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Eco-friendly Chelating Agents for Extraction of Metal from Spent Catalysts of Fertilizer Industry

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Abstract

Green chemistry perceives the concept of developing innovative environmental benign technologies and improving the resource intensity. In order to explore this concept for minimizing the industrial waste and for reducing the environmental impact of hazardous chemicals. The paper focuses on green approach to extract metals like Ni,Cu,Mo, Fe, Zn, Rh and Pd from spent catalyst, which contain substantial quantity of heavy metals and may affect the ecosystem. The chelation technology is an ecofriendly process for extraction of heavy metals from spent catalyst obtained from fertilizer industry. Green chemistry recognizes the concept of developing innovative environmentally benign technologies to protect human health and ecosystems. In order to explore this concept for minimizing industrial waste and for reducing the environmental impact of hazardous chemicals, new greener approaches need to be adopted for the extraction of heavy metals from industrial waste. In this review, new green approaches employed for metal extraction are discussed in brief. Chelation technology, a modern research trend, has shown its potential to develop sustainable technology for metal extraction from spent catalysts and various metal-contaminated sites. However, the interaction mechanism of ligands with metals and the ecotoxicological risk associated with the increased bioavailability of heavy metals due to the formation of metal–chelate complexes. Therefore, a need felt to provide a comprehensive state-of–the-art of aspects associated with chelation technology to promote this process as a green chemistry approach. Chelation technology elucidates the mechanism associated with metal–ligand complexation in order to have a better understanding of the metal extraction process. The effects of various process parameters on the formation and stability of complexes have been elaborately discussed with respect to optimizing the chelation efficiency. Therefore, biotechnological approaches have been assessed to illustrate the possibility of ligand degradation, which will help to look for new environmentally safe mobilizing agents. Chelation technology as a potential ecofriendly method to extract heavy metals from spent catalysts. Chelation technology have been carried out for extraction of transition metals from spent catalyst samples obtained from fertilizer and petrochemical industries using different biodegradable chelating agents(NTA ,EDDS,IDSA ,MGDA & GLDA).

Keywords: Spent catalysts, chelation technology, chelating agents, biodegradability, solid wastes minimization, fertilizer industry, metal extraction, pollution, ecofriendly approaches,

Introduction

Metal catalysts play an ineluctable role in chemical industries for industrial growth and technology development. These catalysts facilitate difficult hydro-treatment and hydrodesulphurization processes with high selectivity for converting heavy oils and residues to more valuable distillates and feedstock's for petrochemicals & fertilizer industry (Kaufmann et al., 2000, Breysse et al., 2003, Song, 2003, Rana et al., 2007). However, activity of the catalyst is deteriorated eventually after certain reaction cycles because of chemical changes during the reaction and deposition of impurities such as coke, metal sulfides and oxides on the surface of the catalyst. At this stage, they need to be replaced with the fresh catalysts for subsequent reaction cycles in order to maintain the desired productivity and selectivity. The discarded catalysts are referred to as “spent catalysts” which contain a significant amount of heavy metals in it and are a threat to the ecosystem if not disposed off in proper manner. The spent catalysts removed from residue desulfurization process at the end of each cycle run contain several metals including vanadium, molybdenum, nickel, cobalt, and aluminum. Spent catalysts from the fertilizer & petroleum industry, generally contain 4–12% Mo, 15–30% Al, 1–5% Ni, 0–4% Co, 5–10% S, 1–5% Si, 0–0.5% V,Zn,Cu & Fe. The quantity of spent catalysts discharged from industries depends on the quantity of fresh catalysts to be used, their lifetime with desirable activity for the reaction and impurities deposition on them during the reaction. Unaccounted disposal of these heavy metals from chemical industries in the form of waste material (spent catalysts) is also an intense source of environmental pollution and therefore, recovery and reuse of heavy metals from waste material are sincere concern in order to prevent environmental pollution and to conserve resources. Several conventional and modern research efforts have been reported in literature for metal extraction. Chelation technology, one of these recent green approaches (Tsang and Hartley, 2014, Voglar and Lestan, 2014) has shown its applicability to recover metals from contaminated sites. Complexation of metal ions with chelating agents in aqueous solution is a ligand substitution reaction where the solvation sphere is substituted by a multidentate ligand to extract, inactivate or mobilize the metal ion. Previous studies (Goel et al., 2009)

suggest that chelation technology as a potential ecofriendly method to extract heavy metals from spent catalysts. Chelation technology have been carried out for extraction of transition metals Ni , Co, Zn, Cu, Rh and Mo from spent catalyst samples obtained from fertilizer and petrochemical industries using different chelating agents (EDTA, NTA, DTPA, EDDS, IDSA, MGDA & GLDA).

