenzoate) anions were also investigated for the extraction of metal ions Ag, Cu, Hg and Pt from industrial and communal waste water[55]. A wide range of ILs applications covering distinct research areas (catalysis, electrolytes and solvents) are currently at an exploratory phase to employ it in industrial processes. However, some ILs may severely contaminate the ecosystem in case of accidental leakage or wastewater disposal. Search for suitable extractants and to understand the complexity of an original aqueous solution due to interference of added chemicals are other problems associated with this approach.[56].

A new term "Green Adsorption" has also been introduced recently for metal extraction from waste water which includes low-cost ecofriendly materials originated from agricultural sources and by-products (fruits, vegetables, food), agricultural residues and wastes[57]. Several authors employed natural bentonite and zeolites[58,59], rice/peanut husk and fly ash[59-61], banana and orange peel[62], anaerobic granular sludges[63-65] for metal extraction. Inspite of having economic potential, these adsorbents are not preferable due to their low adsorption capacities and therefore, chemical modification of these materials is required to improve the performance[66-69]. Rice hull was investigated as a chemically modified adsorbent using ethylenediamine for Cr^{+3} metal removal[70] and it was observed that chemical modification of rice hull enhanced its adsorption capacity. Fig. 1 demonstrates the structural configuration of some green extractant which have been used in literature for metal removal.

Fig. 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (A) DEHPA (Di-(2ethylhexyl phosphoric acid) (B) Aliquat-336 (*N*-Methyl-*N,N,N*-trioctyl-octan-1-ammonium chloride) (C) Cyanex 272 (*Bis*(2,4,4-trimethylpentyl)phosphinic acid) (D) Cyanex 301 (*Bis*(2,4,4-trimethylpentyl) dithio-phosphinic acid) (E)1-*N*-butyl-3-methylimidazolium salts (F) LIX-84-IC (2-hydroy-5-nonyl acetophenone oxime) (G) Tributyl Phosphate (H) Acorga M5640 (active substance 2- hydroxy-5-nonylbenzaldehyde oxime) (I) Amberlite Resin 400 (J) Dowex M-4195 Resin

Some authors also employed modified biopolymer adsorbents derived from chitin, chitosan and starch for metal removal from contaminated sites[6]. Repo et al.[71] investigated the adsorption properties of modified chitosans using different chelating agents in the aqueous solutions of Co^{+2} and Ni^{+2} ions. Results indicated that adsorption efficiency of ethylenediaminetetraacetic acid (EDTA) modified chitosan was 99.2% for Co^{+2} and 99.5% for Ni^{+2} while diethylenetriaminepentaacetic acid (DTPA) modified chitosan removed 96.7% of $Co^{+2}$and 93.6% of Ni^{+2} at the similar reaction conditions which could be explained on the basis of crosslinked structure of DTPA-chitosan and lower surface coverage of DTPA compared to EDTA. In the similar manner, Wang et al.[72] applied adsorption process to extract Pb^{+2} and Cu^{+2} in micro-polluted water source using PS-EDTA resin. It was illustrated that at optimum reaction conditions, PS-EDTA surface adsorbs Cu^{+2} much better than Pb^{+2} and seems to be a better adsorbent for removal of both ions from aqueous solutions. Dzulkefly et al.[73] used chelating resin Amberlite IRC-718 for extraction of Ni^{+2} from spent catalyst samples, obtained from hydrogenation of palm and palm kernel oils. Oil content was removed from the catalyst by soxhlet extraction using n-hexane. Amberlite resin showed more than 90% extraction efficiency for Ni^{+2} with higher than 90% purity with regard to other metals Mg and Ca in the catalyst samples. Kolodynska[74] studied the effect of weak base chelating resin (Dowex M 4195) as ion exchanger for Cu^{+2}, Zn^{+2}, Ni^{+2} as well as Cd^{+2} and Pb^{+2} sorption in the presence of complexing agents glutamicdiacetic acid (GLDA) and ethylenediaminedisuccinic acid (EDDS). It was observed that at low pH there are some deprotonated nitrogen atoms capable of interacting directly with metal ions. Dowex M 4195 was reported to have higher sorption capacity with GLDA than EDDS. These green adsorbents offers certain advantages such as low-cost, easy operating conditions and wide pH range, however low selectivity and waste generation are the major drawbacks which inhibit its applicability at large scale.

Membrane filtration[75-77], electrodialysis[78-79] and photocatalysis[80-81] are also being considered as green approaches for metal extraction from industrial effluent. These methods need regeneration of membranes after certain intervals which increase operational cost and energy requirement for the process, still high separation selectivity make these processes feasible for metal removal. Photocatalysts consume photons from the UV-near visible region and may induce degradation of organic pollutants as well as recovery of metals in one-pot systems. Traces of the target compounds can also be identified using this method. However, metal removal using photocatalysis process is still a new research area and therefore cannot be judged at this stage.

It is believed that technical applicability, operational simplicity and economic feasibility are the key factors in selecting the most suitable technology for metal extraction[6]. Chelation technology, evolved over the century for being used in metal-intoxication, has also been emerged as a green chemical engineering approach for metal extraction from contaminated sites (soil, waste water, spent catalyst) in recent years. Several studies have been conducted to evaluate performance of chelation agents as adsorbents, extractant, coating materials to prepare modified composites etc. This article reviews the technical applicability of chelation technology for metal removal from contaminated sites and also illustrates recent developments in this particular research area.

3. Chelation Technology: A path to Green Economy

‘Chelation’ is defined as formation of stable metal ligand complexes which are soluble in water. Though, ‘chelation’ term defines the mobilization of metal ions from contaminated sites using multidentate ligands (chelators) as reagents, however, some authors assumed hydration of metal ion as an initial step (reaction takes place in aqueous solution) and then, multidentate ligand tend to substitute water molecules from metal-water complexes in order to form metal-ligand complex[82,83]. In this article, chelation is demonstrated as the process of ligand replacement of monodentate ligands in metal complexes by multidentate ones. Metal ions present in these complexes do not exhibit chemical activity as uncomplexed ions[84].

Chelating agents may be either organic or inorganic compounds. Polyphosphates are the best known inorganic chelating agents however these are hydrolytically unstable at high temperature and pH. Among the organic chelating agent, aminopolycarboxylates are the frequently used chelant which accounted the largest share (39%) in the world wide consumption of chelating agent in year 2012[85]. These aminopolycarboxylates e.g. EDTA, nitrilotriacetic acid (NTA), DTPA have stronger binding capacity than polyphosphates and better sequestering ability than hydrolytic acid type chelating agents[86,87]. A new discipline 'greener chelating agent' is also gaining researcher's concern these days and contributes to 15% of the overall world consumption of aminopolycarboxylate chelating agents[88] and the demand is expected to increase upto 21% till year 2018 due to replacement of conventional chelating agents by new range of biodegradable chelating agents. EDDS, GLDA, Iminodisuccinic acid (IDSA) etc. are the examples of biodegradable green chelating agents which may significantly share the chelating agents market in forthcoming years to avoid environmental risks associated with non-biodegradable chelators. Fig. 2 demonstrates molecular arrangement of some newly synthesized biodegradable chelating agents.

Fig. 2 : Molecular arrangements of some newly synthesized biodegradable chelating agents (A) *N*-2-acetamidoiminodiacetic acid (ADA) (B) Ethylenediglutamic Acid (EDGA) (C) Ethylenediamine dimalonic Acid (EDDA) (D) *N,N-bis*(Carboxymethyl)-*L*-Glutamic Acid Tetrasodium Salt (GLDA) (E) Iminodisuccinic acid (IDS) (F) Ethylenediamine disuccinic acid (EDDS) (G) Methyl glycine diacetic acid, trisodium salt (MGDA) (H) *N-bis* [2- (1,2-dicarboxy methoxy)ethyl] glysine (BCA3) (I) *N-bis* [2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCEEAA) (J) 2,6-Pyridinedicarboxylic acid (DPA)

The major key factors driving chelating agent growth in the market include strict environmental legislations, rising demand of biodegradable chelating agents and diverse applications of chelating agents. It was forecasted by Global Industrial

Analyst (GIA) that the global market for chelating agents is expected to reach 438 thousands metric tonnes by the year 2017[89].

Extraction of metals with chelating agents does not require high temperature and the chelating agents can be reused after the extraction of metals. Due to its recoverable nature, this process is more economical than any other process. This process is ecofriendly due to easy recovery of chelating agent used for the process, non-corrosive environment and no any hazardous byproducts are liberated during the process. High efficiency of metal extraction and moderate thermodynamic stabilities of the metal complexes make this technology more favorable than any other technology for metal recovery.

3.1. Metal-chelate complex formation

Chelation concept is based on coordinative incorporation of a metal ion into a heterocyclic ring structure. Metal ions in solution always make bonds with ligands and form complex ions. Alfred Werner proposed the concept of transition metal complex formation in 1893[90] and unriddled the puzzling aspect of having higher valences than requisite for transition-metal compounds. This work suggests the existence of secondary valence in addition to a “primary” valence of appropriately charged counter ions for transition metal complexes[91]. The word ‘chelate’ was introduced in 1920 for these caliperlike ligands which function as two associating units and hold the central metal ion in order to make ring structures[92]. The coordination environment around the metal ions is demonstrated by Werner’s theory according to which metal ions are coordinated by neutral or negatively charged ligands whose arrangement around the centre depends on the oxidation state of metal[93].

Metal-chelate complex formation mechanism refers to the step by step analysis of reactions involved in the conversion of reactants to products. The general reaction profile for metal (M) – ligand (L) interaction can be given as eq. (1) -

$$\begin{array}{ccccccccc} M + L & \rightleftharpoons & [ML]^* & \rightleftharpoons & [ML] & \rightleftharpoons & [ML]^{**} & \rightleftharpoons & ML \\ \textbf{Energetic Collision} & & \textbf{Transition State} & & \textbf{Intermediate} & & \textbf{Transition State} & & \textbf{Final Product} \end{array} \qquad (1)$$

It can be seen in eq. (1) that there are two transition states where the ligand substitution may take place. Schematic representation of eq. (1) is given in Fig. 3 which suggests that metal and ligand interact due to energetic collision of both the molecules. Energetic collisions between molecules cause stretching and bending of the interatomic bonds which makes them more susceptible to cleavage. Distortion of the bonds can also allow their associated electron clouds to interact with other reactants that may lead to the formation of new bonds. There are different transition states and intermediate stages between the reactant conversion and product formation. An intermediate occurs at the local energy minima whereas the transition state always occurs at an energy maxima point and cannot be isolated.

Fig. 3: Metal-ligand interaction – General Mechanism

The mechanism of metal-ligand complex (ML) formation can also be demonstrated in terms of a rapid pre-equilibrium. Reaction is carried out in an aqueous phase and the water molecules are replaced by another ligand in the coordination sphere of the metal. The reaction mechanism can be performed in two steps –

1) Metal- water complexation (Formation of an outer sphere complex $[M(H_2O)]^{+a}$
2) Metal-chelate complexation (Replacement of water molecule by the ligand).

The reaction mechanism of metal-chelate complexation in aqueous system is demonstrated in Fig. 4 which depicts that initially the metal-complex contain water molecule as a ligand and then the other ligand is substituting the first one in the rate determining step. Thus, metal-ligand complex formation reaction can be considered a ligand substitution reaction.

Fig. 4: Schematic representation of the reaction mechanism for metal-complex formation in aqueous system.

The reaction for the ligand substitution can be given as eq. (2) -

$$[ML_nX]^{Z+} + Y^- \rightleftharpoons [ML_nY]^{Z+} + X^- \qquad (2)$$

Different mechanisms (associative, dissociative and interchange) for the ligand substitution reaction are demonstrated in Fig. 5.

Fig. 5: Ligand Substitution Mechanisms – (a) Associative (b) Dissociative (c) Interchange

Reedjick[94] studied the applicability of heavy metal Pt^{+2} and Ru^{+2} as an anticancer drug when coordinated with the appropriate ligand. It was observed by investigating the reaction kinetics that ligand exchange reaction depends on both the metal and the coordinated ligand. Square-planar Pt^{+2} compounds exchange their ligands via associative ($S_N{}^2$) process, where the incoming ligand coordinates as a new ligand and the original ligands dissociates. Associative mechanism takes place in just one step and well-defined intermediates are not observed. Octahedral Ru^{+2} coordination compounds, on the other hand, tend to lose a ligand first (to generate a five-coordinate intermediate), after which the new ligand comes in, and thus follows a dissociative ($S_N{}^1$) mechanism.

Metal extraction process using chelating agents is a heterogeneous process because of the transportation of chelated metal ions from catalyst to the aqueous solution. Thus, it can also be explained as 'solid-liquid' extraction process. The final product of extraction process does not depend on whether the reaction takes place at the interface or in the aqueous phase. However, it depends on the electron-count of the metal complex undergoing the ligand substitution. Contribution of mass transfer rate to the total rate of the process must be taken into consideration. The process can be considered a 'diffusion controlled' process at low rate of phase mixing, whereas a 'kinetic region' can be achieved by increasing the mixing and lowering the particle size[15,95]. Thus, rate of individual chemical stages of the process can be known in the region of 'mixed kinetics' if the rates of mass transfer and of chemical reactions are comparable in magnitude.

3.2 The Chelate Effect

Formation constant for any chelation process can be computed by the thermodynamic relationship as given in eq.(3):

$$\Delta G^\circ = -RT\ \ln(K) = \Delta H^\circ - T(\Delta S^\circ) \quad (3)$$

Enthalpy (ΔH) contributes to the thermodynamics of complexation process in the form of ligand repulsion, distortion and crystal field stabilization energy[96] whereas the entropy (ΔS) includes all probability factors which control the stability of the complex.

Schwarzenbach[97] delineated the combined effect of these two terms (enthalpy and entropy) as the 'Chelate effect' which refers to the enhanced stability of a metal-ligand complex due to chelation process. It was concluded in Schwarzenbach work on EDTA versus the corresponding iminodiacetate that the chelating species can be stabilized with a favourable entropy change[97]. Adamson[98] investigated the effect of standard thermodynamic states and concluded that asymmetry in the choice of the standard thermodynamic states causes the chelate effect.

The enthalpy change in chelation reaction was assumed to be non-significant till the Myres[99] investigation which suggests that enthalpy difference in aqueous solution of ligands is a significant contributor to Gibbs free energy (ΔG^0). The significant entropy effect of ligand solution and of coordinated metal ion solution was also studied. An increase in translational entropy was reported when molecules are released in solution during the chelation process. The entropy of solution of the monodentate and chelated cations did not differ much whereas the enthalpy deviated from ideal solution by more than 4.8 kcal[99].

Chung et al.[100] illustrated an example of chelation for octahedral complexes and suggested that the entropy change of a chelation reaction is a combination of different entropy forms. It was deduced that the solvation entropy and internal rotation entropy play a negative contribution on overall energy. The reason behind the negative magnitude of solvation entropy is the difference in solvation entropies of the ligands and the different standard states employed. The solvation factor in organic solvents will be less significant than in aqueous solution, therefore, the entropy change of chelation in the gas phase or in an organic solvent will be larger than that in aqueous solution. It was also suggested that the internal rotation of free ligands and the complexes containing monodentate ligands are lost in the chelation reaction and therefore, the decreasing magnitude of entropy can be observed with the increasing size of chelate ring.

