Extraction of Nickel from Spent Catalyst Using EDTA as Chelating Agent

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ABSTRACT

The extraction of nickel from spent catalyst of primary steam reformer from a nearby fertilizer plant using chelation method is reported in this paper. The chelation was carried out using a di-sodium salt of EDTA (ethylene diamine tetra acetic acid) as a chelating agent. The Ni-EDTA complex formed was dechelated using nitric acid as a solvent resulting into the formation of nickel nitrate (NiNO$_3$) and recovery of EDTA. The recovered EDTA was used for subsequent experiments. The objective was to evaluate nickel removal efficiency of EDTA and reusability of recovered EDTA. The effect of EDTA concentration, time of chelation, catalyst to liquid ratio (S:L) and temperature of chelation were studied in detail. The extraction was up to 95% under the following conditions: 1M concentration of EDTA, solid to liquid ratio 1:10 (g/mL), particle size 1-2 mm, pH 10, 7 hours of chelation time, 400 rpm and 90°C.

INTRODUCTION

The importance of catalysis to chemical processes is enormous. An estimated 90% of the chemical production processes are based on catalytic technologies, encompassing four major market sectors: fuel refining, polymerization, chemical production and environmental remediation. Nickel is widely used as a catalyst in several technological processes like steam-reforming of methane (Singh 2009, Al-Mansi & Abdel Monem 2002), hydrogenation, hydrodesulphurisation, hydrorefining, vegetable oil hydrogenation (Ni, Mo/Al$_2$O$_3$, NiO/Al$_2$O$_3$, Raney nickel alloy respectively), refinery hydrocracking (NiS, WS$_2$/SiO$_2$Al$_2$O$_3$), methanation of carbon oxide from hydrogen (Thomas 1970, Mulak et al. 2005, Mulak & Miazga 2008), etc. The world primary nickel consumption is about 1 million tons, which is growing by an average of 3.1 per cent per year. Amongst all the base metals, nickel is the most volatile owing to its strong demand and tight supply.

One of the major problems related to the use of catalysts in the chemical industry is loss of catalytic activity with time due to loss of surface area, sintering and/or deposition of various compounds like coke, sulphur, etc. The changes provoked by the catalyst deactivation play a significant role for a large number of industrial processes. Spent nickel catalysts are considered as solid wastes and also the replacement cost with fresh catalyst is quite high. Spent catalysts have been classified as hazardous wastes by the United States Environment Protection Agency (USEPA). The dumping of catalysts in landfills is unacceptable as the metals present in the catalysts can be leached into groundwater, resulting in an environmental catastrophe (Clark et al. 1996, Furimsky 1996). In addition to the formation of leachate, the spent catalysts, when in contact with water, can liberate toxic gases

as well. In addition to all these environmental concerns and stringent disposal laws, efforts are being made to recover metals from spent catalysts. The factors considered for the recovery of metals from spent catalysts are: chemical composition, metal price, distance from chemical industry to recycling industry, operational costs and environmental concerns (Marafi & Stanislaus 2003, Rapaport 2000, Chen et al. 2006, Starck 2001, Arslan et al. 2002, Kar et al. 2004, Rane et al. 2005, Valverde et al. 2008, Trimm 2001). The efforts are being made to rejuvenate, recycle and convert the spent catalyst to an environmentally acceptable safe material for reuse (Marafi & Stanislaus 2003, Chen et al. 2006, Trimm 2001, Yoo 1998).

There are two methods used for the recovery of nickel from nickel spent like pyrometallurgical in which product is ferronickel obtained at high temperature, and second is hydrometallurgical in which nickel salts are obtained using leaching with various acids. Hydrometallurgy processes have been used to recover metals from industrial wastes due to their flexible, environment friendly and energy saving characteristics (Kinoshita et al. 2003). The leaching of different metals using variety of reagents such as NaOH, NH$_4$, NH$_3$-(NH$_4$)$_2$SO$_4$, H$_2$O$_2$, H$_2$SO$_4$, HNO$_3$, HF and aqua regia is reported in the literature (Angelidis et al. 1995, Sun et al. 2001, De Lima et al. 2005, Raisoni & Dixit 1988, McPartland & Bautista 1990, Sastre et al. 2002, Yang et al. 2003). However, the leaching methods described in the literature have certain limitations. Use of acid solutions with pH < 1 for leaching out of nickel complicates the process of selective recovery of nickel from a solid matrix and also lead to formation of byproducts.