Spent catalysts are major source of solid wastes in the fertilizer industry. Indian fertilizer Industry is the third largest producer of fertilizer in the world. In India, there are about 56 major nitrogenous and 72 single super phosphate plants, the production of fertilizer in large capacity does release wastes into the environment in various form and is bound to be significant. Ammonia is very important chemical which used as raw material for manufacturing of different chemicals such as nitrogenous fertilizer, nitric acid, cyanide, amine and organic compounds. In the 19th century, ammonia was obtained from natural saltpeter or recovered from coal. In order to meet the increasing demand for nitrogenous fertilizers, a variety of methods were tried to fix nitrogen from air at the beginning of the 20th century. Catalytic ammonia synthesis from N2 and H2 was developed by Fritz Haber, and then Carl Bosch applied this process to industrial production successfully at the beginning of 20th century. Because of the extensive use of nitrogenous fertilizers, catalytic ammonia synthesis plays an important role in agriculture and other industries.

Synthesis of ammonia in different plant depends on raw materials and catalysts used in synthesis process. Ammonia is basically produced from water, air and energy. The source of energy is normally coal or hydrocarbons which are reacted with water at high temperature and electricity to drive the compressors. Natural gas is generally the preferred hydrocarbon: some 77% of world ammonia production capacity is currently based on natural gas and more than 99% of world nitrogenous fertilizer production is based on ammonia. In ammonia production plant different type of catalysts are used (Sing, B., 2009).After periodical use of the catalysts, due to poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst, they will become inactive or spent or poisoned due to loss of surface area.

Environmental laws concerning spent catalyst disposal have become increasingly more severe in recent years. Disposal of spent catalyst is a problem as it falls under the category of hazardous industrial waste. Spent catalysts have been classified as hazardous wastes by the United States Environment Protection Agency (USEPA) therefore spent catalyst should be again utilize an environmentally acceptable safe materials for recycle (USEPA, 2003). These metals exert wide variety of adverse effects on human being. Some of the metals have extremely long biological half-life that essentially makes it a cumulative toxin. Also some metals are carcinogenic in nature. Hence, these solid waste materials which are causing serious environmental problems can act as artificial ores. The valuable metals can be recovered from these spent catalyst waste. Recovery of metals from spent catalysts solid wastes has been an important issue not only from economic aspect but also for recycling rare natural sources and reducing the spent catalyst waste to prevent the environmental pollution. Several alternative methods such as disposal in land fills, reclamation of metals, regeneration/ rejuvenation and reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with the spent catalyst problem. The choice between these options depends on technical feasibility and economic considerations. Among all these methods metal reclamation has attained maximum attention as the recovered metals from spent catalysts.

SPENT CATALYST (SOLID WASTES)

Different types of catalysts are used in ammonia synthesis plant of fertilizer industry. The improvement of catalysts not only increases the efficiency of production of ammonia, but also saves consumption of the power. Although a lot of technology progress has been achieved, the basic principles and process in modern ammonia plants are essentially the same as original ones developed by Haber and Bosch, a century ago. More than 77% of world ammonia production capacity is currently based on natural gas. During ammonia synthesis, the major reaction of production and purification of synthesis gas and the ammonia, all are carried out over different catalysts (Prajapati, R. P., Sharma Anand and Tiwari, D. R., 2011). At least eight kinds of catalysts are used in the whole process, where natural gas or naphtha is used as feedstock and steam reforming is used to produce synthesis gas. These catalysts are Co-Mo hydrocarbon catalyst, zinc oxide desulfurizer, primary and secondary steam reforming catalysts, high and low temperature shift catalysts, methanation catalyst and ammonia synthesis catalyst etc. Details of the various catalysts used in the ammonia synthesis plant are given in table-1. The eight kinds of catalysts may be roughly classified as “protective catalysts and economic catalysts”. Co-Mo hydrogenation catalyst and zinc oxide desulfurizer are the protective catalyst for the primary steam reforming catalysts. The high-temperature shift catalyst protects the low-temperature shift catalyst, and the methanation catalyst is the protective catalyst for ammonia synthesis catalyst (Shen J.(ed.) ,2001).

The catalysts for primary and secondary steam reforming, low-temperature shift and ammonia synthesis are responsible for the conversions of raw materials and the yield of products, and have direct effect on economic benefits of the whole plant, and are thus called as “economic catalysts”. The amount of catalysts used depends on the process and raw material.

Spent catalysts could be used as a cheap source for the valuable metals. Chelation-dechelation technology very important for the extraction of heavy metals from spent catalysts. Nearly closed loop eco-friendly technology has also been developed in order to extract metals from multimetallic spent catalysts using biodegradable chelating agents. The present study review article explores all the aspects of this technology to promote the chelation process as an eco-

friendly chemical approach. Therefore, innovative processes are required within an eco-friendly framework that should recognize the global necessity of resources (metals) and significantly reduce hazardous waste on the environment, without compromising the economics of the process (Sillanpaa, M.,.Pirkanniemi,K.,2001). One possible method for extraction of heavy metals from spent catalyst of fertilizer industry is chelation technology that has a high potential for metal extraction by biodegradable chelating agents and the chelating agents can be reused in the extraction process itself.