Temperature dependence for association constants of metal chelates and complexes was investigated by identifying ligand-dependent correlations of partial molar entropy of association (ΔS_r) of the complexes and chelates with the standard-state entropies ($\Delta S°$) of the aqueous cations at 298K and 1 bar[101]. Quantum chemical calculations were also performed to study the chelate effect of the metal complex formation reaction in aqueous system[102]. It was concluded that the rotation and vibration entropy contributions are also as important as the translation entropy contribution to the total entropy of reaction. ΔH° of reaction also play a significant contribution to the ΔG_0 of reaction in complex formation reactions, and therefore, the strong stability of chelate complexes can be considered a combined effect of enthalpy and various forms of entropy of the reaction.

3.3. Factors affecting the metal-chelate complexation

Formation of metal-chelate complex may be considered a heterogeneous chemical reaction which depends on certain process parameters such as reaction pH, molar concentration of chelating agents, reaction temperature, various competing equations in aqueous phase etc. This section briefly discusses the effect of various important factors on metal-ligand complexation process which play a dominant role to increase the extraction efficiency.

3.3.1. Effect of reaction pH

Extraction of metal-ligand complex compounds is represented by eq. (4):

$$M^{+n} + nHL \rightleftharpoons ML_n + nH^+ \qquad (4)$$

The extraction constant (K_{ex}) for the above metal-ligand (ML_n) complexation reaction can be given as eq. (5)[103] :

$$K_{ex} = [ML_n]\,[H^+]^n / [M^{n+}][HL]^n \qquad (5)$$

Here, if the formation of intermediate complexes with the reagent and side product formation due to hydrolysis or competing reaction in aqueous phase is neglected for a certain pH range, then eq. (5) can be rearranged as eq. (6):

$$K_{ex} = E\,([H^+]^n/[HL]^n) \qquad \text{where } E = \text{distribution coefficient} \qquad (6)$$

$$\log E = \log K_{ex} + npH + n\log[HL]^n \qquad (7)$$

Thus, it can be depicted from eq. (7) that the curve between log E (distribution coefficient) and pH of the solution should be a straight line with slope n which indicates that if molar concentration of chelating agent [HL] is constant, then extraction of heavy metals will be completely dependent on reaction pH.

Several authors studied effect of reaction pH on chelant assisted metal extraction from industrial waste, soil and other contaminated sites. Tandy et al.[104] studied the effect of solution pH on efficiency of various biodegradable and conventional chelating agents for metal extraction from noncalcerous soils which have been demonstrated in Fig. 6. EDTA was found to be the most effective chelating agent over the entire pH range for Cu, Zn and Pb as shown in Fig. 6. EDDS can be observed as better metal extractant for Cu and Zn than EDTA at pH>6 and low stoichiometric ratio of chelating agent to metal. NTA also showed comparable extraction of Zn as EDDS at neutral pH however NTA was not found to be an effective chelating agent for Cu extraction. IDSA and methylglycinediacetic acid (MGDA) performed better Cu extraction efficiency than EDTA at neutral pH when ratio of chelating agent to metal is equimolar. Stronger complexation of Pb with EDTA than other chelating agents resulted in the highest extraction efficiency of EDTA for Pb metal, however, EDDS also showed similar Pb extraction efficiency as EDTA for pH>7.

Fig. 6: Effect of reaction pH on extraction efficiency of various chelating agents for Cu (Blue markers), Zn (Red markers) and Pb (Green markers)[104]

Begum et al.[105] demonstrated effect of different extraction variables (reaction pH, chelating agent to metal ratio, stability constants of metal/chelating agent and solid phase distribution of metals) on metal extraction from artificially contaminated soils. EDDS showed the best extraction efficiencies among the biodegradable chelating agents for extraction of Cu, Pb, and Zn at pH = 7. It was also observed that *dl*-2-(2-carboxymethyl)nitrilotriacetic acid (GLDA) performed better than other employed chelating agents for the extraction of Zn, Cd and Cu at pH = 4, while EDTA illustrated the highest efficiency for lead removal. Average extraction efficiency at neutral pH was observed to be either lower or comparable than that of acidic or alkaline reaction conditions. Acidic pH conditions may increase the concurrent release of the other metal ions and an exchange of H^+ ion from functional groups present at soil surface[106] whereas alkaline pH conditions may be responsible for increasing the reactive species L^{n-} in aqueous solution and higher formation rate of the soluble coordination compounds[107] which could be the possible reasons for improved extraction efficiency at acidic and alkaline pH.

Chatreewongsin[108] studied metal extraction from soil samples by EDTA chelation in a microwave system and concluded that amount of extracted Cu was dependent upon reaction pH for classical chelation technique. Higher dissociation of EDTA molecules was observed at alkaline pH which could be related with the protonated stages of EDTA species (HL^{3-} and L^{4-}) in alkaline medium. Soil surfaces may also contain large number of negative surface charges at alkaline pH, thus Cu-EDTA complexes possessing negatively charges are preferable in the aqueous solutions. Goel et al.[13] extracted Ni from spent catalyst of a fertilizer industry using EDTA and illustrated that extraction efficiency of EDTA increased with an increase in pH value upto 10, however after pH =10, extraction starts to decrease. Authors did not explain the reason associated with the decrease in extraction efficiency with increase in pH. Existence of anionic complexes of ML^{-}_{n+1} in the solution or hydrolysis of the metals may be the possible reasons for this observation. Fangueiro et al.[109] suggested that solution pH may affect the aqueous metal species concentrations (and consequently the stability of metal chelates), the solubility of chelating agents, trace metal sorption/desorption, ion exchange phenomena, as well as re-adsorption mechanisms of newly formed metal–chelant complexes and thus strongly affects the performance of the chelating agents for extracting metals from contaminated sites. Chauhan et al.[15] investigated the performance of biodegradable chelating agent EDDS to extract Ni from spent catalyst and concluded that EDDS requires narrower pH range for chelation-dechelation process than EDTA due to lower stability constants of Ni-EDDS complex. It has also been reported that EDDS can extract higher amount of heavy metals at neutral pH than that of EDTA.

Thus, effective pH range for extraction of a particular element may differ for different ligands which may be explained on the basis of the percentage distribution of protonation stages of ligands[96]. Curves representing the percentage (%) distribution of various protonation stages for some ligands (3,6-dioxaoctane-1,2,4,5,7,8-hexacarboxylic acid (TDS), EDTA, EDDS, and DTPA) have been reproduced here for reader’s ready reference and shown in Fig. 7(A) - Fig. 7(D).

Fig. 7 : % Distribution of protonation stages of various chelating agents (A) TDS (B) EDTA (C) EDDS (D) DTPA[96]

It is elucidated that each ligand has its certain pH range for different protonation stages. TDS has more acidic species than EDTA, EDDS and DTPA whereas, DTPA has a wider pH range for the protonated H_2L^{-2} form. HL^{-3} is predominant for the pH value 7 to 9 in case of EDDS while, a wider pH range (pH = 6 to pH = 10) can be observed in case of EDTA for the same protonation stage. This deviation in the % distribution of various protonation stages strongly affects the effective pH range for a ligand. It can also be seen from Fig. 7 that the fully protonated H_6L^{+n} form predominates at the most acidic pH value (pH = 1-2), and as the reaction moves towards alkaline pH, hydrogen availability for displacement decreases and deprotonated forms are prevalent, therefore, after a certain increase in pH value, no further improvement in extraction efficiency can be observed[9]. It should also be kept in consideration that the favorable pH range for the efficient extraction of heavy metals may correspond to the precipitation range of the corresponding chelate, which can be determined either by stability constants[15] or distribution constants of the complexes[103].

3.3.2. Effect of molar concentration of chelating agent

Molar concentration of chelating agent also plays a significant role in metal extraction process. Distribution coefficient (E) largely depends on reagent concentration in solution at constant pH as shown in eq.(7) and a straight line with a slope of charge n of the metal cation is obtained by plotting a curve between log E and log [HL]. Relationship between pH and concentration of the reagent has also been explicated in the literature as given in eq.(8)[103]:

$$pH_{50} = (-1/n) * \log K_{ex} - \log [HL] \qquad (8)$$

Eq.(8) suggests that as the molar concentration of the ligand [HL] increases by one order of magnitude, pH_{50} decreases by one unit. Here pH_{50} indicates the value of pH corresponding to 50% extraction of metal ion when distribution coefficient is unity[103,107]. Effect of ligand concentration on metal extraction efficiency has been investigated elaborately in literature[13,74,104,105,110-112]. Jiang et al., 2011[26] varied the chelating agent concentration from 0.1g/L to 0.4g/L to extract Cu and Ni from artificially contaminated soil and illustrated a significant effect of molar concentration of chelating agent on extraction efficiency. Metal extraction efficiency improved with increase in reagent concentration, however, after a certain amount (when the dose of chelating agent is enough for soil requirement), extraction efficiency becomes nearly constant. Some authors have also reported molar concentration of chelating agent in terms of stoichiometric ratio of chelating agent to metal (MR). Kim et al.[113] studied effect of various factors (solution to soil ratio, presence of major metal cations in samples and stoichiometric ratio of chelating agent to metal ions) responsible for metal extraction from Pb-contaminated soils and observed the high dependence of extraction efficiency on molar concentration of chelating agent. Extraction efficiency was also found to be dependent on the properties of soil samples and therefore, at a given stoichiometric ratio, extraction efficiency varied for different soil samples as shown in Fig. 8. However, if sufficiently large amount of EDTA was applied, most of the Pb may be extracted.

Fig. 8: Effect of chelating agent (EDTA) to metal stoichiometric ratio (MR) on Pb extraction from different soil samples[113].

Similar observations were reported for Cu, Pb and Zn extraction using various biodegradable chelating agents[104] and data have been redrawn in Fig. 9. It can be observed from Fig. 9 that as the concentration of chelating agent increases in the solution, metal extraction efficiency increases. Cu extraction was enhanced significantly for all investigated chelating agents at an equimolar ratio between chelating agent and metal. EDTA showed a significant improvement in Cu extraction at higher chelating agent to metal ratio which was explained by the speciation calculations. These calculations suggests that at a high MR, most of the EDTA was present in uncomplexed form and therefore, probability of metal-ligand complex formation increases, whereas, 90% of total EDDS is always accounted as uncomplexed EDDS and therefore, enough free EDDS is available to extract further Cu even at low MR. Therefore, Cu extraction efficiency of EDDS is nearly comparable at low and high MR values, while significant difference in Cu extraction was observed using other chelation agents[104]. When MR is increased (10:1), EDTA was observed to be more effective than other chelating agents for all the three metals at neutral pH.

Fig. 9 : Effect of chelating agent to metal stoichiometric ratio (MR) on metal extraction using different chelating agents[104]

Research has also been carried out to investigate the effect of liquid to solid (L/S) ratio on metal extraction from contaminated sites using chelating agent. Effect of L/S was investigated for Co and Mo extraction from spent catalyst at constant MR and results suggested an increase in extraction efficiency with an increase in L/S[9] to a certain extent. Increase in L/S ratio corresponds to the decrease in concentration of chelating agent in the aqueous solution and therefore beyond the optimum (required) L/S ratio for efficient mixing, extraction efficiency starts to decrease. However, if the L/S ratio is too low to prepare chelating agent solution and to minimize the external resistance by performing efficient mixing of particles, then extraction efficiency will be less, therefore, optimization of L/S is also requisite to achieve high extraction efficiency. Chauhan et al.[112] performed design of experiments and statistical analysis to optimize the process parameters for metal extraction process using different chelating agents (EDTA, DTPA, EDDS, NTA). Authors illustrated a significant mutual interaction effect of MR and L/S on Ni extraction. Kim et al.[113] varied L/S from 3 to 10 for lead extraction from contaminated soils and concluded that L/S did not show any effect on Pb extraction from soil. The possible reason for this observation could be the presence of excess amount of chelating agent from which only a small fraction was effectively utilized to extract Pb from soil. The remaining amount of chelating agent may be freely available in the solution or may form complexes with other metal cations, therefore, no effective increase in extraction efficiency can be observed beyond a certain L/S value when concentration of reagent is enough for the metal extraction. Manouchehri et al.[114] also urged that L/S cannot be considered an indicator to ensure the maximum metal extraction efficiency, however, this ratio must be investigated with respect to all the extractable metal ion present in the contaminated sites.

It is recommended that the molar concentration of chelating agents should be greater than that of the target metal species present in contaminated site to minimize the competing effect of other undesirable ions[115,116] however some reports also suggest that after a certain extent, extraction efficiency either becomes unaltered or starts decreasing with increase in concentration, which could be related with the higher dose of reagent concentration than the requirement of contaminated site for metal extraction[12]. Some other limitations may also arise due to higher concentration of chelating agent such as the reagent is difficult to remove and its residual traces may reduce the accuracy of the determination. Using a lower concentration of ligand and high L/S ratio may be beneficial in order to prevent clogging of the solid particles during leaching and to provide better mixing[117]. However, generation of large amount of wastewater after the extraction process may enhance the treatment cost and pollution possibility which is not desirable. Therefore an optimized value of the concentration of chelating agent and L/S ratio are necessary for effective extraction.

3.3.3 Effect of Reaction Temperature and Pressures

Understanding of thermodynamics aspects associated with chelating agent assisted metal extraction process is necessary in order to optimize the process parameters. Several studies have been carried out to investigate the effect of reaction temperature on metal extraction efficiency. Chauhan et al.[9] varied the reaction temperature from 100-140°C for extraction of Co and Mo from spent catalyst using EDTA and reported an increase in extraction efficiency with increase in reaction temperature. The increase in (%) metal extraction with increase in temperature may be related with Arrhenius behavior of the surface reaction which may enhance the reaction kinetics to dissolve the metal. 80.4% Co and 84.9% Mo recovery was reported at an optimized reaction temperature of 120°C within 4h of reaction time.

Fig. 10 demonstrates extraction of Ni using EDTA from spent catalyst at different reaction time and reaction temperatures under atmospheric and autogenous reaction conditions. It can be depicted from Fig. 10 that 95% Ni recovery was achieved under hydrothermal condition in an autoclave at reaction temperatures of 150ºC, over a 4h reaction time[14]. High temperature may also cause an autogenous pressure build up in the reactor. Extraction experiments were performed under atmospheric reflux conditions at reaction temperature of 90°C and a significant difference in extraction efficiency was observed[15] when results were compared with that of autogenous reaction condition at similar process parameters[14] as shown in Fig. 10.

Fig. 10 : Effect of reaction temperature on Ni extraction from spent catalyst

This could be due to the autogenous pressure in autoclave and better mixing of particles which is necessary for effective extraction process. Higher extraction efficiency of EDDS was observed at low reaction temperature which suggested superiority of EDDS over EDTA at low temperature. Increase in vessel pressure upto

2.7 atm at temperature 140°C was observed in literature[9,14] during chelation process for metal extraction which favours the rate of forward reaction, hence metal extraction efficiency improves. Extraction process at similar reaction condition was performed under atmospheric reflux conditions at reaction temperature 100°C, and about 58% Mo was extracted which was nearly 12% less than the extraction efficiency obtained under autogenous conditions[9]. Hong et al.[118] also investigated pressure assisted Pb extraction from soil samples and concluded that soil particles may break into smaller fractions due to high pressure and therefore, lower particle size enhance the metal extraction efficiency by controlling the internal diffusion. Therefore, autogenous reaction conditions are preferable for chelation process.