The present study investigates the use of EDTA as a chelating agent for extraction nickel from spent catalyst. The

objective was to evaluate nickel removal efficiency of EDTA and reusability of the recovered EDTA.

MATERIALS AND METHODS

Pre-oxidation of samples: The spent catalyst used in this investigation was provided by a local fertilizer company, the composition of which is shown in Table 1. The shape of spent catalysts was cylindrical with a particle size of 1.5 cm o.d., 1 cm i.d. and 1 cm length. The 100 g of spent catalyst was crushed to 5 mm size followed by coke removal at 600°C for 6 h. Before furtherer treatment, spent catalyst samples were crushed and screened to a particle size of 1-2 mm.

Chelation route: A solution of EDTA (ethylene diamine tetra acetic acid) was prepared by adding NaOH slowly till EDTA completely dissolved and the pH 10-12 was attained. 5 g of the spent catalyst was added to the EDTA solution in a batch reactor and the reaction was carried out for 4-6 h. EDTA formed a complex with nickel which was precipitated in the solution upon addition of nitric acid and aged for few hours. It was then filtered to obtain spent EDTA and a nickel salt (nickel nitrate) solution. The operating parameters are shown in Table 2. The EDTA, recovered as a powder was washed with hot distilled water several times, dried in oven at 80°C and was reused.

EDTA forms a complex with nickel depending upon the concentration of EDTA as per the following reaction:

$$NiO\text{-}Alumina_{(s)} + EDTA_{(l)} \rightarrow [Ni\text{-}(EDTA)]^{2+}_{(l)} + Alumina_{(s)} \quad ...(1)$$
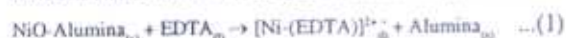
After the chelation, the residue material (alumina) was separated from the complex solution by filtration. Filtrate was subjected to de-chelation process in which metal-chelate was separated by changing the pH of solution depending on the type of complex. Generally, Ni-EDTA complex is not stable in acidic solutions. Therefore, nitric acid was used to de-chelate the formed complex during the chelation process. The entire flowsheet for the recovery is shown in Fig. 1.

$$[Ni\text{-}(EDTA)]^{2+}_{(l)} + HNO_{3(l)} \rightarrow Ni(NO_3)_2 \cdot 6H_2O_{(l)} + EDTA_{(s)} \quad ...(2)$$

After complete settling of precipitated EDTA, it was sent for a filtration process. The EDTA was separated as a spent chelating agent and nickel was extracted as a nickel nitrate solution. The recovered EDTA was further purified and reused.

Atomic absorption spectrometer (AAS, Shimadzu AA6300) and UV Visible Spectrophotometer (UV Vis, Shimadzu UV1800) were used to determine the nickel content. The nickel concentration of the solution obtained after recovery of nickel from spent catalyst was measured using UV-Vis spectrophotometer as follows: Standard samples were prepared from known nickel concentrations (nickel nitrate, nickel sulphate or nickel chloride) in 250 mL of

Table 1: Specifications of the spent catalysts collected from local fertilizer unit.

Component	Primary reformer
Nickel oxide	16%
Alumina	78%
Calcium oxide	< 6%
Silicon	< 0.1%

All % are by wt.

Table 2: Parameters varied for recovery of nickel from spent catalyst.