Table-1 catalysts used in the ammonia synthesis plant (fertilizer industry)

S.N	Process	Catalyst	Catalytic Reaction	Life (years)	Nature of spent catalyst
1	Hydrosulfurisation	$Co/Mo/Al_2O_3$	$R_2S+2H_2 \rightarrow 2RH+H_2S$	5-7	Pyrophoric
2	Desulphurisation	ZnO	$H_2S+ZnO \rightarrow ZnS+H_2O$	depends on the S-content in Natural gas	Non-pyrophoric
3	Primary reforming	NiO	$CH_4+H_2O \rightarrow CO+3H_2$	5-7	Pyrophoric
4	Secondary reforming	NiO	$CH_4+1/2O_2 \rightarrow CO+2H_2$	5-7	Pyrophoric
5	High temperature shift converter	$Fe_2O_3 \& Cr_2O_3$	$CO+H_2O \rightarrow CO_2+H_2$	5-7	Pyrophoric
6	Low temperature shift converter	$CuO, ZnO \& Al_2O_3$	$CO+H_2O \rightarrow CO_2+H_2$	5-7	Pyrophoric
7	Methanation converter	Ni	$CO/CO_2+6H_2 \rightarrow CH_4+H_2O$	5-7	Pyrophoric
8	Ammonia Converter	Fe_3O_4	$N_2+3H_2 \rightarrow 2NH_3$	5-7	Pyrophoric

BIODEGRADABLE CHELATING AGENTS

Globally, there is an urgent need to look for new green reagents for metal extraction from industrial waste water, soil and spent catalyst. This excogitation is now assisting researchers to move towards ionic liquids, novel resins, polymeric composites, chetating agents and others green extractants. Chelating agents have been used for many years by industry and analytical chemists because of their sequestering or masking properties: that is the ability to suppress the activity of a dissolved metal ion without its physical removal from the solution (Neal, J.A. & Roshe, N.J., 1973). Chelating agents may be either organic or inorganic compounds. However, these are hydrolytically unstable at high temperature and pH. Among the organic chelating agents, aminopolycarboxylates are frequently used chelants and accounted for the largest share (39%) in the world-wide consumption of chelating agents in 2012. These aminopolycarboxylates, e.g. EDTA, nitrilotriacetic acid (NTA) and DTPA, have stronger binding capacities than polyphosphates and better sequestering abilities than hydrolytic acid-type chelating agents. A new discipline, 'greener chelating agents', is also gaining the attention of researchers; such agents contribute 15% of the overall world-wide consumption of aminopolycarboxylate chelating agents and the demand is expected to increase up to 21% by 2018, due to the replacement of conventional chelating agents by a new range of biodegradable chelating agents. EDDS, GLDA, iminodisuccinic acid (IDSA), etc., are examples of biodegradable green chelating agents which may significantly share the chelating agents market in forthcoming years to avoid the environmental risks associated with non-biodegradable chelators. Their biodegradability is an important focus because of the renewed attention towards environmental protection issues. Some biodegradable chelating agents described in detail along with their molecular arrangement given below.

1. IDS

Iminodisuccinic acid (N-1-2-dicarboxyethyl)-D,L-aspartate acid, present in four possible stereoisomer's (R,R,), (S,S), (R,S) and (S,R). However, the two meso forms (R, S) and (S, R) are identical. The isomeric mixture of IDS consists of 25% (S, S), 25% (R,R), and 50% (R,S) form. IDS exhibits extremely rapid biodegradation, which equals approximates 80% after just 7 days. It is characterized by excellent calcium binding properties, stability in a wide pH, good complexation of heavy metals ions and low environmental impact due to low toxicity and good biodegradability according to the OECD (Organization of Economic Cooperation and Development) test. It was found that in the dilute solutions of IDS more than 90% of metal ions are bound over a a wide pH range (Hyvonen,et al.,2003). . IDS can be also applied for production of micronutrient fertilizers. The chemical structure of IDS given in figure -1