Moreover, metal extraction process using chelation technology would be adopted in a practical industrial plant where process has to be carried out in stirred autoclaves. Therefore, chelating agent assisted metal extraction process under autogenous reaction conditions is considered a feasible and efficient way of metal extraction on industrial platform. However, very high reaction temperatures can adversely affect process economics, in terms of consumption of steam utilities and equipment cost.

3.3.4 Effect of competing reactions in aqueous phase

Chelation reactions in aqueous phase involve the interaction of ligands with metal cation and result in the formation of metal-ligand complex, however some other products may also form during the process which may interfere in efficient extraction of target metals. Formation of lower complexes with chelating agents, hydrolysis and complex formation with extraneous complexing agents are major examples of competing reactions in aqueous phase[103]. If all compounds are mononuclear and ML_n is the only target species, then the distribution coefficient is calculated as shown in eq. (9) where effects of all other competing reactions are also considered.

$$E = [ML_n]_0 / ([M] + \Sigma_{i=1} [ML_i] + \Sigma_{j=1} [M(OH)_j] + \Sigma_{q=1} [MX_q]) \qquad (9)$$

$[ML_i]$ is concentration of metal-ligand complex including $[ML_n]$; $[M(OH)_j]$ is concentration of all hydroxylated components, and $[MX_q]$ is concentrations of complexes formed with the extraneous complexing agents[103].

In et al., 2008[119] employed the solvent extraction process with chelating agent salen-$(NEt_2)_2$ to extract Cu^{+2}, Mn^{+2} and Zn^{+2} from water samples and investigated the effect of concomitant ions on metal extraction process. It was illustrated that Mg^{+2} interfered with the extraction of Mn^{+2} and extraction of Mn^{+2} decreases, however no any significant effects were observed on extraction of Cu^{+2} and Zn^{+2}. It was also reported that if Mg^{+2} coexists in the solution at a very high concentration (>150000 times the Mn^{+2}), then Mn^{+2} cannot be determined due to strong interference. Manouchehri et al.[114] illustrated the significant effect of concentration of chelating agent and type of solid matrix on the extraction and reactivity of various metals (Pb, Cu, Cd, Al, Fe, Ca and Mg). Different competitive reactions were seen for major elements (Al, Ca, Fe and Mg) towards chelating agent EDTA depending on the soil Ca content. Calcareous soils preferred the formation of Ca–EDTA due to abundance of Ca in soil, while Al–and Fe–EDTA complex formations dominate in non-calcareous soil. Relatively weak bonding strength of Ca to certain soil fractions during the concurrent extraction process in calcerous soils may cause preferable Ca dissolution and displacement of other metals at higher reaction times. Tandy et al.[104] observed a strong competitive reaction between target metals and Ca as an important factor for extraction using EDTA, but not with EDDS which consequences in a decrease in extraction efficiency for EDTA compared to EDDS. Valverde et al.[120] illustrated that Fe may be neglected during speciation of EDDS in soil samples whereas a contradictory result was reported[104] which suggested that Fe-EDTA decreases with increase in reaction pH due to Ca interference while Fe-EDDS was observed relevant species at neutral pH.

Species in aqueous solution exist in formation-dissociation equilibrium, and consequently, displacement reactions of metal ion or ligand by another reactant may occur, therefore metal-ligand complexation depends on the displacement equilibrium constants when a chelating agent is added to the solution containing two or more metal cations. It is suggested that a ligand must overcome competing metal precipitation, surface complexation and precipitation of solid particles to achieve an effective extraction of metals from the contaminated site[114]. Therefore, enough molar concentration of chelating agent in the solution is also desirable to combine with the target metal and other ions which can displace the target metal. Chelating agent should have different stability constants for two metals, if selective reaction of one metal is required in presence of the other[121].

3.4. Factors affecting stability of Metal-ligand complex

Metal-ligand complex process can be represented as shown in eq. (10) and (11):

$$M^{+n} + nL^{-} \rightleftharpoons ML_n \quad ; \quad \beta_n = [ML_n] / [M^{+n}] [L^{-}] \qquad (10)$$

$$[ML_n] = ML_{n(0)} \quad ; \quad P_{ML} = [ML_n]_0 / [ML_n] \qquad (11)$$

where β_n and P_{ML} are the overall stability constant and distribution constant respectively of metal-ligand complex, If eq. (10) and (11) is combined with the eq.(5), it can be rewritten as eq.(12):

$$K_{ex} = (\beta_n P_{ML} K^n_{HL})/P^n_{HL} \qquad (12)$$

Where K^n_{HL} is dissociation constant and P^n_{HL} is the distribution constant of the molecular form of reagent.

$$\log K_{ex} = \log (\beta_n P_{ML}) - n\log (P_{HL}/K_{HL}) \qquad (13)$$

Eq.(13) suggests that stability constant of the complex and acid dissociation constant of the reagent are interconnected. Consequently distribution constants of the reagent and of the complex are also complected[103]. Thus, stability of metal-ligand complex depends primarily on ligand properties. Ligands are classified on the basis of their charge, size, identity of the coordinating atom(s), and number of electrons donated to the metal ion (denticity). Ligands can be further characterized into monodentate, bidentate and polydentate depending on the number of donor atoms present in the ligands which allows attachment of two or more donor atoms to the same metal ion simultaneously and produces one or more rings. This ring formation is the major characteristic of chelation distinguishing it from monodentate metal coordination by increasing stability of the resultant chelate complex, therefore, stability constants of chelating agents for equal number of similar coordinated donor atoms are from one to several orders of magnitude greater than those of the monodentate complexes. Five and six-membered rings are considered the most stable in chelation reaction. Formation of three membered ring structures is proscribed due to presence of coordination angles on the metal atoms. On other hand, more than seven membered rings are also not desirable due to an unconvincing probability of ring closure. Thus, size and number of rings, substituents on the rings and the nature of the metal and donor atoms are the common factors which affect the stability of a metal-ion complex. Formation of each additional ring by the same ligand provides extra stability to the metal-ligand complex due to displacement of coordinated solvent molecule. DTPA is a more stable chelating agent than EDTA due to presence of more donor atoms (8 binding sites) than EDTA (6 binding sites), however NTA is considered relatively biodegradable and forms a less stable complex due to availability of only 4 binding sites for complexation[112]. Larger the complex formation constant, the more stable is the species. Steric hindrance also contributes to the stability of a chelating agent due to the presence of bulky groups attached to a donor atom. This interaction may cause mutual repulsion between the ligands, hence stability of the metal-ligand bond decreases. EDDS has lesser stability than EDTA (in spite of having same number of binding sites) complex due to presence of two six membered rings in EDDS which causes steric hindrance and weakens the metal – ligand bond[121]. Biodegradable properties of a chelating agent also depend on the stability constants of the ligands. Aminoploycarboxylate which form complexes with relatively low stability constants (e.g., IDSA, NTA, EDDS) are readily degradable, whereas those forming stronger complexes (e.g., EDTA, DTPA) are relatively resistant to biodegradation. Complex formation constants of selected metal complexes are presented in Table 2 for reader's reference.

Table 2 : Complex formation constants of 1:1 metal-ligand complexes at 25°C and ionic strength of 0.1 M. Values are expressed as log *K*.[135]

Thus, assessment of the most suitable and ecofriendly alternative should be performed very carefully by considering all the above described factors such as pH range, molar concentration of reagent and element, liquid to solid ratio required for efficient metal extraction process, other competing reactions in the aqueous phase, solubility and stability of metal complex in different reaction conditions, protonation, and stability constants.

4. Environmental Scrutiny of Chelating Agents

Chelating agents have been utilized widely in various domestic and industrial applications for many years and recently gaining attention in the field of metal extraction from various contaminated sites to minimize the environmental pollution. A high resistance to biodegradability is requisite to attain the stability of metal-chelate complex in industrial processes, however, non-biodegradable chelating agents itself may cause certain deleterious effects to the ecosystem. Chelating agents may perturb the natural speciation of metals and may cause a dissolution effect of heavy metals adsorbed in sediments[136,137]. Chelating agents contain nearly 10% nitrogen which may eventually present in the aquatic system, thus chelating agents may pose a significant effect on the eutrophication process[138]. Literature suggests relatively high concentration of EDTA, the major chelating agent used in various industrial and domestic applications, in surface water and drinking water due to its high persistency in the ecosystem[139,140]. According to publications by European Aminocarboxylates Committee[141] and the European Chemical Bureau[142], the predicted no effect concentration in the aquatic environment (PNEC$_{aqua}$) for EDTA is 2.2 mg/l based on no-effect concentration (NOEC) of EDTA for *Daphnia Magna* (22 mg/l). The guideline value for EDTA concentration in drinking water is 0.6 mg/l published by World Health Organization[143].

Stringent environmental regulations are coercing industries across the globe to increase utilization and production of biodegradable chelating agents. The biodegradation of these conventional chelating agents (EDTA, DTPA, organophosphonates) was investigated using various isolated bacterial strains[144,145]; still, these compounds do not satisfy the criteria for biodegradability[146]. Thus, environmental concerns associated with the non-biodegradable chelating agents have been the predominant reason to stimulate the demand for more ecologically-viable chelant. Biodegradable chelating agents are likely to capture a significant share of chelating agents market in coming years, owing to potential health and environmental hazards associated with use of nonbiodegradable organic chelating compounds. Sykora et al.[147] suggested that biodegradability of a complexing agent depends on the functional group available on the ligand and the number of nitrogen atoms present in ligands. NTA contain a single nitrogen atom in the molecule and therefore, it is relatively subject to biodegradation. Another important observation suggested that resistance to biodegradability increases with the number of tertiary amino groups (EDTA, DTPA). Optical isomerization is also considered as an important factor for biodegradability e.g. *[S,S]*-EDDS stereoisomer is subjected to easy degradation whereas the *[R,R]* isomer remains undegraded and the *[R,S]* isomer degrades very slowly and incompletely[83,148].

OECD Guidelines for testing of chemicals described internationally used standard test methods in year 1993 to investigate the biodegradability of chemicals[149]. A brief description of biodegradability tests have been listed in Table 3.

Table 3: Internationally used standard test methods for investigating biodegradability of chemicals[150]

It is vital to mention that different biodegradation tests (Coupled units test, Zahn-Wellens test, MITI test, AFNOR test, Sturm test, OECD screening test and Closed bottle test) reported in literature were carried out for EDTA by Gerike and Fischer[151] and results suggest that the most frequently used chelating agent EDTA is not biodegradable at all. The European Union risk assessment report also confirms the non-biodegradability of EDTA[152].

Studies with more readily biodegradable complexing agents were performed extensively in last few years. Biotechnologically produced EDDS has been an important reagent to investigate for its biodegradability, instead of being a structural isomer of EDTA. MGDA showed a good stability in a wide pH range and also satisfied the OECD criteria[146]. Boroweic et al.[153] illustrated GLDA as a biodegradable and non-toxic chelating agent for the ecosystem. Lanham et al.[154] investigated ethylenediamine-*N,N*-diglutaric acid (EDDG) whereas, ethylenediamine-*N,N*-dimalonic acid (EDDM) was synthesized by Aoki and Hara[155] as a biodegradable chelating agent. Recently, pyridine-2,6-dicarboxilic acid (PDA) has also been established as a biodegradable ligand with efficiency to chelate metals in a ligand to metal ratio of 2:1[156]. Some other biodegradable chelating agents such as *N-bis*[2-(carboxymethoxy)ethyl]glycine (BCA3), *N-bis*[2-(1,2-dicarboxyethoxy)ethyl]glycine (BCA5), *N-bis*[2-(1,2,dicarboxyethoxy)ethyl]aspartic acid (BCA6), and *N-bis*[2-(methylcarboxymethoxy) ethyl] glysine *(MBCA3)*, IDSA have also been investigated in literature[96].

Several new methodologies are being investigated in past few decades to find out new ways of degrading chelating agents. Advanced oxidation processes (AOP) have been considered a promising technology for the degradation of recalcitrant organic pollutants. These processes apply combinations of radiation, oxidants (ozone, hydrogen peroxide and molecular oxygen) and catalysts for degrading the target compounds[157]. EDTA was effectively eliminated with ozone dose of 1400 mg/l from bleaching effluent[158]. UV radiation were employed for the degradation of Fe and Cu complexes of NTA, EDTA, DTPA, and EDDS, whereas Mn^{+2} complexes were observed to be more recalcitrant to UV induced degradation than other metal-EDTA or metal-DTPA complexes[159].

Biodegradation of chelating agents using pure bacterial cultures is also considered a beneficial approach in order to minimize the metal mobilization into the ecosystem. Several microorganisms have been reported to degrade chelating agents under aerobic conditions[160,161]. *Agrobacterium* sp.[162], the bacterial strain DSM 9103[163] and the bacterial strain BNC1[160] were considered as the most efficient enrichment cultures for degradation of EDTA, however, still no bacterial strain was found in literature to be able to degrade DTPA[157]. It has also been mentioned that bacterial culture which is responsible for the degradation of NTA, cannot degrade EDTA, however the EDTA degrading bacterial strain BNC1 can grow on both EDTA and NTA[164]. The biochemistry of NTA degradation suggested iminodiacetate (IDA) as the major degradation product which can be obtained either by the NTA monooxygenase of *Chelatobacter heintzii (C. Heintzii)*[165] or EDTA monooxygenases of BNC1 and DSM 9103[166,167]. IDA is transformed to glycine and glyoxylate by a membrane-bound IDA dehydrogenase in *C. Heintzii*[168]. New genes were also identified with the determined N-terminal amino acid sequence and overexpressed in *Escherichia coli to investigate the* IDA oxidase activity[169].

Degradation of EDTA is reported by the EDTA monooxygenases of strains BNC1 and DSM 9103 which oxidize EDTA to ethylenediaminetriacetate (ED3A) and then to ethylenediaminediacetate (EDDA)[163,166,167] and IDA oxidase oxidizes EDDA to ethylenediamine (ED). The bacterium BNC1 may further metabolize ED to get nitrogen present in it.

Degradability of ligands is not only affected by their chemical structure, it may also influenced by the metal ions present in the complex and has been demonstrated for NTA, oxalate, citrate and EDTA in literature[170,171]. Kluner et al.[164] studied the metabolism of EDTA and its metal chelates using whole cells of the strain BNC1 and the cell-free extracts prepared from it and observed that metal-EDTA chelates with relatively low thermodynamic stability constants (K), such as Ba($10^{5.5}$), Mg($10^{6.4}$), and Ca-EDTA ($10^{8.4}$), were readily degraded by growing or resting cells of strain

BNC1, however, metal-EDTA chelates with stability constants above 10^{12}, such as Fe(III)-, Co-, Cd-, Pb-, Ni-, and Cu-EDTA could not be metabolized by whole cells. This observation explained the fact that the degradability should decrease with increasing stability constants of metal complexes. It was also illustrated that slow metal exchange kinetic plays a significant role in the biodegradation of ligands because of the strict speciation requirements[164].

Computer simulations have also been an appropriate way of studying the degradation pathway by studying the C-N bond dissociation energy using computer simulations. Chen et al.[83] employed molecular simulation (density functional theory at B3LYP/6-31G* level) to define the dissociation energy of metal-EDTA and metal-EDDS to investigate the superior biodegradability of EDDS than EDTA. Fig. 11 gives a collection of proposed and identified degradation pathways of EDTA. Many of the primary and secondary degradation products of EDTA may form soluble complexes with metal ions, such as ED3A, EDDA, and IDA, whereas some of the degradation products are expected to be even more recalcitrant to degradation than EDTA or DTPA themselves, such as 2-ketopiperazine-1,4-diacetic acid (KPDA), 2-ketopiperazine-1/4-acetic acids (KPMAs), and ketopiperazine[172].

