



EXTRACTION OF NICKEL FROM SPENT CATALYST COMING OUT FROM FERTILIZER INDUSTRY

Ramprakash Prajapati*¹ and Rashmi Singhai²

¹Associate Professor of Chemistry, ²Professor of Chemistry.
Department of Chemistry (DESM) Regional Institute of Education (NCERT) Bhopal 462013 India.

Corresponding Author: Ramprakash Prajapati

Associate Professor of Chemistry Department of Chemistry (DESM) Regional Institute of Education (NCERT) Bhopal 462013 India.

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ABSTRACT

Literature suggests that 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 chelating agent [S,S]-ethylene-diamine-disuccinic-acid ([S,S]-EDDS) can be considered as an environmentally benign substitute for EDTA due to its easy biodegradation capability. The present study focuses on the effectiveness of biodegradable chelating agent [S,S]-EDDS for extraction of nickel from the spent catalyst of fertilizer industry. Experiments were carried out in batch mode under reflux conditions and process design parameters were optimized to maximize the extraction efficiency. Ni extraction of 84% was attained at optimum reaction condition in one cycle run. Dechelation of Ni-EDDS complex was performed at pH 5 where more than 96% EDDS was recovered. Results of the present study were compared with the previously studied chelating agent EDTA at optimum reaction conditions reported in literature. It was observed that [S,S]-EDDS requires a narrower pH range as compared to EDTA for chelation-dechelation process. Thus milder reaction conditions were employed for metal extraction using EDDS which is favorable to select the material of construction of equipment, in addition to the added advantage of biodegradability.

KEYWORDS: Biodegradable chelating agent, spent catalyst, fertilizer industry ecofriendly, recovery and chelation-dechelation.

INTRODUCTION

Heavy metals serve as an ineluctable contributor in process industries for industrial growth and technology development. With increasing demand of metallic composite and alloy materials in industrial processes, supplies of metals are being stepped down regularly today and will eventually be exhausted. At the same time, stringent environmental regulations must also be taken into consideration. Hence, it becomes imperative to develop an ecofriendly method for the recovery of these valuable metals. One possible method for extraction of heavy metals from spent catalyst is chelation technology that has a high potential for metal extraction. A classical aminopolycarboxylate chelating agent, ethylene-diamine-tetraacetic acid (EDTA), has been used for many years to extract heavy metals. In spite of being an effective chelating agent, environmental risks associated with its use are an appealing issue to solve. Major concern of using EDTA is its complexation strength which inhibits its degradation. 1-3 EDTA accumulates in the environment as a tenacious organic pollutant. In recent years, the easily biodegradable greener chelating

agent [S,S]-ethylene-diaminedisuccinic acid ([S,S]-EDDS) has been proposed as a safe and environmentally benign substitute of EDTA for metal extraction from soils and sewage sludge. 4-6 EDTA and EDDS both are aminopolycarboxylate chelating agents. 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. 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 4. Spent catalysts generated in the fertilizer industry deactivate over a lifespan of about 5–7 years because of the harsh conditions in the primary and secondary reformer. More than 3000 t/year of spent catalyst is generated by China and India and 150 000–170 000 t/year of spent catalyst is generated worldwide because of increasing demand for fertilizer. In 2010, about 568.64 tons of spent catalyst was generated from Indian refinery industries, compared to just 203.39 tons in 2007. The increasing amount of industrial waste and disposal of these solids is an issue of concern. Therefore attempts are being made for the recovery of valuable metals from these spent catalysts using ecofriendly methods. The objective of the present study was to look into the effectiveness of biodegradable chelating agent [S,S]-ethylenediamine disuccinic acid ([S,S]-EDDS) as a potential alternative for metal extraction from spent catalyst and to compare its efficiency with traditional chelating agent EDTA

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. Ammonia is produced from atmospheric nitrogen and hydrogen from a hydrocarbon source. Natural gas is the most commonly used hydrocarbon feedstock for new plant; other feedstock's that have been used include naphtha, oil and gasified coal. 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).

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

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.

Extraction Of Nickel From Spent Catalyst Using Biodegradable Chelating Agent

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. 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., contribute to the metal extraction efficiency and therefore the effect of each parameter must be studied in order to optimize the extraction efficiency. The non-biodegradability issue associated with EDTA is the major constraint of using it on a large scale. 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. The exchange behavior of Ni from primary reforming waste catalyst used in the fertilizer industry towards the chelating agents EDTA and DTPA. 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., 2003). 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.

CONCLUSION

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. In the present study, 84% of the Ni present in the spent fertilizer catalyst could be extracted in one cycle.. The recovered EDDS can be recycled during the process after treatment. Maximum 5% reduction in Ni extraction efficiency was observed with first cycle recovered EDDS as compared to fresh EDDS. 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.

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