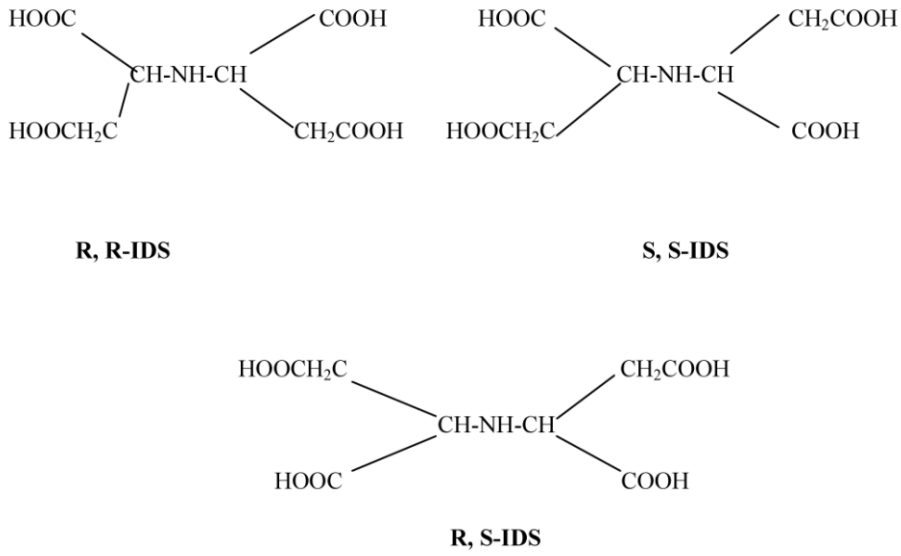

Fig.1 The structural isomers of IDS

2. EDDS

Ethylenediamine-N,N-disuccinic acid (EDDS) is a structural isomer of EDTA. It forms four isomers , S,S-EDDS (25%),R,R-EDDS(25%),R,S-EDDS(50%) and S,R-EDDS(50%). The S,S-isomer of EDDS, based on the naturally occurring amino acid i.e.L-aspartic, is readily biodegradable. According to the OECD 83% of S,S-EDDS convert to CO2 within 20 days (Jaworska,et al., 1999). However, the others are partly or completely non-biodegradable (Tandy,et al.2006a). The structure of EDDS isomers is given in Fig.2.

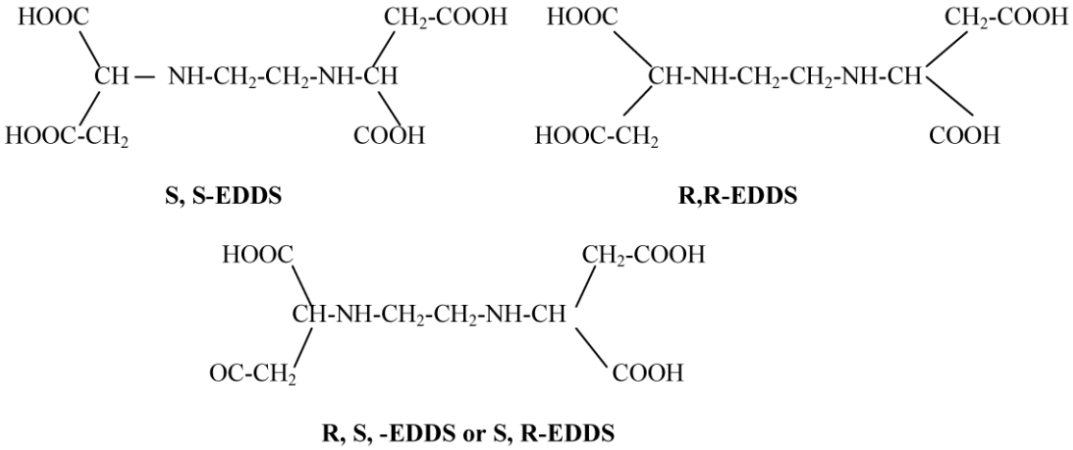

Fig. 2 Structural isomers of EDDS

3. GLDA

A novel readily biodegradable chelating agent, tetrasodium of N,N-bis(carboxymethyl)-L- glutamic acid, the carbon source of GLDA is primarily biobased. Therefore, GLDA is the only chelating agent with green carbon atoms. The biodegradation of GLDA is initiated by mono-oxygenases catalyzing the removal of carboxymethyl groups. According to the Swedish Society for nature conservation GLDA is 86% based on natural, raw materials. It also possesses good solubility at both low and high pH. Greater than 60% of L-GLDA degrades within 28 days., The structure of L-GLDA-Na4 is given in Fig.3.

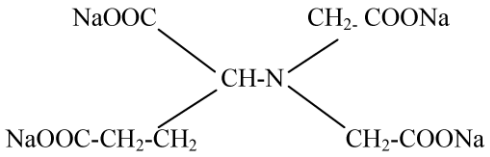

Fig. 3 **L-GLDA-Na_4**

4. MGDA:

Methyl glycine diacetic acid, trissodium salt (MGDA) also known as glycine-N, N-diaacetic acid. MGDA is readily biodegradable and does not require adapted bacteria for decomposition, instead is degraded under the standard conditions. In the case of MGDA high stability throughout the entire pH range and even at elevated temperatures is found. Furthermore, the metal complexing power of MGDA is stronger than that of citrates. The complexes formed by it are characterized by high stability over a wide range of both pH and temperature.

5. DS

Polyaspartic acid (DS) is excellent Ca (II) tolerance, corrosion inhibition properties, stability in a wide pH range as well as low environmental impact by low toxicity and good biodegradability. It is also an effective chelating agent of a new generation which can be applied for heavy metal ions removal. . The properties of the above described chelating agents are given in table-2.

Table 2: The properties of the above described biodegradable chelating agents

Se. No.	Properties/ Chelating agents	IDS	EDDS	GLDA	MGDA	DS
1.	Molecular weight	337.1	358.1	351.1	271.0	-
2.	Appearance	colourless to light yellow	colourless to yellowish	colourless to yellowish	clear yellowish	clear reddish
3.	pH	10.3-11.4	9.2	13.5	11.0	9.5-10.5
4.	Density	1.32-1.35 g/mL	1.26 g /mL	1.38 g/mL	1.31g /mL	1.3g/mL
5.	Solubility in H_2O	in any ratio	in any ratio	in any ratio	in any ratio	in any ratio
6.	Biodegradability	more than 80%	more than 60%	more than 83%	more than 68%	more than 60%

Chelating agents are used as components or process chemicals in wide variety of application, however, according to fig.-5 only pulp and paper, cleaning, chemical processing, agriculture and water treatment constitute 80% of their consumption. Chelating agents have already proven their applicability in, medicines. Nevertheless, extensive research is being carried out on metal detoxification using chelating agents. Chemical engineers &chemists are now moving towards research on chelating agents by applying their metal complexation properties in various applications, such as recovery of heavy metals from waste materials, phytoremediation, and many more. The biodegradability issue associated with classical chelating agents has also been a matter of concern for chemical engineers and chemists.