Fig. 11: Identified degradation products and pathways of EDTA[135].

Degradation of EDDS was also predicted by calculating the dissociation energy of all C-N bonds present in EDDS[83]. *N*-(2-aminoethyl) aspartic acid (AEAA) was obtained as the first catabolism product of EDDS. The anticipated mechanism and energy profile of the *[S,S]*-EDDS depicted N-H bond formation and C-H bond cleavage due to intramolecular transfer of hydrogen atom from the preferential carbon atom to nitrogen atom.

Thus it can be concluded from the above section that the more stable a metal-ligand complex is, lesser the possibility for it to degrade. Various methods which are available for degrading the chelating agents are still not enough to provide an efficient solution to develop an ecofriendly alternative; however, it can move towards new direction to find out the better alternative.

5. Applications of Chelation technology for metal extraction from contaminated sites

The global market is witnessing the increasing demand of chelating agent and emergence of many new chelating products. Developed economies capture the largest share of chelating agent market as stated by the new market research report on chelating agents[173]. Asian market are also expanding at a growth rate of over 4% annually and thus represents wide applicability for chelating agents in developing countries too. It is reported that more than 70% of the global demand of chelating agents comes from domestic applications, water treatment and pulp & paper industries; however, chelating agents are now finding increasing scope in various applications in order to minimize pollution into ecosystem. Literature available on the interaction of chelating agents with the environment suggests a wide range of applications in medicines, microbial growth, soil remediation and metal extraction from waste materials. The first study was published in 1950 to study the effect of EDTA on microbial growth and the bioavailability of metal complexes[174]. In 1951, Fe(III)-EDTA complex was investigated as iron fertilizer for plants[175]. Lysine, glyoxaline-4-5-dicarboxylic acid and histidine have also been reported in 1953 as chelating agent for the preparations of Keilin horse-heart succinoxidase[176]. Fig. 12 demonstrates the continuously increasing number of publications every year based on application of chelating agents in various areas[177]. It can be depicted from Fig. 12 that chelating agents are being used in medicines for nearly six decades and it is still one of most important discipline in metal intoxication. Application of chelation concept in reactions (adsorption and complexation) was published first time in year 1955 and till then chelating agents are constantly being employed in reactions which are self explanatory with the increasing number of publications as shown in Fig. 12. In 1960s, research was mainly addressed to the application of chelating agent in soil, plant and water samples.

Fig. 12 : Cumulative number of publication for last six decades on 'application of chelating agents in various areas' (metal extraction from water includes natural water resources and waste water; reactions include adsorption, complexation, surface reactions; environment includes biodegradability, ecotoxicological effects; soil remediation includes phytoextraction, metal mobilization)[177]. (Database : Scopus; accessed on July 2014)

The soil related research expanded its area to the soil remediation (extraction of metals and phytoremediation), and effect of chelating agents on biodegradability aspects till the decade of 1990. In the 1990s, applications of chelating agents were also investigated in ground water, waste water and the surface reaction that occur with natural ions. Since then, the versatility of chelating agents has stimulated the continuing research on the uses and environmental effects of chelating agents. Chelation concept has been also employed, in recent years, for metal extraction from industrial wastes (spent catalysts) and from waste electrical and electronic equipments (WEEE). The wide range of leading research areas accompanying applications of chelation agents are shown in Fig.13 which demonstrates that highest numbers of publications were dominated in the research area of biochemistry, genetics and molecular Biology with 27% publications of total number of publications for “chelating agents”[177].

Fig. 13 : Leading research areas in terms of number of research publications for ‘Chelating Agents’[177] (Databased : Scopus; accessed on July 2014)

Chelating agents have already been proved its applicability in medicines. Still, an extensive research is going on metal intoxication using chelating agents. Chemical engineers are now moving towards research on chelating agents by applying its metal complexation property in various applications such as recovery of heavy metals from waste material, phytoremediation and many more. The biodegradability issue associated with classical chelating agents has also been a matter of concern for chemical engineers and chemists.

5.1 Chelating agent used for metal extraction from spent catalysts

Applicability of chelating agents in metal extraction from spent catalysts is recently flourishing as a wide research area for the aid of industrial, economical and ecological benefits. Heavy metals are extensively used for the preparation of various catalysts in petrochemical and fertilizer industries. The market demand for hydrotreatment catalysts is estimated to increase with an annual growth rate of 4.4%[178]. These catalysts start to lose their activity after certain process cycles due to deposition of metal sulphides and coke on catalyst pores. At this stage, they need to be replaced with the fresh catalysts and are considered as “Spent Catalysts”. These spent catalysts contain significant amount of heavy metals in it and may be a substantive source to release heavy metals into environment, if not disposed off in proper manner. Spent catalysts obtained from the petroleum industry contains 4-

12% Mo, 15–30% Al, 1–5% Ni, 0–4% Co, 5–10% S, 1–5% Si, 0–0.5% V. Disposal of spent catalysts requires compliance with stringent environmental regulations. The avoidance of (heavy) metal release from spent catalysts to the environment is one important motivating factor. Another one is the exploitation of those wastes with respect to metal recycling from economic point of view. Reuse of spent catalysts after regeneration is prudential and therefore, an environmentally benign way should be opted for the safe disposal of spent catalysts at the end of the catalyst life. It has been reported that recycling of metal scraps is an eco-efficient way in order to manage 33% less energy consumption and 60% less pollutants generation than the production of fresh fuel[179]. The high amount of valuable metals present in spent catalysts has also attracted the researcher's attention to explore various new methods for metal extraction in order to develop an efficient processing.

Numerous hydrometallurgical and pyrometallurgical approaches have been adopted for the recovery of heavy metals from spent catalyst. Pyrometallurgical process involves smelting of the spent catalyst to metal alloys and slag in the gaseous environment or recovering the metals in the liquid environment, preceded by roasting or wet oxidation of the spent catalyst[180]. However, these methods are energy intensive due to high temperature requirements and may liberate toxic gases into the environment. Several hydrometallurgical approaches such as leaching[181], solvent extraction[182,183] and biological methods[184,185] have also been reported to recover metals from spent catalyst, soil and other industrial wastes which involve use of aqueous chemistry and recovery occurs at temperatures lower than the boiling point of the aqueous media. Combinations of pyro- and hydro-metallurgical processes have also been employed for metal recovery from spent catalysts due to complex nature of spent catalysts[186,187]. Chlorination process was also adopted for metal recovery, however corrosive nature and toxicity of chlorine gas or any mixture of it inhibits the operation[188,189]. All these processes have shown potential in removing metals from industrial wastes; however, use of hazardous chemicals, secondary pollution possibility by these chemicals, less acceptance of biological process in the environment and high process cost restrict their use on large scale. Therefore, search for an efficient and ecofriendly technology to extract metals from spent catalyst is needed.

Extraction of metals with chelating agents does not require high temperature and the chelating agents can be reused after the extraction of metals which make it more economical than any other process. Goel et al.[13] used spent catalyst from fertilizer industry for recovery of Ni using EDTA as chelating agent and 96% Ni was recovered in the form of $NiSO_4$ with EDTA concentration 0.8M, L/S = 50, reaction time = 10h, particle size 100μm, 700rpm stirring sped, temperature 100°C, and pH 10. However, very high L/S in this study is a sincere concern due to large space requirement and increasing possibility of large amount of waste water generation. Recovered EDTA was reused in the successive experiments with more than 73% Ni recovery over four cycles. The authors suggested that interference of competing sulfur ions in the recycled extracted EDTA may be the reason for decreasing extraction efficiency with recycled EDTA solution. Various reaction parameters such as molar concentration of chelating agent, solid to liquid ratio, stirring speed, particle size, reaction pH, reaction temperature, reaction time etc. contributes to the metal extraction efficiency and therefore effect of each parameters must be studied to optimize the extraction efficiency. The non-biodegradability issue associated with EDTA is the major constraint of using it at a wide scale. Therefore, a biodegradable chelating agent *[S,S]*-EDDS was first time employed for the extraction of Ni from spent catalyst in batch mode under atmospheric reflux condition and recovered 84% Ni at optimum reaction conditions in one cycle[15]. The effectiveness of *[S,S]*-EDDS was also compared with the traditional chelating agent EDTA and it was concluded that *[S,S]*-EDDS requires a narrower pH range as compared to EDTA for "Extraction" and "Solvent/chelator regeneration" process. The complete process flow chart is shown in Fig. 14.

Fig. 14 : Process flow chart for "Solid-liquid extraction and regeneration of chelating agent"

Goel et al.[8] studied the exchange behavior of Ni towards chelating agents EDTA and DTPA from primary reforming waste catalyst used in fertilizer industry. It was concluded that extraction of metal depends on the complexing affinity of a chelating agent for metal and on the affinity between solid and metal. EDTA has six binding sites (4 acid and 2 amines sites) that make coordination bond with metal while DTPA has eight sites (3 amine and 5 acid sites), which show stronger binding capacity than

EDTA and higher extraction efficiency than EDTA, but cannot be recovered easily due to a complicated process to break the coordination bond.

Extraction efficiency of recovered EDTA was investigated and significant extraction of Co and Mo was observed upto five cycles using recovered EDTA at optimum reaction conditions[9], however nearly 20% loss in extraction efficiency was observed for the fifth cycle recovered EDTA than the fresh EDTA. The loss in extraction efficiency can be related with the loss in number of metal-binding sites due to repetitive precipitation of EDTA[9] and added number of impurities during each cycle[13,15].

Therefore, it can be concluded that metal extraction from spent catalyst using chelating agent is a good idea on economic and ecological platform. Due to its recoverable nature, this process is more economical than any other process. Table 4 provides an economic evaluation of chelation process in comparison with other methods employed in literature. It can be depicted from Table 4 that that material cost of chelation technology is less than other methods. Though it may also be seen that cost factor of 0.62$ for alkaline leaching and 0.61$ for chelation technology are nearly equal to each other. However, this fact cannot be denied that alkaline reagent cannot be reused for next alkaline leaching cycles while chelating agent can be reused at least four times for chelation experiments without significant loss in extraction efficiency. Thus, by comparing cost factor for 4 cycles using these two methods, cost for alkaline method will be 2.44$ while only 0.74$ cost to four chelation cycles using recovered EDTA. Thus, recycling possibility with good extraction efficiency reduces the process cost significantly and makes the process more convincing than other available methods.

Table 4: Economical Evaluation of available technologies for metal extraction from spent catalyst

This process is ecofriendly also due to easy recovery of chelating agent used for the process, no corrosive environment and no any hazardous byproducts are liberated during the process. High efficiency of metal extraction and moderate thermodynamic stabilities of the metal complexes make this technology more favorable than any other technology for metal recovery. Chelation technology (solid-liquid extraction) takes place in two step while pyrometallurgical process (high temperature requirement) can be performed in just one step , still chelation technology offers advantage over pyrometallurgical process in terms of lower energy consumption. Another crucial advantage of chelation technology is related to the final product formation. It is always easier to prepare salts, oxides or complexes using a liquid-phase process which can be reused in catalyst preparation whereas high temperature process would yield the metals in metallic state.

However, many things are still left to find out in this particular research area, not much work has been reported in literature on the extraction of metal from spent catalyst. Search for new biodegradable chelating agents may be helpful to develop new ecotechnie processes. Generation of new adsorbent beds and resins by coating of chelating agent will provide direction to develop a continuous process for metal extraction on an industrial scale. Recovery of chelating agent is another important research area which still needs more investigation. Literature still do not state complete recovery and efficient recycling of chelating agents, therefore new methods needs to be find out to make efficient recovery during the process.

5.2 Chelating agents used for metal extraction from soil

Soil contamination due to exposure to heavy metals has become a serious concern that affects crop yields, soil productivity and leads to bioaccumulation of metals in the ecosystem. Heavy metal sorption at soil surface can be explained on the basis of surface complexation concept. The active functional groups present on soil surface (S) bind with metal (M) through covalent interactions which can be explained as shown in eq. (14)[194].

$$S - OH + M^{+n} \rightleftharpoons S - OM^{+n-1} + H^{+} \qquad (14)$$

It can be depicted from eq. (14) that metal sorption to the soil matrix is a pH dependent reaction. Surface adsorption sites become saturated and sometimes surface polymerization possibility increases with increasing metal concentrations in soil matrix which may result in metal precipitation. Various soil remediation techniques are being adopted these days in order to remove metal pollutants from soil or transform these metals into non-toxic form. Davis and Singh[195] compared chlorination, acid leaching and chelation technology using EDTA, DTPA to extract Zn from artificially contaminated soil column. Highest removal efficiency was obtained using chelation process at optimized flow rate. Kocialkowski et al.[196] evaluated performance of different chelating agents for extraction of heavy metals Cu, Zn, Pb and Mn from arable soil samples and concluded EDTA as the best chelating agent for extraction of all metals. Lim et al.[197] investigated the extractability of EDTA for removal of divalent metals Cd, Pb and Ni from soil. They also developed a cost effective closed loop utilization of EDTA by recovering and reusing it for metal extraction. Hong et al.[118] checked the extraction, recovery, and biostability of DTPA as a remediation agent for soils contaminated with metals. It was observed that DTPA was capable of extracting Pb from the contaminated soils and could be recovered by the use of cationic and anionic precipitants in alkaline pH conditions. Palma et al.[198] investigated the effectiveness of extractant EDTA, its structural isomer EDDS, rhamnolipids and citric acid for heavy metal removal from a contaminated harbour sediment by varying concentration of chelating agent and overall washing time. EDTA and EDDS showed the comparable metal extraction efficiency (~70%) whereas lower removal efficiency was achieved using rhamnolipids and citric acid. Tandy et al.[104] compared the traditional chelating agent EDTA with biodegradable chelating agents *[S,S]*-EDDS, IDSA, MGDA and NTA for the extraction of heavy metals from contaminated soil. The authors optimized the reaction time 24h and higher concentration of chelating agent was considered favourable for higher metal extraction. Less pH dependence and less difference in extraction efficiency of various chelating agents was also observed at higher molar concentration of complexing agents. Extraction with EDDS at pH = 7 showed the optimum extraction efficiency for Cu, Zn, and Pb and loss of Ca and Fe from the soil. The work was extended to compare the efficiency of batch and column extraction of Cu, Zn, and Pb from polluted soils using the biodegradable chelating agent EDDS[199]. Table 5 gives a list of chelating agents which have been used for metal extraction from soil in literature.

Table 5 : Chelating Agents used for metal extraction from soil in literature.

Yip et al.[204] employed EDDS for the extraction of Cu, Zn and Pb from artificially and field contaminated soil samples and developed an empirical model using the initial metal distribution to estimate the extraction efficiency at equilibrium. It was also observed that higher extraction rates can be achieved in multi metal contaminated soil samples than mono-metallic contaminated soils due to presence of large proportion of carbonated and exchangeable fraction of heavy metals. Batch kinetic and equilibrium experiments were conducted to study the influence of EDDS to metal molar ratios (MR), solution pH and soil to solution ratio on metal extraction from contaminated soil under EDDS deficiency (i.e.MR< 1)[205].