Parameter	Range
Acid concentration	10-80 % by volume
Digestion temperature	30-90°C
Digestion time	0-8 h
Solid:Liquid (S:L)	1:5 to 1:30 g/mL

deionised water. Calibration chart was prepared with these standard samples based on peaks obtained, and fitted to a Beer's law type equation at wave length of 394 nm. The concentration of an unknown solution was then determined using the prepared calibration curve of respective solution at the wave length of 394 nm. The equation (3) was obtained from the calibration curve that relates the absorbance and concentration of metal ion.

$$Y = 0.00009X + 0.0038 \quad ...(3)$$

X = absorbance on the spectrophotometer
Y = concentration in ppm

RESULTS AND DISCUSSION

Chelation technique: It is generally observed that solubilization of metals increases with EDTA concentration (Goel et al. 2009). The effect of concentration of EDTA on cation leaching was determined by varying concentration of EDTA from 0.1M to 1.0M. Fig. 2 shows the effect of EDTA concentration on metal extraction at pH 10 and 400 rpm using 1-2 mm particles. Upon increasing EDTA concentration from 0.1M to 1.0M, there is a gradual change in the percentage extraction of nickel. It indicates that excess reactant EDTA pushes the reaction forward for the reversible reaction. As evident from the Fig. 2, the maximum recovery was obtained at 1M EDTA. Goel et al. (2009) studied the recovery of nickel from a spent catalyst using EDTA-disodium salt as a chelating agent after which sulphuric acid was added to obtain NiSO₄. They reported the extraction up to 95% under the following conditions: 0.8M concentration of EDTA, S:L ratio 1:50 (g:mL), particle size 100 μm, pH 10, chelation time 10 h, 700 rpm and 100°C.
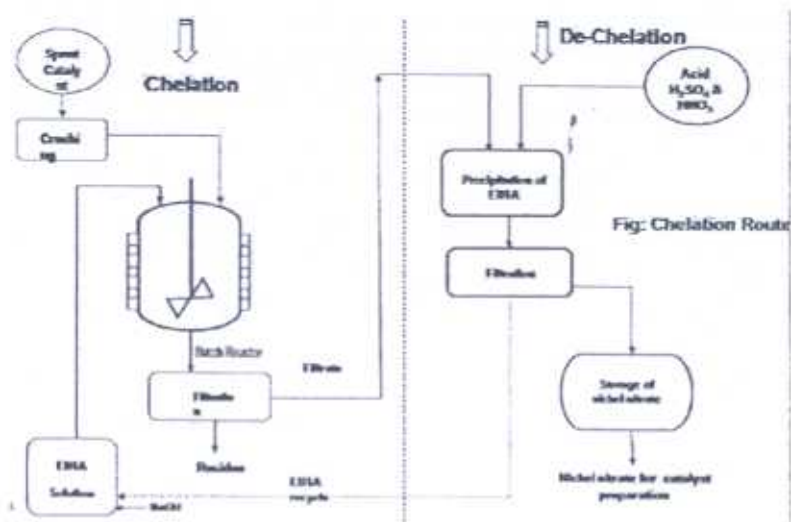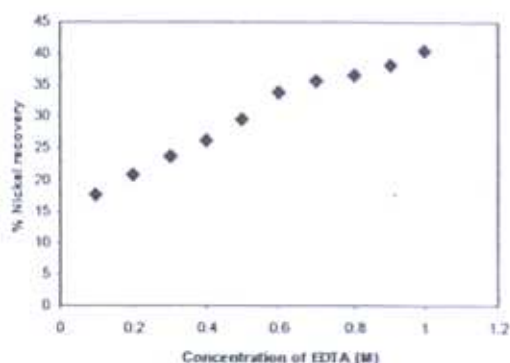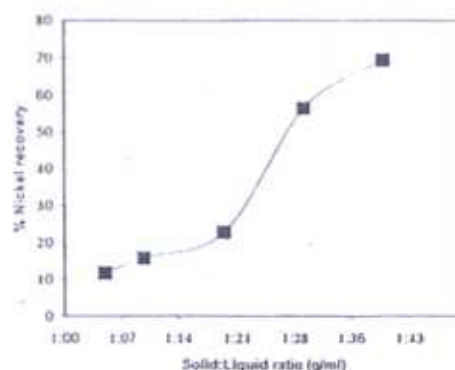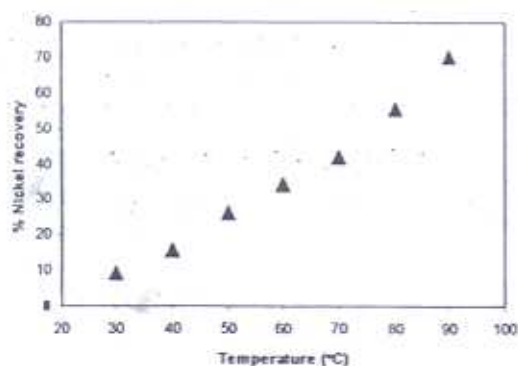
Fig 1: Flow sheet for the recovery of metal using EDTA.