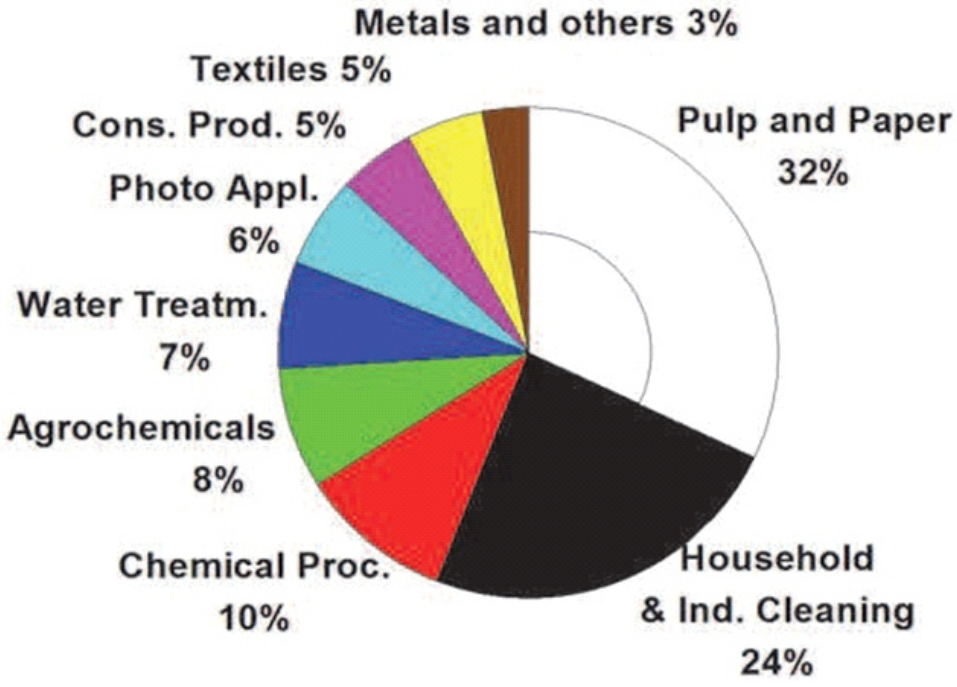

Fig.5 The percentage applicability of chelating agents in different field.

CHELATION TECHNOLOGY: AN ECO-FRIENTLY PATH FOR ENVIRONMENT

Chelant extraction of heavy metals from spent catalyst has several advantages, such as high potential extraction efficiency, high specificity for metals and potential for recovery and reuse of the chelant molecules. EDTA (Ethylenediamine tetraacetic acid) is one of the most commonly used complexing agents and has been intensively studied. It has proven to be very effective in heavy metal removal from spent catalysts and contaminated sites due to its ability to form strong complexes with many transition metals (Elliot and Brown 1989, Chen et al., 1995, Hong et al., 1999, Sun et al., 2001). .Recently several biodegradable chelants have been investigated such as MGDA (Methylglycine-diacetic acid), IDSA (Iminosuccinic acid) and EDDS (Ethylenediamine disuccinic acid). Their ability to extract heavy metals were investigated by .They found that among the biodegradable chelants investigated, EDDS showed the best overall performance. Its use for remediation purposes of metal polluted soils has also been proposed by other authors, because it shows high affinity for many heavy metals, was found to be readily biodegradable and only weakly toxic (Grcman et al., 2003, Jaworska et al. ,1999, Vandevivere et al., 2001a, Vandevivere et al. ,2001b).

'Chelation' is defined as the formation of stable metal–ligand complexes which are soluble in water. Although the 'chelation' term defines the mobilization of metal ions from contaminated sites using multidentate ligands (chelators) as reagents, some authors have assumed hydration of the metal ion as an initial step (as the reaction takes place in aqueous solution), followed by the multidentate ligand tending to displace water molecules from the metal–water complex in order to form a metal–ligand complex. Chelation is demonstrated as the process of ligand replacement of monodentate ligands in metal complexes by multidentate ones. The metal ions present in these complexes do not exhibit the chemical activity of uncomplexed ions. Chelating agents may be either organic or inorganic compounds. The applicability of chelating agents in metal extraction from spent catalysts has recently been flourishing as a wide research area for industrial, economical and ecological benefits. Heavy metals are extensively used for the preparation of various catalysts in the petrochemical and fertilizer industries (Yuan, Z.; Van Briesen J.M. ,2008). The large amount of valuable metals present in spent catalysts has also attracted the attention of researchers to explore various new methods for metal extraction in order to develop efficient processing. Numerous hydrometallurgical and pyrometallurgical approaches have been adopted for the recovery of heavy metals from spent catalysts. Pyrometallurgical processes involve smelting of the spent catalyst to metal alloys and slag in a gaseous environment or recovering the metals in the liquid environment, preceded by roasting or wet oxidation of the spent catalyst(Chauhan, G.; Pant, K. K.; Nigam, K. D. P., 2013) . 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, solvent