Phytoextraction is now-a-days an appealing technology for metal extraction from soils and also known as 'green remediation' which involves desorption of metals from the soil matrix and metal mobilization to the rhizosphere for uptake by plant roots. It can be categorized into phytoextraction (plant harvesting to accumulate metals in shoots), phytomining (use of plant biomass), phytovolatilization (use of microbes to transform soil elements into volatile forms), and phytostabilization (conversion of heavy metals into less toxic and biodegradable forms). But due to the limited plant species with a high capacity to accumulate metals and to produce a large amount of biomass, chelation technology has been incorporated with phytoextraction to improve the uptake of metals by high biomass plants[206-207]. Blaylock et al.[208] demonstrated the application of Brassica juncea (Indian mustard) as a hyper-accumulator with synthetic chelating agents to extract Pb from soil. It was observed that combined effect of EDTA and acetic acid led to nearly two times higher accumulation of Pb in mustard shoots compared to the extraction efficiency of EDTA alone. Vassil et al.[209] also suggested similar results for extraction of Pb using Indian mustard along with EDTA and concluded that coordination of Pb transport by EDTA enhances the mobility within the plants of insoluble Pb^{+2} ion whereas high concentrations of Pb-EDTA may cause reductions in transpiration rate and shoot water content due to presence of free protonated EDTA (H-EDTA) in the hydroponic solution. Luo et al.[210] investigated the chemically enhanced phytoextraction using EDTA, EDDS and citric acid on the intake of Cu, Pb, Zn and Cd by corn (*Zea mays L.)* and bean (*Phaseolus vulgaris L.)* plants. Results indicated EDTA as more efficient chelating agent than EDDS in the extraction of Pb and Cd, whereas EDDS is more effective in the extraction of Cu and Zn. Meers et al.[211] also compared the performance of biodegradable chelating agent EDDS, NTA and citric acid with EDTA to enhance shoot accumulation of Cd, Cu, Cr, Ni, Pb and Zn in *Helianthus annuus*. Similar results were obtained to justify the applicability of EDDS for phytoextraction of heavy metals. Evangelou et al.[212] investigated the influence of EDDS and EDTA on the uptake of Cd and Cu from soil with tobacco *Nicotiana tabacum*. Effect of EDTA and citric acid on the phytoextraction of heavy metals (Cd, Cu, Pb and Zn) from industrially contaminated soil with hyper-accumulator *Sedum alfredii Hance* were investigated by Sun et al.[213].

Thus, valuable studies conducted by many researchers have endorsed the use of chelating agents in phytoextraction to amend the metal extraction process. However, some areas are still under investigation for the successful implication of chelating agent induced phytoextraction. An effective prevention of leaching into groundwater, need of more field studies to have a better outlook of phytoextraction possibilities and justified reasons for different observations by various researchers are the most important factors before phytoextraction can be considered as a promising solution.

6. Future Research Aspects – Statistical and Computational approach for chelation

Chelation experiments are performed in the laboratory and need lots of efforts and accuracy to optimize the metal extraction process. Therefore, in the present computational era, it is consistent to find out some new technologies to minimize experimental efforts and to achieve better accuracy in observations. Design of experiments, computational fluid dynamics, molecular and computational simulations can be considered a better approach for designing and optimizing metal extraction process. Mohd. Salim et al.[214] employed a face-centered cube design (FCD) in response surface methodology to evaluate the relationship between the extraction parameters and the metal chelating activity of *Centella asiatica* (CA) and *Erythroxylum cuneatum* (EC). The experiments were designed for 30 experimental runs including six replications at centre point and concluded that response surface methodology reduced the extraction time, temperature and stirring speed. This methodology also helped to subsequently improve the chelating activity of the plants in comparison to the conventional method. Chauhan et al.[112] explained that ‘one variable at a time (OVAT)’ approach does not consider the interaction effect of process variables and cannot be an efficient approach for multivariate analysis. Therefore, box-behnken design (BBD) was coupled with RSM to optimize the process parameters using statistical analysis and to provide the elaborated quality of information. Response surface plots demonstrated the optimum reaction conditions (molar ratio of chelating agent to Ni, S/L and reaction time. MR = 3.6, S/L = 1/22.3, reaction temperature of 85.2°C, reaction time of 8.2h and pH = 7.3) for Ni extraction from spent catalysts using various aminopolycarboxylate chelating agents. It was also suggested that optimization studies using computational methods may prove useful on industrial scale to minimize manual efforts and to achieve better efficiency at low processing costs.

Pinto et al.[148] performed computer simulations in order to assess the selectivity of various chelating agents to transition metals in medium with excess of Ca and Mg ions and the ability of compounds to complex Ca and Mg ions at high concentration. Results demonstrated the pH range for various chelating agents at which it can complex more than 80 % of the respective transition metals (Fe, Mn, Cu, Pb, Cd, and Zn) in excess of Ca and Mg ions. This metal speciation calculations and computer simulations at different pH range may provide an idea about the most favorable chelating agent in different industrial processes. It was also suggested that NTA, EDDS, MGDA, and PDA can be used in paper and pulp industry due to its favorable pH range[148]. Experimental studies[215] also suggest the similar observation at specific pH range in pulp and paper industries. It was also concluded that still, no any biodegradable chelating agent has the superior efficiency than EDTA for Pb removal from soil which is in concordance with the experimental studies[103,105,114,115,120].

Density functional theory (DFT) methods have also been employed for the static and dynamics structure calculations of various chelating agents to investigate the coordination properties of chelating agents with metal ions[216-219]. Chen et al.[83] calculated the free energy changes for hydration and complexation process and demonstrated the metal complexation process as a substitution reaction of the coordinated water molecules by the chelating agents. Degradation pathways were also deduced for EDTA and EDDS by calculating the dissociation energy of various C-N bonds of the ligands. Sillanpaa et al.[220] performed geometry optimizations, continuum-solvation and mixed cluster–continuum model, Car–Parrinello molecular dynamics simulations to study the complexation of amino polycarboxylic acids with different divalent metal ions. The work presented a good estimation on the metal ion complexation constant with different ligands. Paola et al.[221] investigated the Jahn-teller distortion and effect of spin states on different palladium clusters and concluded that ligand and kinetic effects play a significant role in driving the formation of ligand-stabilized clusters. Coskuner et al.[222] demonstrated the stable nature of the crystalline structure of octahedral Al-EDTA in aqueous solution.

Thus, computational approaches may reduce manual efforts and provide elaborated quality of information in different research aspects. However, more studies are still needed in the area of computational simulation to make it more convenient to researchers. Computational fluid dynamics may also be helpful in order to study hydrodynamics associated with the metal-extraction process and to have an approximation of various process parameters in order to perform pilot plant studies.

7. Summary and Outlook

Chelation technology for extraction of heavy metals from contaminated sites (soil, water, industrial waste) is drawing sincere concern these days in order to develop new promising green methods which should be efficient on the ecological and economical platform. Various R&D studies are currently underway to identify process parameters which may affect the formation and stability of metal-ligand complex. Higher extraction efficiency, reusability of chelating agents and diverse applicability make it a convincing technology, however, still a number of challenges need to be addressed. Synthesis of new biodegradable mobilizing agents and identification of their degradation pathways by means of molecular simulation or biological methods, are open research field with immense opportunities for further development in the field of chelation technology. Different possible methods to recover and recycle the chelating agents should also be explored to bring about an efficient ‘closed loop’ chelation process. Successful application of the chelation technology for metal extraction from contaminated sites is a very elegant example of ligand substitution mechanism, though the industrial application of the process is still restricted by the lack of adequate knowledge about competing reactions which may affect the metal-ligand complexation. More experimental studies will be helpful to have a better perceptivity of the ligand substitution mechanism and to explore the diverse applicability of chelation technology. It is conceived that modern computational tools may suggest an ongoing renaissance of research activities in chelation technology to carve-out the new territory of metal-ligand complexation. Thus, future attempts should focus on sustainability, economics and environmental impact of the process to accomplish the growing industrial demand.

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Table 1 : Studies performed to investigate recovery of heavy metals from spent catalyst using different hydro/pyro metallurgical methods

References	Spent Catalyst	Metals	Reagent/ Micro-Organism	Reaction conditions	Metal Recovery	Advantages	Limitations
Bio-Leaching							
Bhardwaj et al.[37]	spent hydrotreating catalyst	Fe, Ni and Mo, and Al	*acidophilic thermophile Acidianus brierleyi*	Spent medium leaching, 1% w/v pulp denstiy	Nearly 100% Fe, Ni, Mo and 67% Al	No harmful effects to environment. High extraction efficiency for heavy metals. Low energy requirements.	Longer leaching time. Microorganisms can not withstand at high temperature. Dependency on several atmospheric conditions Sensitive to any contamination possibility.
Gerayeli et al.[38]	spent refinery catalysts	Al, Mo, Ni	*Acidianus brierleyi*	pH 1.6, pulp density 0.6% (w/v), inoculation 4% (v/v) and elemental sulfur concentration 4 g/L	35% Al, 83% Mo and 69% Ni		
Amiri et al.[39]	Spent Refinery Catalyst	Al, Mo, Ni	*Aspergillus Niger*	Particle size 150–212 µm, Sucrose 93.8g/L, Pulp density 3% w/v, and pH 7.	99.5±0.4%Mo, 45.8±1.2%Ni, 13.9±0.1%Al.		
Amiri et al.[40]	Tungsten rich spent hydro cracking catalyst	Ni, Mo, Fe, W, Al	*Penicillium simplicissimum*	Particle size < 150µm, Pulp Density 3% w/v, 30°C, shaking speed 120 rpm, 14 days incubation time. (Two Step Bioleaching)	100% W, 100% Fe, 92.7% Mo, 66.43% Ni, 25% Al		
Belochini et al.[41]	spent refinery catalysts	Ni, V, Mo	mixed culture of three strains of Fe/S oxidizing bacteria	21 days cultivation time, 30°C and 175rpm shaking speed, Catalyst concentration 10 g/L, modified 9K medium	83±4% Ni and 90±5% V; 30-40% Mo		

Acid Leaching							
Banda et al.[42]	spent hydro processing catalyst	Mo, Co	Hydrochloric Acid (HCl)	Acid Conc. : 3mol/L, Reaction Temp. : 90°C, Rection Time : 60 min, Particle Size : 250µm, pulp density : 5%(w/v)	97% and 94% of Mo and Co,	High metal recovery. Better recirculation possibilities (Mishra et al., 2010; Zeng & Cheng, 2009). Shortest Process time.	Usage of Hazardous chemicals. May generate corrosive environment. Requires specific material of construction to avoid corrosion. May liberate toxic gases to environment. High Energy Requirement High operational Cost Not applicable to highly contaminated ores (Asghari et al., 2013).
Mazurek[43]	Spent vanadium catalyst	V, K, Fe	Oxalic Acid	Acid Conc. : 2%, Reaction Temp. : 50°C, Reaction Time: 4 hr, Particle Size: 180-250µm, pulp density: 4 %(w/v).	91% V, 92% K, 63% Fe		
Parhi et al.[44]	Spent refinery catalyst	Ni, Al, Fe	Hydrochloric Acid	Acid Conc. : 1M, Reaction Temp. : 50°C, Rection Time : 120 min, Particle Size :50-71µm, pulp density : 0.2%(w/v).	99.9% Ni, 1% Al		
Al-Sheeha et al.[45]	Spent Hydro-processing Catalyst	Mo, V, Ni	Organic Vs. inorganic acids	Acid Conc. : 10% Reaction Temp. : 50°C, Reaction Time : 6h, Particle Size < 500µm, pulp density : 2.5%(w/v).	Organic acids showed better leaching than inorganic acids.		
Barik et al.[46]	spent hydrodesulphurization catalyst	Co, Mo, Al and S	Sulphuric Acid along with different oxidants.	Acid Conc.: 0.5M, Reaction Temp. : 50°C, Reaction Time : 120 min, Particle Size : 51-70µm, pulp density : 1%(w/v), [H_2O_2] as oxidant : five times stoichiometric	99.87% Mo, 96.25% Co and 11.03% Al		

Alkali Leaching							
Huang et al.[47]	Spent hydro-desulphurization catalyst	Mo, Ni, Al	NH_3·H2O, Na_2CO_3, NaOH under normal pressure and autoclave conditions	Temperature 160 °C, NaOH dosage 1.2 times the stoichiometric amount, solid/liquid ratio 1:4, retention time : 120 min and stirring rate 300 rpm.	NH_3, Na_2CO_3 : < 85% Mo NaOH : <93% Mo; NaOH auto-claving : > 96% Mo with 0.2% Al leaching.	High Extraction Efficiency Short reaction time	Usage of hazardous chemicals. Large quantity of chemicals needed. May pose harmful effects to human health and environment. Leaching of support materials along with desired metal affect the extraction efficiency.
Al-Sheeha et al.[45]	Spent Hydro-processing Catalyst	Mo, V, Ni	Ammonium Hydroxide (NH_4OH), Ammonium carbonate ((NH4)$_2$CO$_3$), Ammonium persulphate ((NH4)$_2$S$_2$O$_8$)	Reagent Concentration : 1 molar solution Reaction Temperature: 50 °C.	NH_4OH : 79.4% Mo, 65.4% V, 22.4 % Ni, 2.9% Al. $(NH_4)_2CO_3$: 86.8% Mo, 70.6% V, 25.4 % Ni, 0.3% Al. $(NH_4)_2S_2O_8$: 46.7% Mo, 83.7% V, 82.7% Ni, 17.7% Al.		
Katsiapi et al.[48]	Co–Mn hydroxide precipitates	Co	Ammonical Leaching	$NH_3/(NH_4)_2CO_3$: 200 g/200 g and solid to liquid ratio : 10%	93% co with less than 0.05% Mn leaching		
Mazurek et al.[49]	Spent Vanadium Catalyst	V, K, Fe	Urea Solution	Particle size : 180-250µm, Reaction Time: 60 min., Reaction temperature : 20°C Reagent Concentration : 40% urea solution, solid to liquid ratio : 10%,	78%V, 90%K and 29%Fe		

Pyrometallurgical Methods							
Al-Sheeha et al.[45]	Spent Hydro-processing Catalyst	Mo, V, Ni	Soda Ash Roasting using NaOH or Na_2CO_3	Reaction Temperature : 550°C and 700°C	More than 97% Mo and V; Ni and Al remain as residue with Na_2CO_3, while Al leached out in case of NaOH and affect efficiency.	Extraction of highly pure alumina which can be reused as support material. Short reaction time.	High energy requirement and High cost. Difficult to operate and liberate toxic gases to environment during thermal treatment. May Cause major changes in catalyst properties (surface area, phase change) due to sintering. Not an economical approach for extraction of metals from less concentrated raw materials of
Chen et al.[50]	Spent hydro-deulphurization catalyst	Ni, Co, Mo, V, Al_2O_3	Roasting	roasting at 750°C, Roasting time 30 min, Na_2O: Al_2O_3 = 1.2.	97.2%Al,, 95.8% V and 98.9%Mo		
Kar et al.[30]	Spent hydro-refining catalysts	Mo, Ni, S, CO, Fe	Salt Roasting using NaCl	roasting temperature : 900°C, Salt conc.: 20wt.%, roasting time : 60 min.	More than 90% Mo		

							complex Composition.
Chlorination							
Upadhyay et al.[51]	Spent Automotive Catalyst	Pt, Pd, Rh	Chlorination using electro generated chlorine	HCl (6.0 mol L^{-1}), current density 714 A m^{-2}, temperature 363 K, pulp density 20 g L^{-1}, and agitation speed - 700rpm	71 % Pt, 68% Pd and 60% Rh	Significant extraction efficiency, short reaction time.	Large amount of HCl needed HCl and generated chlorine are toxic.
Ojeda et al.[52]	Alluvial material	Au	Chlorination + Pyro-metallurgical process	873 K and 5400 s, flow rate 1.67 X 10^{-3} m^3 and molar fraction of chlorine equal to one.	98.73% recovery	High extraction efficiency Short reaction time	High temperature requirement. Chemicals needed for reaction are hazardous to handle may liberate toxic gases to the ecosystem.