Fig. 2: Effect of EDTA concentration on recovery of nickel via chelation technique. (T=30°C; S:L=1:10 g/mL., 400 rpm; t= 5hrs)

Fig. 3: Effect of solid-liquid ratio on recovery of nickel via chelation technique. (T=30°C; EDTA concentration=1M, 400 rpm ; t= 5 hrs)

Fig. 4: Effect of temperature on recovery of nickel via chelation technique. (EDTA concentration=1M; S:L=1:10 g/mL; 400 rpm; t= 5 h)
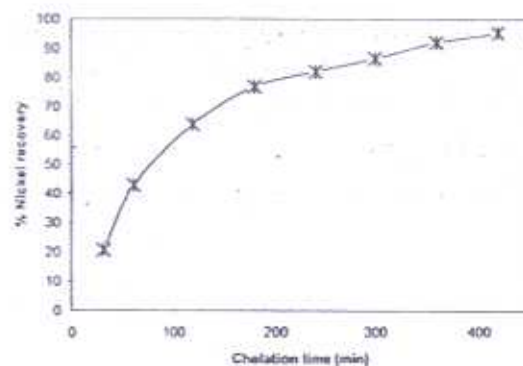
Fig. 5: Effect of chelation time on recovery of nickel via chelation technique. (EDTA concentration=1M; S: L=1:10 g/mL; T=90°C; 400 rpm)

The effect of solid-liquid ratio on the nickel recovery was studied by performing experiments at 1:5, 1:10, 1:20, 1:30 and 1:40 (g:mL) respectively. Fig. 3 reveals that the percentage extraction was influenced by the S:L ratio, the recovery increased as ratio increased. The 69% conversion at S:L ratio 1:40 (g:mL) was observed; however, very high S:L ratio is not advisable as it leads to increase in the volume of reactor, solid-liquid handling problems, etc. Therefore, in the present study an S:L ratio of 1:10 (g:mL) was used for all other experiments.

The effect of temperature and reaction time on nickel recovery is displayed in Figs. 4 and 5 respectively. The recovery increased as a function of temperature with 70% recovery at 90°C. At temperatures beyond 90°C, recovery was almost constant. Fig. 5 reveals that the percentage extraction increased as the time of chelation increased at pH 10 and 400 rpm using 1-2 mm particles. A maximum recovery of 95% was observed after 7 h of chelation time. The advantage of the chelation route compared to conventional acid leaching route is that there is no interaction with the alumina support.

CONCLUSION

The use of catalysts, and hence, catalyst wastes have rapidly been increasing worldwide. Recovery of valuable elements from spent catalysts becomes an unavoidable task not only for reducing the inventory cost of catalysts but also for reducing the catalyst waste to prevent environmental pollution. For the recovery of nickel from spent catalyst using chelating agent the 95% nickel recovery was obtained in 7 h at EDTA concentration of 1M, S:L = 1:10 (g:mL), pH 10, 400 rpm and 90°C. Almost all the EDTA could be recovered from solution without interaction with alumina support. The main attractiveness of the present research in addition to effective recovery of nickel is recovery of EDTA from Ni- EDTA complex which can be used several times for extraction of nickel from spent catalysts. The process becomes economically more viable because of complete recycling of EDTA. In all the cases, EDTA was recovered up to 97-99%, which could be recycled back to the process.

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