extraction and biological methods have also been reported for the recovery of metals from spent catalysts, soil and other industrial waste that involve the 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 the complex nature of spent catalysts. The chlorination process was also adopted for metal recovery; however, the corrosive nature and toxicity of chlorine gas or any mixture of it inhibits the operation. All these processes have shown potential in removing metals from industrial waste; however, the use of hazardous chemicals, possibility of secondary pollution by these chemicals, lower tolerance of biological processes in the environment and high process costs restrict their use on large scales. Therefore, the search for an efficient and ecofriendly technology to extract metals from spent catalysts is needed .

Aminopolycarboxylates, are chelating agents widely used in several industrial, agricultural, and domestic applications. However, the fact that they are not biodegradable leads to the presence of considerable amounts in aquatic systems, with serious environmental consequences. The replacement of these compounds by biodegradable alternatives has been the object of study in the last three decades. The most relevant studies towards the use of environmentally friendly chelating agents in a large number of applications: oxidative bleaching, detergents and cleaning compositions, scale prevention and reduction, remediation of soils, agriculture, electroplating, waste treatment, and biocides (Marafi M., and Stanislaus, A., 2003) . Nitrilotriacetic acid (NTA), ethylenediaminedisuccinic acid (EDDS), and iminodisuccinic acid (IDS) are the most commonly suggested to replace the nonbiodegradable chelating agents depending on the application, the requirements for metal complexation might differ. Metal chelation ability of the most promising chelating compounds [NTA, EDDS, IDS, methylglycinediacetic acid (MGDA), L-glutamic acid N,N-diacetic acid (GLDA), ethylenediamine-N,N′-diglutaric acid (EDDG), ethylenediamine-N,N′-dimalonic acid (EDDM), were used for Fe, Mn,Ni, Mo, Cu, Pb, Cd, Zn, Rh, and Ru metal extraction from spent catalysts which are byproduct of fertilizer industry.

EXTRACTION OF METALS FROM SPENT CATALYSTS USING CHELATION TECHNOLOGY

The extraction of metals from spent catalyst using biodegradable chelating agents can be make it more economical than any other process (Goel et al.,2009). The extraction of metals with chelating agents does not require high temperatures and the chelating agents can be reused after the extraction of the metals. Due to its recoverable nature, this process is more economical than any other process. This process is ecofriendly due to the easy recovery of the chelating agent used for the process, the non-corrosive environment and the fact that no hazardous byproducts are liberated during the process. The 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 (Hyvönen, H. & Aksela, R. ,2010). The ethylene-diamine-tetraacetic acid (EDTA) has been proved as a successful chelating agent for the extraction of metals from soils and spent catalysts. EDTA, however, is quite persistent in the environment due to its low biodegradability, thus its use becomes a matter of environmental concern. Therefore, to minimize the potential environmental risks, a new biodegradable chelating agent [S,S]-ethylene-diamine-disuccinic-acid ([S,S]-EDDS),IDS,GLDA & MGDA can be considered as an environmentally benign substitute for EDTA due to its easy biodegradation capability.Many researchers have investigated the effectiveness of biodegradable chelating agent [S,S]-EDDS for extraction of nickel from the spent catalyst of fertilizer industry. Chelating agents such as EDDS and NTA, which form complexes with relatively low or moderately high formation constants, are readily degradable, while those forming strong complexes, such as EDTA and DTPA, are resistant to degradation and not easily degraded. Ethylene-diamine-disuccinic acid (EDDS) is an efficient transition metal chelator. It is a structural isomer of EDTA. Literature suggests that only the [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. Thus, [S,S]-EDDS is considered as the favorable isomer for extraction of metals (Tandy, S., Ammann, A., Schulin, R. & Nowack, B. ,2006a). The major geometrical difference between [M([S,S]-EDDS)]2− and [M(EDTA)]2− is the size of chelate rings. The hexadentate chelation of EDTA4− gives rise to five five-membered rings, including one ethylenediamine ring (E ring), two β-alaninate rings, and two R glycinate rings. The complex [M([S,S]-EDDS)]2−, however comprises a five-membered E ring, two five-membered glycinate rings, and two six-membered β-alaninate rings. Increasing the size of the carboxylate rings allows the complexes to attain octahedral angles closer to the ideal. Many researchers have investigated EDDS as a biodegradable chelating agent for soil washing and sewage sludge. Copper was extracted from sewage sludge using biodegradable chelant EDDS at solid to solution ratio 1:50. It was reported that without chelant, extraction efficiency decreases with increasing pH, while by addition of EDDS, extraction efficiency increases within range of pH 3−10. In pH range 1−3, efficiency decreases due to lesser solubility of EDDS in acidic medium . Higher nickel extraction capacity along with good biodegradability makes [S,S]-ethylene-diamine-disuccinic acid a promising alternate chelating agent for the extraction of metal from spent catalyst. The, 84% of the Ni present in the spent fertilizer catalyst could be extracted in one cycle. Therefore, [S,S]-EDDS has been demonstrated to be an efficient and green chelating agent with a mobilizing capacity that can be considered comparable with that of EDTA.