Table 2 : Complex formation constants of 1:1 metal-ligand complexes at 25°C and ionic strength of 0.1 M. Values are expressed as log *K*.[135]

Metal ion	EDTA	NTA	DTPA	β-ADA	BCA-5	BCA-6	HEDTA	EDDS	IDSA
Ca^{+2}	10.6[122,123]-10.7[124]	6.4[122,123]	10.8[123,124]-10.9[125]	5.0[123]	7.4[130]	7.7[130,131]	8.2[125]	6.3[132,133]	2.59[127]
Cd^{+2}	16.4[723]	9.8[123,125]	19[122,123]-19.3[125,127]	8.2[123]	-	-	-	12.7[134]	5.7[127]
Cr^{+3}	23.4[124]	>10[126]	22.1[125]	-	-	-	-	-	-
Cu^{+2}	18.8[124]	12.9[122,123]	21.1[125]-21.5[125,127]	9.3[129]-12.6[123]	9.6[130]	13.1[130,131]	17.6[128]	20.4[132]	10.6[127]
Fe^{+2}	14.3[122-124]	8.3[123,125]-8.8[126]	16.0[127]-16.5[122,123]	8.9[123]	-	-	12.2[125]	-	5.8[127]
Fe^{+3}	25.0[123]	15.9[123,125]-16.3[126]	27.3[127]-28.0[123]	13.3[125]-16.1[123]	12.6[130]	15.5[131]-17.3[130]	19.8[125]	23.6[132]	10.9[127]
Pb^{+2}	18.0[125]	11.3[125]	18.9[125]	-	-	-	-	14.4[134]	7.45[127]
Ni^{+2}	18.5[123]-18.6[122,124]	11.5[123,125,126]	20.2[122,123,125,127]	11.4[123]	-	-	17.1[125]	18.5[134]	8.19[127]
Mg^{+2}	8.7[125]-8.8[123,124]	5.4[126]-5.5[123,125]	9.0[125]-9.3[123,124]	5.3[123]	5.9[130]	5.9[131]-6.0[130]	7.0[125]	7.7[134]	2.94[127]
Mn^{+2}	13.8[122,123]-13.9[124]	7.4[126]-7.5[122,123,135]	15.5[123]-15.6[124,125,127]	7.3[123,125]	7.5[130]	9.2[131]-9.3[130]	10.8[125]	10.7[132,133]	-
Zn^{+2}	16.4[122,123]-16.5[124]	10.7[122,123,125]	18.3[123], 18.6[125]	10.0[123]	8.1[130]	11.3[130]	14.6[125]	15.3[134]	7.03[127]
Co^{+2}	16.2[122,128]	10.4[122]	19.3[127]	-	-	-	-	13.6[134]	6.97[127]

Table 3: Internationally used standard test methods for investigating biodegradability of chemicals[150]

Major Categories	**Sub-categories**	**Basis of testing**	**Test duration**
Ultimate biodegradability screening tests	Modified Sturm test/OECD 301B Modified MITI test/OECD 301C Closed Bottle test/OECD 301D Manometric Respirometry test/ OECD 301F BODIS test (BOD test for Insoluble Substances, ISO 10708	By measuring the analytical parameters of mineralisation (CO_2 evolution or O_2 consumption)	4 weeks (Batch Tests)
	DOC die-away test/OECD 301A Modified OECD Screening test/ OECD 301E	By determining the extent of ultimate biodegradation by DOC removal	
Inherent biodegradability screening tests	Modified Zahn–Wellens test/ OECD 302B	By measuring carbon removal, high sludge inoculums is used to obtain high bacterial concentration	28 days
Continuous activated sludge (CAS) test	Coupled Units test/OECD 303A.	By Carbon removal (DOC) measurement using activated sludge	3h, continuous mode of experiment

Table 4: Economical Evaluation of available technologies for metal extraction from spent catalyst

***(Cost to each material corresponds to the cost listed on vendor's website).**

Technology	Reaction Condition	Extraction Yield	Chemicals needed	Amount of chemicals and prices	Material Cost for the process	Reference
Acid Leaching	50% H_2SO_4, S/L =1/20, 85°C, 2.5h	94% Nickel	Sulphuric acid	10g catalyst → 200 ml solution, 100ml H_2SO_4 (4.25$ for 500ml H_2SO_4, FS) = (4.25/500)*100 = 0.85$	0.85$ for 10g catalyst processing	Abdel-Aal & Rashad[190]
Acid Leaching	67% H_2SO_4, S/L = 1/14, 80°C, 2.33h	85% Nickel	Sulphuric acid	10g catalyst → 140 ml solution, 93.8 ml H_2SO_4 (4.25$ for 500ml H_2SO_4, FS) = (255/500)*93.8 = 0.79$	0.79$ for 10g catalyst processing	Idris et al.,[191]
Bioleaching	30°C, 175 rpm shaking, 21 days treatment	83% Ni, 90% V and 30% Mo	9K media - $(NH_4)_2SO_4$,KCl, H_2HPO_4, $MgSO_4.7H_2O$, $Ca(NO_3)_2$, Agar Gel, $FeSO_4$, catalyst digestion – HCl, bacterial cultures	10g catalyst, 70ml solution of 9K medium + 30ml $FeSO_4$ solution to make 100 ml solution 0.21g of $(NH_4)_2SO_4$*0.092$ /g = 0.019$ 0.01g of KCl * 0.074$ /g = 0.00073$ 0.05g of H_2HPO_4 *0.131$ /g = 0.0065$ 0.05g of $MgSO_4.7H_2O$ * 0.0078/g = 0.00033$ 0.001g of $Ca(NO_3)_2$ * 0.142$ /g = 0.00098$ 0.5g Agarose Gel * 0.9128$ /g = 0.456$ 4.91g $FeSO_4$ * 0.011$ /g = 0.054$ 50% HCl = 50ml HCl * 0.0067$ /ml = 0.34$	0.87$ + price of bacterial culture	Belochini et al.,[192]

Bioleaching	35°C, 180 rpm shaking, 240h treatment, particle size - 106 µm,	85-95% Ni , V	9K media, bacterial culture, 10% HCl for dilution, $HgCl_2$	9K media price same as above + HCl and $HgCl_2$ price according to requirement	0.87$ + price of bacterial culture	Kim et al.,[193]
Alkaline leaching followed by acid washing	Time - 1h, temperature - 30°C, and pulp density - 10%	97% Ni, 99% V, 84% Mo	$(NH_4)_2CO_3$ H_2SO_4	10g → 250 ml solution 40g/ L $(NH_4)_2CO_3$ => 10g in 250 ml solution. 10g $(NH_4)_2CO_3$ * 0.0505$ /g = 0.5055$ 1M H_2SO_4 = 13.6 ml in 250 ml solution. 13.6 ml H_2SO_4 * 0.0085$ /g = 0.1156$	0.621$	Mishra et al.,[32]
Chelation technology	0.4M EDTA, S/L =1:15, 4h, 130°C,	>90% Ni, 88% Mo, 84% Co	EDTA, NaOH/ H_2SO_4 (98% conc.=18mol/L) for adjusting pH	10g → 150 ml solution 0.4M EDTA => 22.3g/150 ml solution 22.3 g EDTA * 0.0276$ /g = 0.616$ 0.1M NaOH => 0.02g in 5ml solution 0.02g * 0.00733$ /g = 0.000147$ 0.2M H_2SO_4 = 0.108 ml in 10 ml solution 0.108ml * 0.0085$ = 0.00091$	0.617$ (for one run using fresh EDTA) 0.74$ to conduct 4 run using recovered EDTA	Chauhan et al., 2012[15], 2013[9]

Table 5 : Chelating Agents used for metal extraction from soil in literature.

Type of soil	Chelating agent	Heavy metals	Reference
Superfund site soil	EDTA	Pb	Ellis et al.[200]
Soil from battery recycling facility	EDTA, NTA	Pb	Elliot and Brown[12]
Quartz-rich sediment and soil samples	NTA	Pb, Ni, Zn	Howard and Shu[201]
Wetland soil	Acetic acid, EDTA , DTPA	Zn, Fe, Mn, Ca, Cd, Mg, K, Al, Na, Cu, Pb	Sistani et al.[202]
Industrially contaminated soil, agriculture soil	EDTA, EDDS, IDSA, MGDA, NTA	Zn, Cu, Pb, Cd, and Ni	Tandy et al.[104]
Soil from 25-50cm below ground surface near a bay.	EDDS	Cu,Zn, Pb	Yip et al.[203]

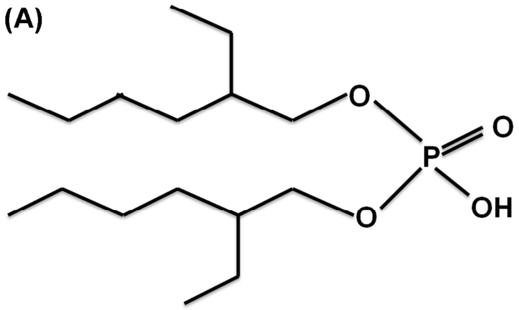

Figure 1 : Newly Synthesized Green Extractants for metal removal from contaminated sites (A) DEHPA (Di-(2ethylhexyl phosphoric acid)
295x208mm (300 x 300 DPI)

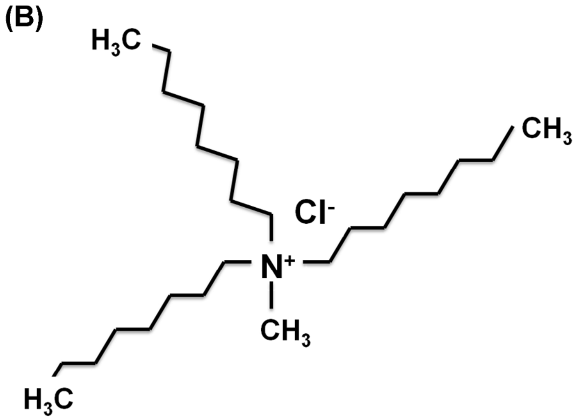

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (B) Aliquat-336 (N-Methyl-N,N,N-trioctyl-octan-1-ammonium chloride)
294x208mm (300 x 300 DPI)

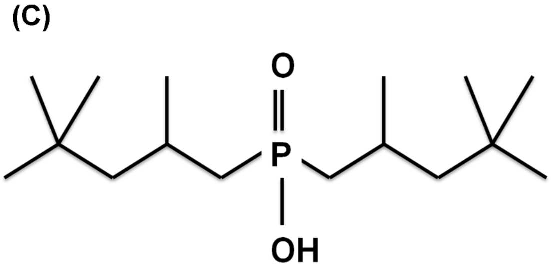

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (C) Cyanex 272 (Bis(2,4,4-trimethylpentyl)phosphinic acid)
295x209mm (300 x 300 DPI)

(D)

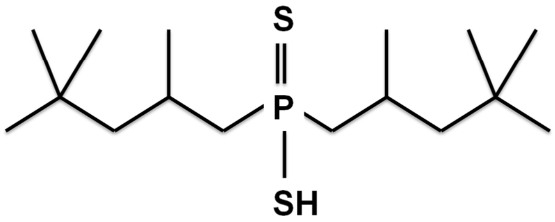

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (D) Cyanex 301 (Bis(2,4,4-trimethylpentyl) dithio-phosphinic acid)
294x208mm (300 x 300 DPI)

(E)

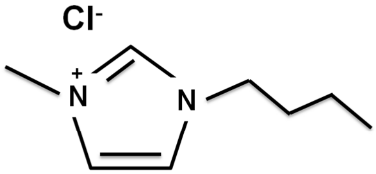

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (E)1-N-butyl-3-methylimidazolium salts
294x208mm (300 x 300 DPI)

(F)

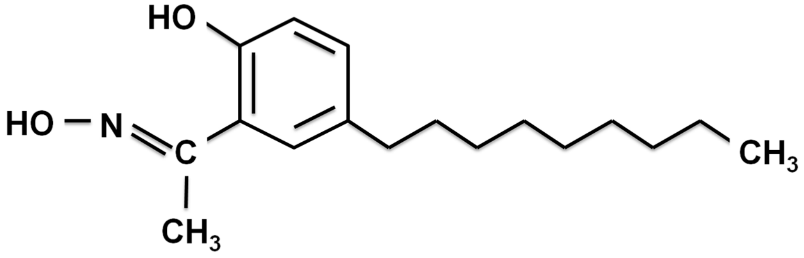

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (F) LIX-84-IC (2-hydroy-5-nonyl acetophenone oxime)
295x209mm (300 x 300 DPI)

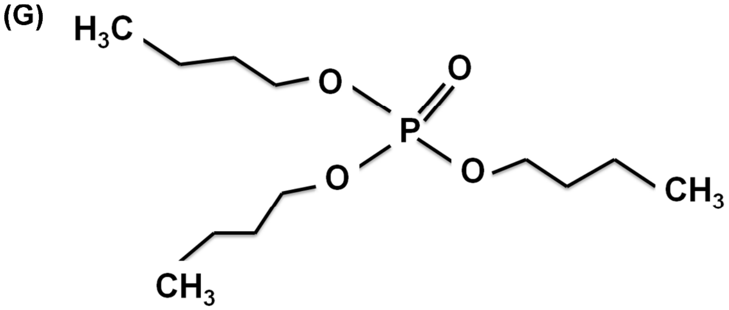

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (G) Tributyl Phosphate
294x208mm (300 x 300 DPI)

(H)

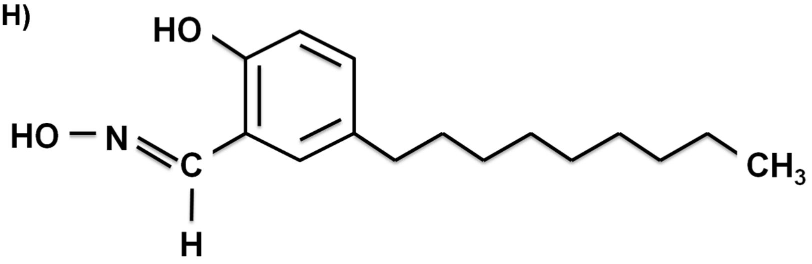

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (H) Acorga M5640 (active substance 2- hydroxy-5-nonylbenzaldehyde oxime)
294x208mm (300 x 300 DPI)

(I)

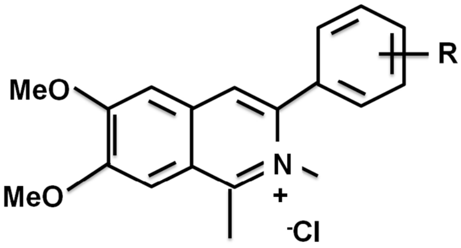

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (I) Amberlite Resin 400
295x208mm (300 x 300 DPI)

(J)