Used spent catalyst from the fertilizer industry for the recovery of Ni using EDTA as a chelating agent. 96% Ni was recovered in the form of NiSO4 with an EDTA concentration of 0.8 M. The recovered EDTA was reused in successive experiments with more than 73% Ni recovery over four cycles. Therefore, a biodegradable chelating agent [S, S] - EDDS was employed for the extraction of Ni from spent catalyst in a batch mode under atmospheric reflux conditions, which recovered 84% Ni in one cycle under optimum reaction conditions. 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 than EDTA for the extraction and solvent/chelator regeneration processes. It was concluded that the extraction of the metal depends on the complexing affinity of the chelating agent for the metal and on the affinity between the solid and metal. EDTA has six binding sites (4 acid and 2 amines sites) that make coordination bonds with the metal, while DTPA has eight sites (3 amine and 5 acid sites), which show stronger binding capacity and higher extraction efficiency than EDTA, but this cannot be recovered easily due to the complicated process to break the coordination bonds. The extraction efficiency of recovered EDTA was investigated and a significant extraction of Co and Mo was observed for up to five cycles using recovered EDTA under optimum reaction conditions; however, a nearly 20% loss in extraction efficiency was observed for the fifth cycle of recovered EDTA compared with the fresh EDTA. The loss in extraction efficiency can be related to a loss in the number of metal-binding sites due to the repetitive precipitation of DTA and the added number of impurities during each cycle.Therefore, it can be concluded that metal extraction from spent catalysts using chelating agents is a good idea on the economical and ecological levels. Due to its recoverable nature, this process is more economical than any other process. An economic evaluation of the chelation process in comparison with other methods employed in the literature. The material cost of chelation technology is less than that of other methods, although it may also be seen that the cost factor of for alkaline leaching and for chelation technology are nearly equal to each other. However, the fact cannot be denied that the alkaline reagent cannot be reused for the next alkaline leaching cycles, while the chelating agent can be reused at least four times for chelation experiments without a significant loss in extraction efficiency (Orama, M., Hyvönen, H., Saarinen, H. & Aksela, R., 2002) . Thus, the possibility of recycling combined with good extraction efficiency reduces the process cost significantly and makes the process more attractive than other available methods. This process is also ecofriendly due to the easy recovery of the chelating agent used for the process, and the fact that no corrosive environment is used and no hazardous byproducts are liberated during the process. The 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 steps while pyrometallurgical processes (which have a high temperature requirement) can be performed in just one step, nevertheless, chelation technology offers an advantage over pyrometallurgical processes in terms of a 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 a high temperature process would yield the metals in the metallic state.

Biodegradable chelant extraction of heavy metals offers an environmentally benign approach for waste management. A number of hydrometallurgical approaches have been reported in literature for metal recovery from spent catalyst and have been listed here in Table -3. These methods include acid and alkali leaching followed by selective precipitation or an ion exchange process to achieve individual metals. Significant metal recoveries have been reported in the literature that use acid-/alkali-leaching processes, however acid is hazardous to handle at higher temperature, and it cannot be recovered and reused in the process(Park, K. H., Mohapatra, D., Reddy, B. R.,2006).Leaching is carried out at high temperature; therefore, generation of corrosive environment and the necessity for expensive material of construction are other concerns associated with the acid-leaching process. Bioleaching has also emerged as a promising technology for recovering metals from waste material in recent years, however, longer leaching time to achieve extraction efficiencies conquers its importance for metal extraction. The associated risk of contamination and less acceptability of microorganisms at high temperatures are other important factors to consider while employing biotechnological approaches (Santhiya, D., Ting, Y. P., 2006). Chelation technology has been employed for study for the extraction of heavy metals from multimetal spent catalysts. It can be seen from Table- 3 that extraction of heavy metals using the chelating agent can give extraction efficiency comparable with that of other conventional methodology. It offers certain incentives to industrial practice as an ecofriendly approach by recovering chelating agents and recycling it for another cycle, thus minimizing the amount of solid wastes and toxic discharge into the atmosphere (Garima, C., Kamal, K.P., Krishna, D.P., 2013). The process can be easily implemented in the lab due to the absence of any hazardous chemicals and byproducts. The high efficiency of metal extraction, high thermodynamic stabilities of the metal complexes, low adsorption of the chelating agent to the catalyst, and minor impacts on the physical and chemical properties of the solid matrix as compared to the effects of acids make biodegradable chelant extraction methodology more convincing than other available methods.