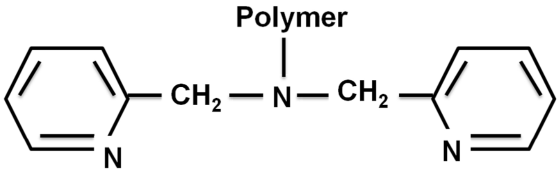

Figure 1: Newly Synthesized Green Extractants for metal removal from contaminated sites (J) Dowex M-4195 Resin
295x207mm (300 x 300 DPI)

(A)

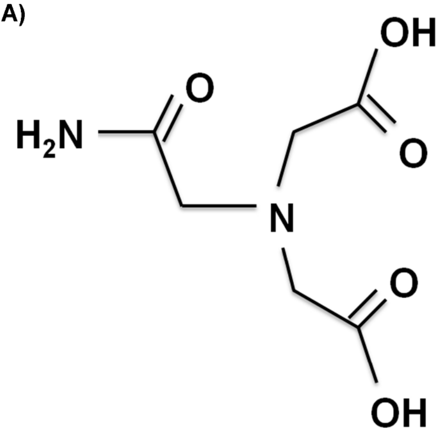

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (A) N-2-acetamidoiminodiacetic acid (ADA)
295x209mm (300 x 300 DPI)

(B)

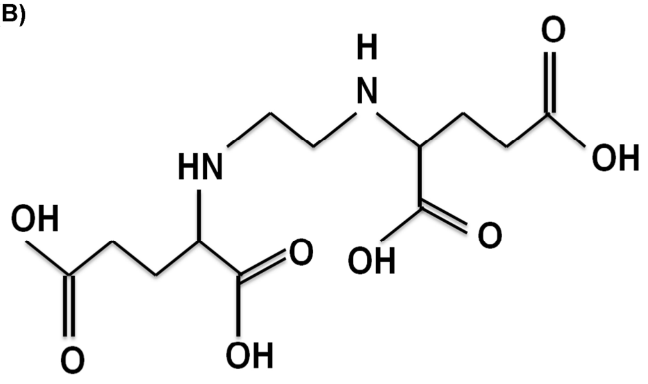

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (B) Ethylenediglutamic Acid (EDGA)
294x208mm (300 x 300 DPI)

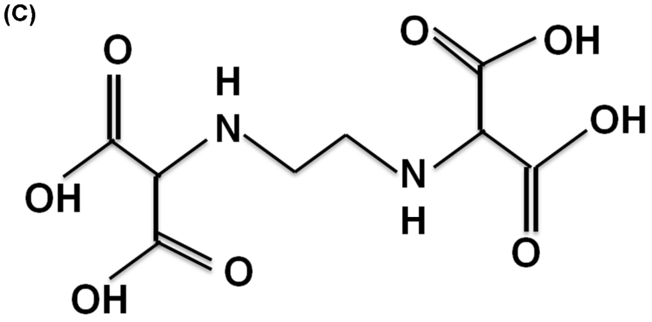

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (C) Ethylenediamine dimalonic Acid (EDDA)
294x207mm (300 x 300 DPI)

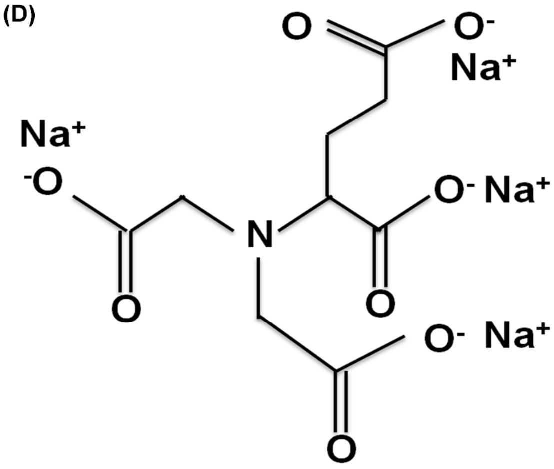

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (D) N,N-bis(Carboxymethyl)-L-Glutamic Acid Tetrasodium Salt (GLDA)
295x209mm (300 x 300 DPI)

(E)

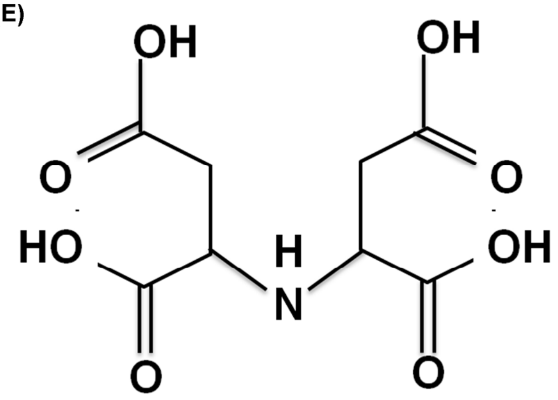

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (E) Iminodisuccinic acid (IDS)
294x209mm (300 x 300 DPI)

(F)

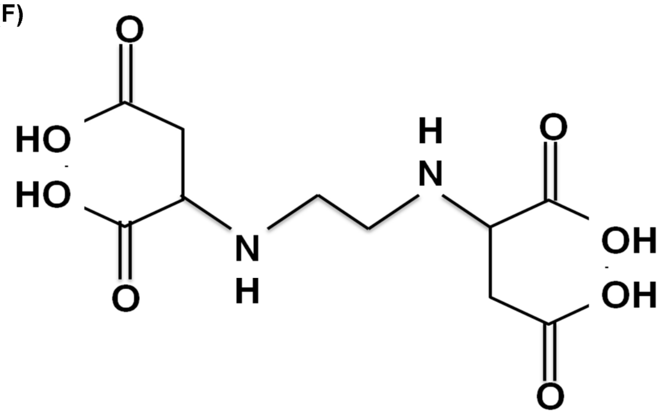

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (F) Ethylenediamine disuccinic acid (EDDS)
294x207mm (300 x 300 DPI)

(G)

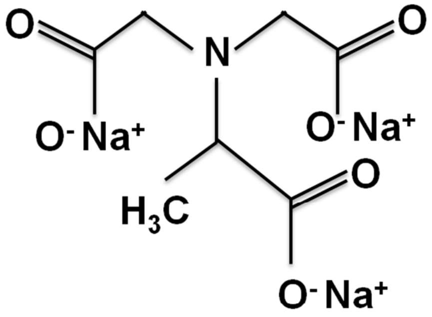

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (G) Methyl glycine diacetic acid, trisodium salt (MGDA)
295x208mm (300 x 300 DPI)

(H)

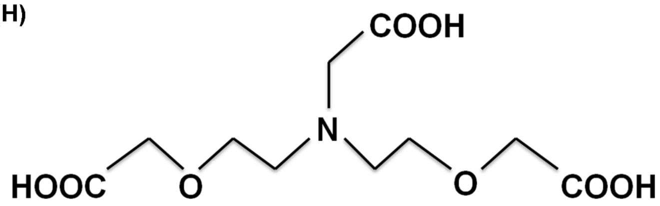

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (H) N-bis [2-(1,2-dicarboxy methoxy)ethyl] glysine (BCA3)
293x206mm (300 x 300 DPI)

(I)

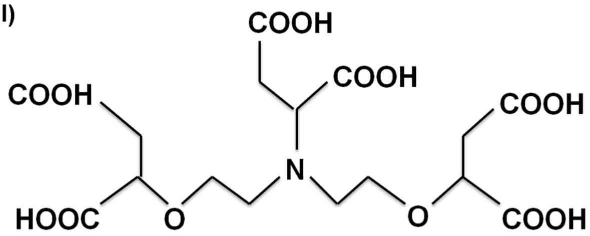

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (I) N-bis [2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCEEAA)
295x209mm (300 x 300 DPI)

(J)

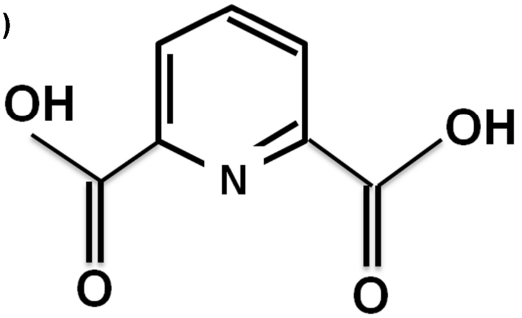

Figure 2: Molecular arrangements of some newly synthesized biodegradable chelating agents (J) 2,6-Pyridinedicarboxylic acid (DPA)
294x208mm (300 x 300 DPI)

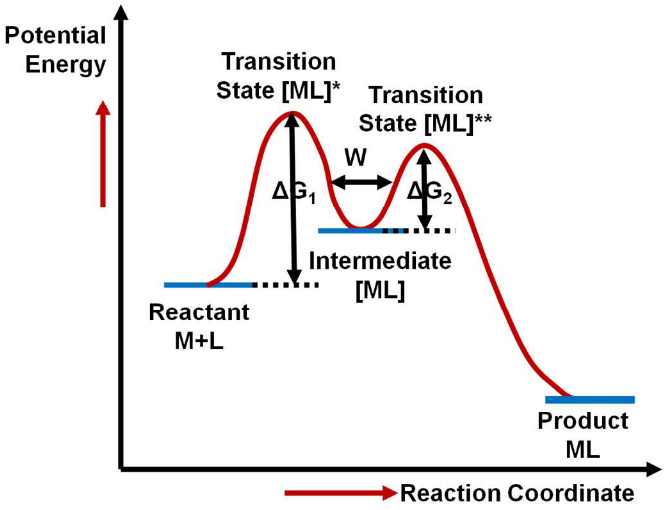

Figure 3: Metal-ligand interaction – General Mechanism
293x209mm (300 x 300 DPI)

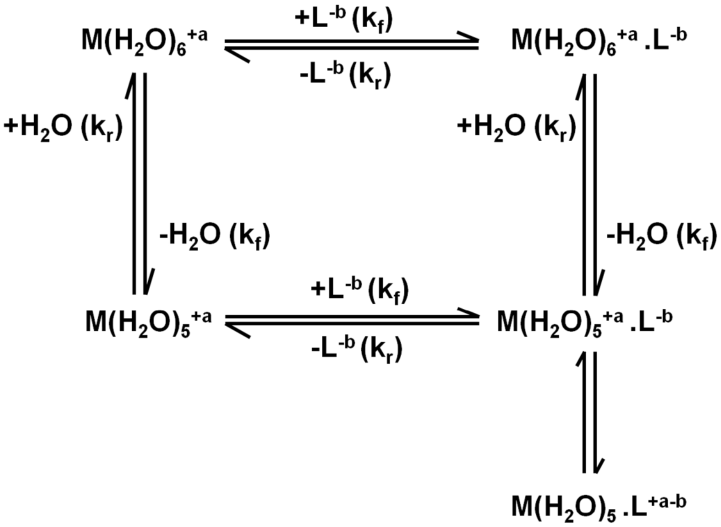

Figure 4: Schematic representation of the reaction mechanism for metal-complex formation in aqueous system
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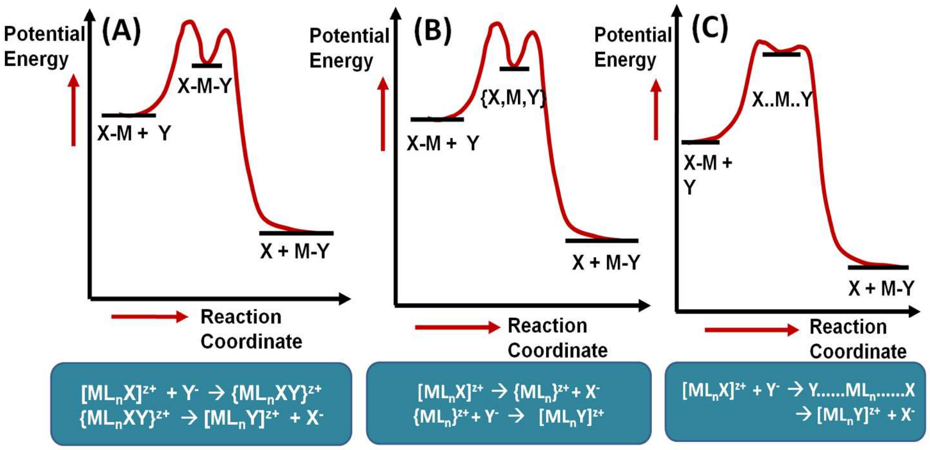

Figure 5: Ligand Substitution Mechanisms – (a) Associative (b) Dissociative (c) Interchange
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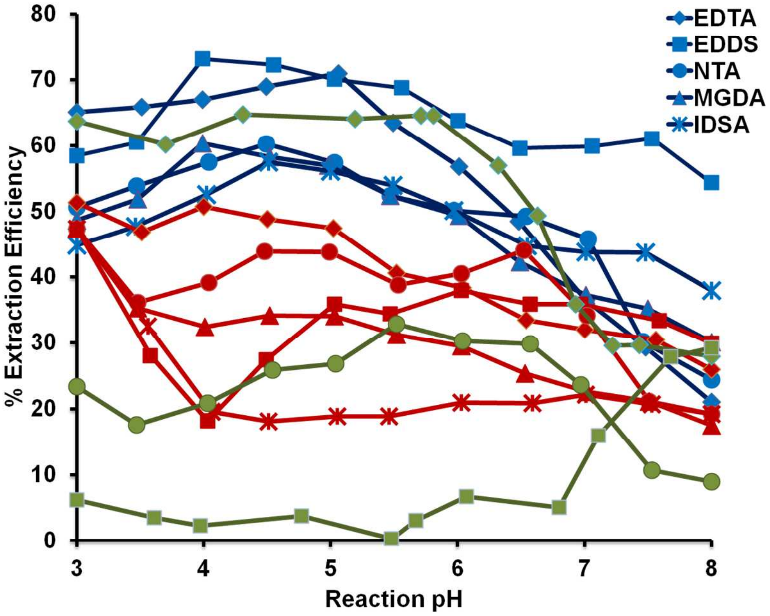

Figure 6: Effect of reaction pH on extraction efficiency of various chelating agents for Cu (Blue markers), Zn (Red markers) and Pb (Green markers)104
294x207mm (300 x 300 DPI)

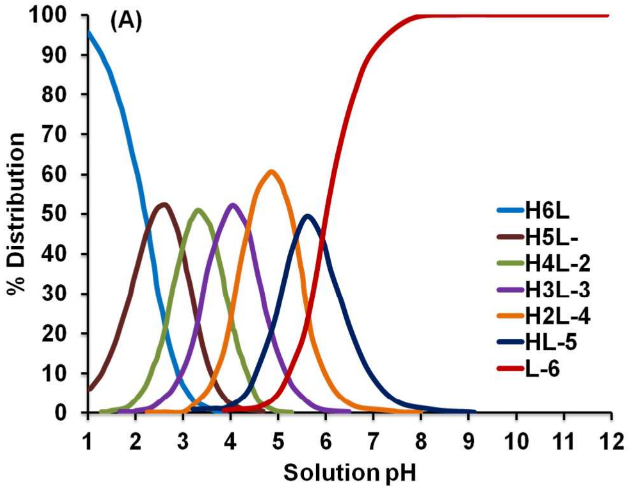

Figure 7 : % Distribution of protonation stages of various chelating agents (A) TDS96
294x209mm (300 x 300 DPI)