S.No.	Catalyst Source	Metals Present	Method of metal extraction	Effi ciency
1.	sulfuric acid production unit	V, K, Fe, Si	Si leaching using urea solution	V (78%), K (90%), and Fe (29%)
2.	spent petroleum catalyst	Ni, V, Mo	leaching with $(NH4)_2CO_3$ followed by washing with H_2SO_4	Ni (90−93%), Mo (12−25%), and V(50−61%)
3.	spent petroleum catalyst	Ni, V, Mo	acid leaching (H_2SO_4)	Ni and V (more than 95%), Mo (28%)
4.	spent hydroprocessing catalyst	Ni, V, Mo	bioleaching using iron/sulfur oxidizing bacteria	Ni (83%), V (90%), Ni and V (50%) in absence of iron; Mo (30−40%)
5.	spent hydrodesulfurization catalyst	Ni, Mo, V	acid leaching + electrolysis process	Mo (14%), Ni (60%) and V (65%)
6.	spent hydrotreating catalysts	CoMo and $NiMo/Al_2O_3$	H_2SO_4 leaching + solvent extraction + ion exchange	Mo (>99.5wt.%), Ni and Co (98.0 ± 0.3 wt.%)
7.	spent hydrodesulfurization catalyst	Ni, Mo, V, Al	Al leaching using oxalic acid solution with H_2O_2 addition	Mo (90%),V (94%), Ni (65%) and Al (33%)
8.	petroleum refining industry	Ni−Mo/ γ-Al_2O_3	alkali leaching (Na_2CO_3/H_2O_2) Mo (>99%) with 99.4% purity, Ni and Al (88%)	Mo (>99%) with 99.4% purity, Ni and Al (88%)
9.	spent refinery processing catalyst	Ni, Mo, Al	bioleaching (Aspergillus niger	Ni (78.5%), Mo (82.3%) and Al (65.2%)
10.	hydro-desulfurization spent catalyst	Co, Mo, Al	chelation technology using EDTA as chelating agent	Co (80.4%), Mo (84.9%) with 91%

ENVIRONMENTAL CONCERN OF CHELATING AGENTS

Chelating agents have been utilized widely in various domestic and industrial applications for many years and have been recently gaining attention in the field of metal extraction from various contaminated sites for minimizing environmental pollution. A high resistance to biodegradability is requisite to attain stability of the metal–chelate complex during industrial processes; however, non-biodegradable chelating agents may have certain deleterious effects on the ecosystem. Chelating agents may perturb the natural speciation of metals and may have a dissolution effect on heavy metals adsorbed in sediments. Chelating agents contain nearly 10% nitrogen which may eventually become present in aquatic systems, and thus chelating agents may have a significant effect on the eutrophication process. Literature suggests that there is a 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 (Jaworska, J. S., Schowanek, D., Feijtel, T. C. J., 1999).

The biodegradation of these conventional chelating agents (EDTA, DTPA, organophosphonates) was investigated using various isolated bacterial strains; still, these compounds do not satisfy the criteria for biodegradability. Thus, the environmental concerns associated with non-biodegradable chelating agents have been the predominant factor that has stimulated the demand for more ecologically-viable chelants. Recently, pyridine-2, 6-dicarboxilic acid (PDA) has also been established as a biodegradable ligand able to efficiently chelate metals in a ligand to metal ratio of 2: 1. Chemists are now moving towards research on chelating agents by applying their metal complexation properties in various applications, such as recovery of heavy metals from waste materials, phytoremediation, and many more. The biodegradability issue associated with classical chelating agents has also been a matter of concern for chemists.

CONCLUSION

Chelation technology for the extraction of heavy metals from spent catalysts and contaminated sites (soil, water, industrial waste) is drawing great attention at present in the development new promising green methods, which should be efficient on

the ecological and economical levels. Various R&D studies are currently underway to identify process parameters which may affect the formation and stability of metal–ligand complexes. Higher extraction efficiency, reusability of chelating agents and diverse applicability make it a convincing technology; however, a number of challenges still need to be addressed. The synthesis of new biodegradable mobilizing agents and the identification of their degradation pathways, by means of molecular simulations or biological methods, are open research fields with immense opportunities for further development in the area 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. The successful application of chelation technology for metal extraction from spent catalysts contaminated sites is a very elegant example of a ligand substitution mechanism, though the industrial application of the process is still restricted by the lack of adequate knowledge about competing reactions that may affect the metal–ligand complexation. More experimental studies will be helpful to provide a better understanding of the ligand substitution mechanism and to explore the diverse applicability of chelation technology .Thus, future attempts should focus on the sustainability, economics and environmental impact of the process to meet the growing industrial demand. The biodegradable chelating agent [S,S]-EDDS showed extraction efficiency similar to that of EDTA for a relatively narrower pH range than that for EDTA, however, the high capital cost of [S,S]-EDDS restricts its pertinency for commercial application. Successful recovery and recycling of recovered chelating agent EDTA for metal extraction minimizes the EDTA mobilization in the environment. Recycling of extracted metals and recovered support material in the synthesis of new catalyst is another apprizing factor of this process which makes this extraction process more convincing for industrial practice. Therefore, the proposed biodegradable chelant metal extraction technology can be considered an environmentally benign approach to recover and reutilize the heavy metals present in waste material (spent catalysts).

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