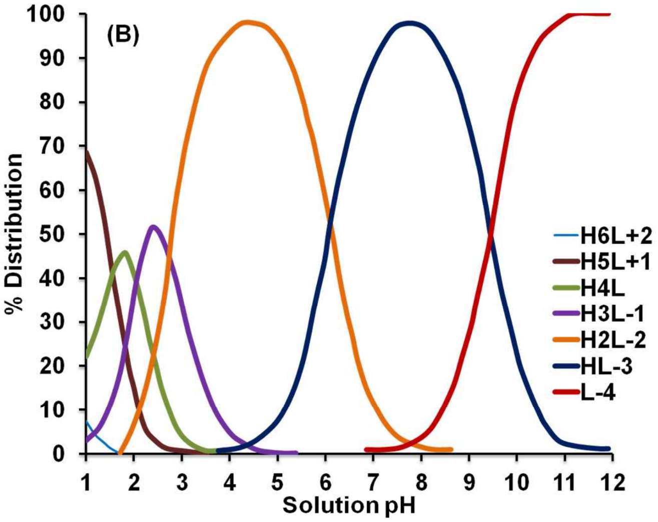

Figure 7 : % Distribution of protonation stages of various chelating agents (B) EDTA96
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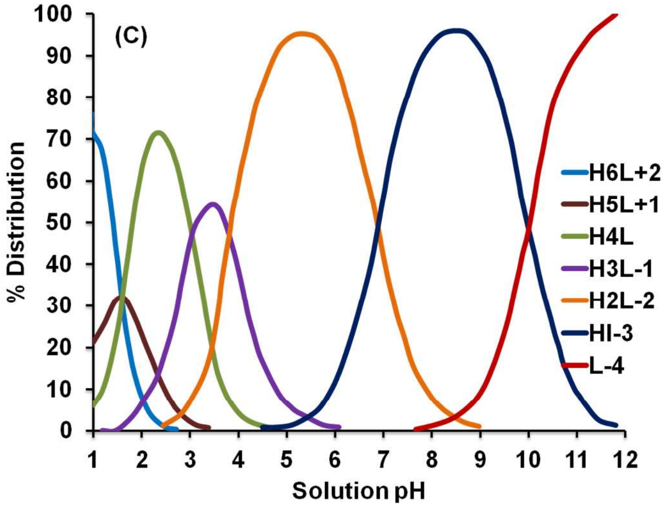

Figure 7 : % Distribution of protonation stages of various chelating agents (C) EDDS96
295x208mm (300 x 300 DPI)

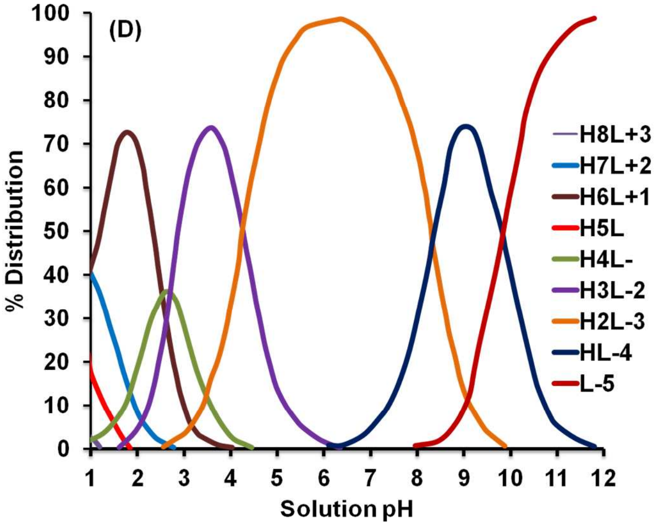

Figure 7 : % Distribution of protonation stages of various chelating agents (D) DTPA96
294x208mm (300 x 300 DPI)

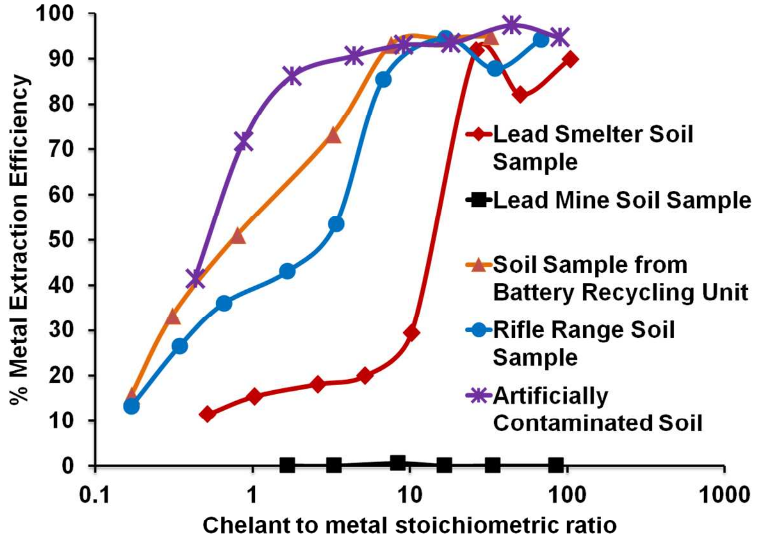

Figure 8 : Effect of chelating agent (EDTA) to metal stoichiometric ratio (MR) on Pb extraction for different soil samples113
294x208mm (300 x 300 DPI)

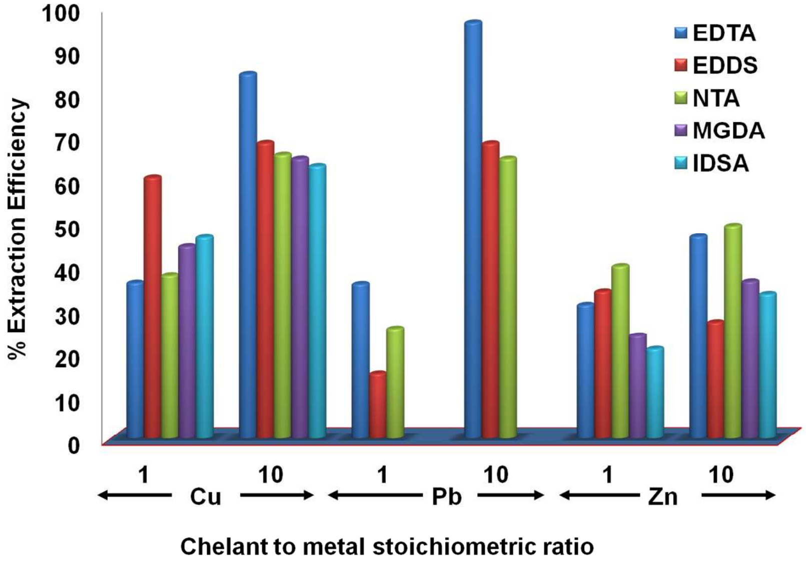

Figure 9 : Effect of chelating agent (EDTA) to metal stoichiometric ratio (MR) on metal extraction using different chelating agent104
295x207mm (300 x 300 DPI)

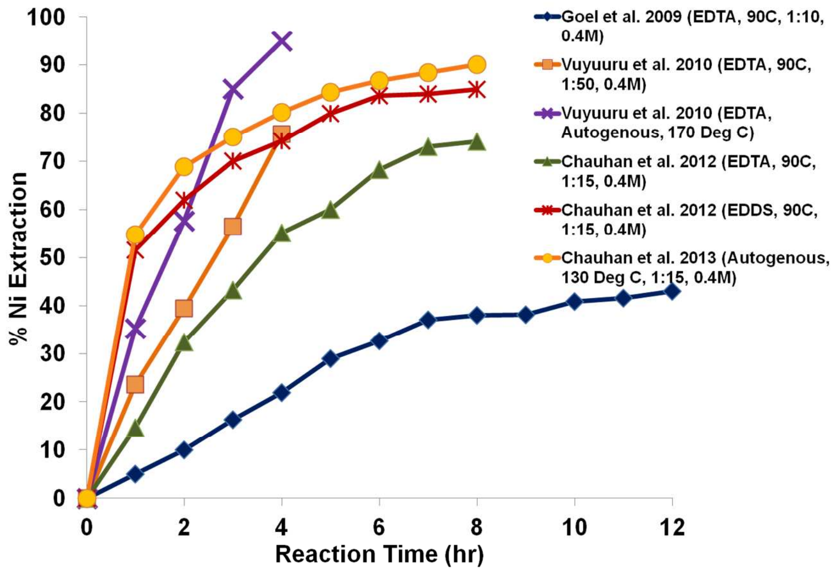

Figure 10 : Effect of reaction temperature on Ni extraction from spent catalyst
294x208mm (300 x 300 DPI)

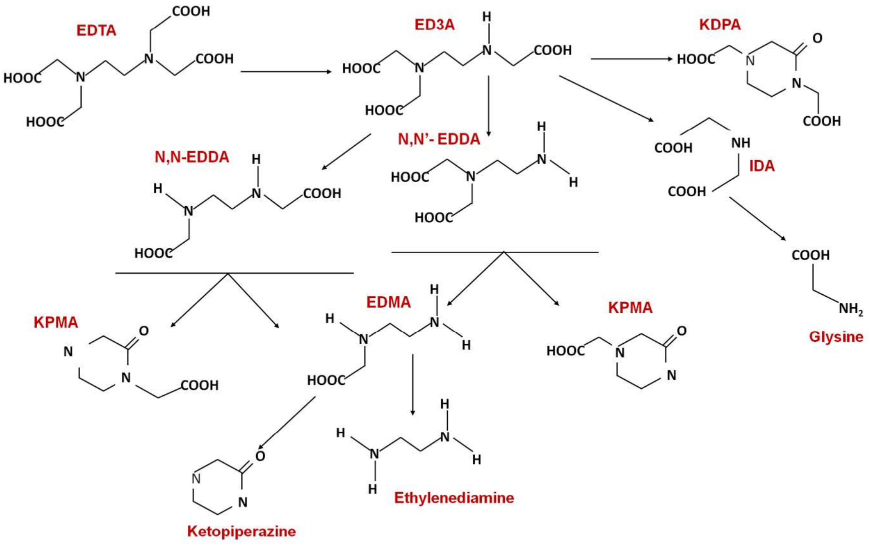

Figure 11: Identified degradation products and pathways of EDTA135
294x208mm (300 x 300 DPI)

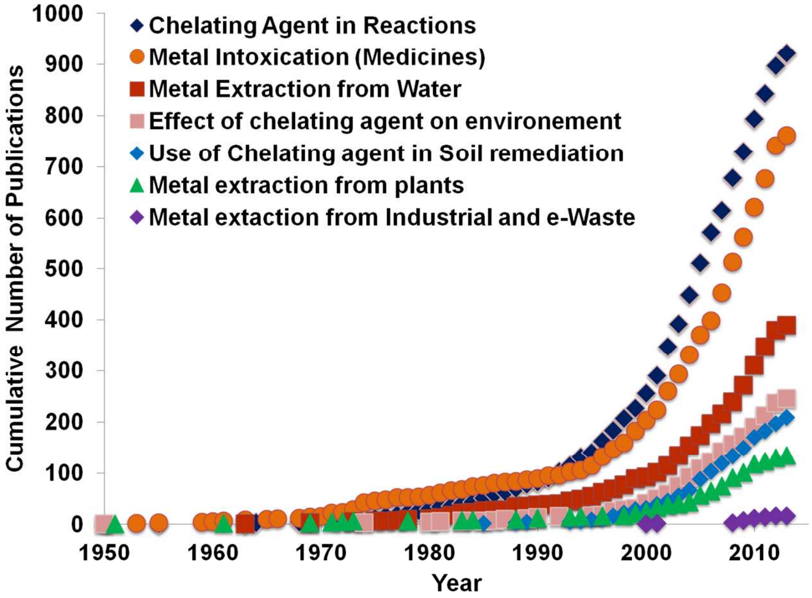

Figure 12: Cumulative number of publication for last six decades on ‘application of chelating agent in various areas’ (metal extraction from water includes natural water resources and waste water; reactions include adsorption, complexation, surface reactions; environment includes biodegradability, ecotoxicological effects; soil remediation includes phytoextraction, metal mobilization)177 (Database : Scopus; accessed on July 2014)
294x208mm (300 x 300 DPI)

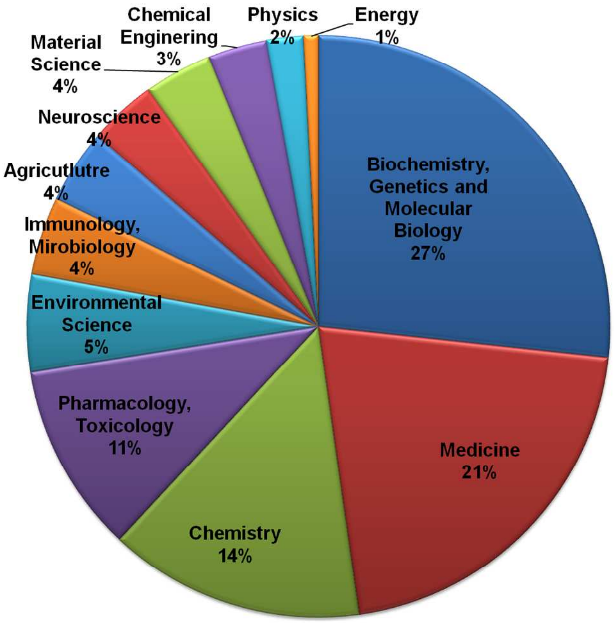

Figure 13: Leading research areas in terms of number of research publications for ‘Chelating Agents’177 (Database : Scopus; accessed on July 2014)
295x208mm (300 x 300 DPI)

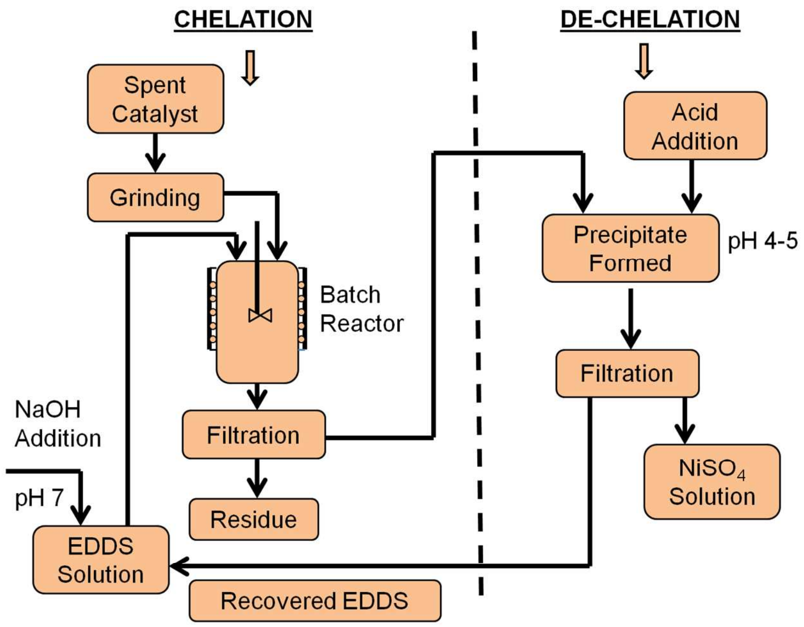

Figure 14: Process flow chart for "Solid-liquid extraction and regeneration of chelating agent"15
294x208mm (300 x 300 DPI)